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Abstracts & Program

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At present day one of the biggest problems over the world is the energy, which usage is increasing more than exponentially, making big damage to the environment. Therefore, it is urgent for materials scientists to propose new materials for energy generation, storage, and transport in order to supply necessary amount of energy and reduce environmental problems. Industrial development for energy production has been performed with a tremendous effort and has already reached the limitation, and it is highly required to study the fundamental aspects of energy issues interning to change drastically the present situation. We, material scientists, now have a good chance to contribute to this important subject. It is necessary to exchange ideas among theoretical and experimental researchers to find the best way to solve this difficult task. Accordingly, we plan to organize International Conference on Functional Materials for Frontier Energy Issues *(ICFMFEI)* to serve good chance for researchers in Asian and other regions to meet and discuss problems face to face.

We hope that you will take the opportunity to network with new acquaintances, and to build upon those relationships that have already been established. We look forward to welcoming our friends and colleagues from Asia, as well as other parts of the world to Novosibirsk, Russia.

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Program

The conference will be held in the House of Scientists (*the Small Hall*) of Siberian Branch of Russian Academy of Sciences located at Morskoy Prospect, 23 (Морской проспект, 23).

	Day 1 (1 Oct)	**Day 2 (2 Oct)**	**Day 3 (3 Oct)**	**Day 4 (4 Oct)**	**Day 5 (5 Oct)**
9:00 – 9:20		Registration			
9:20 – 9:30		Welcome Speech			
9:30 – 11:00		Oral Session *(Invited Speakers)*			
11:00 – 11:30		Coffee Break			
11:30 – 13:00		Oral Session *(Invited Speakers)*			
13:00 – 14:00		Lunch			
14:00 – 15:30		Oral Session			
15:30 – 16:00		Coffee Break			
16:00 – 17:00		Oral Session *(Young Oral Reports)*			
17:00 – 17:30		**Group Photo**			
17:30 – 18:00		Poster Session Preparation			Closing & Award
18:00 – 21:00	Registration & Welcome Party	Dinner & Poster Session		Banquet	

Scientific Program

Day 2 (2 Oct)

Opening Ceremony
9:20 – 9:30 **Welcome Speech**

Session I: Invited Reports
Chair: Mizuseki H.

9:30 – 10:00 **Goto T.**
"Solid-State Thin Film Lithium Battery by Chemical Vapor Deposition"
Institute for Materials Research, Tohoku University

10:00 – 10:30 **Maguire J. F.**
"Multi-Scale Modeling of Materials for Energy Applications"
Scientific Simulation Systems Inc., USA

10:30 – 11:00 **Lee K.-R.**
"Web Based Nano Materials Design Platform"
Computational Science Center, Korea Institute of Science and Technology

11:00 – 11:30 **Coffee Break**

Session II: Invited Reports
Chair: Goto T.

11:30 – 12:00 **Saprykin A. I.**
"Design of Novel High Capacity Anode Materials for Li-Ion Batteries Based on Nanostructured SiC-Graphene Composites"
Nikolaev Institute of Inorganic Chemistry, SB RAS

12:00 – 12:30 **Chen Y.**
"First-Principles Modelling of Formation and Effect of NdO_x Phase in Grain-boundary of Nd-Fe-B"
Department of Nanomechanics, School of Engineering ,Tohoku University

12:30 – 13:00 **Mizuseki H.**
"Computational Materials Design on High-Performance Gas Separation Materials"
Korea Institute of Science and Technology

13:00 – 14:00 **Lunch**

Session III: Oral Reports
Chair: Fugita T.

14:00 – 14:20 **Pikalova E.**
"Electrochemical Properties of Ca Doped Praseodymium Nickelate Oxide Cathodes in Contact With $Ce_{0.8}Sm_{0.2}O_{1.9}$ Electrolyte"
Institute of High Temperature Electrochemistry, UB RAS

14:20 – 14:40 **Shiga K.**
"Ionic Conduction in Single-Crystalline $BaTiO_3$ and $BaTi_2O_5$"
Institute for Materials Research, Tohoku University

14:40 – 15:00 **Snegurov P. A.**
“Molecular Dynamics Simulation of Ionic Conductivity in Yttria-Stabilized Zirconia: the Role of Phase Composition”
Institute of Chemistry, Saint-Petersburg State University

15:00 – 15:20 **Maznoy A.**
“Porous Nickel-Aluminides as Key Elements of Porous Radiant Burners”
Tomsk scientific center, SB RAS

15:30 – 16:00 **Coffee Break**

Session IV: Young Oral Reports
Chair: Bozhko Yu. Yu.

16:00 – 16:15 **Stoporev A. S.**
“Significance of the Disperse Medium in the Nucleation Process of Methane Hydrate in Water-in-Oil Emulsions”
Nikolaev Institute of Inorganic Chemistry, SB RAS

16:15 – 16:30 **Medvedev V. I.**
“Phase Equilibrium for Clathrate Hydrate Formed in Methane + Water + Ethylene Carbonate System”
Gubkin Russian State University of Oil and Gas

16:30 – 16:45 **Maznoy A.**
“Porous Nickel-Aluminides as Metal Support for Solid Oxide Fuel Cells”
Tomsk scientific center, SB RAS

16:45 – 17:00 **Maznoy A.**
“Porous Penetrable Sialon Ceramics Produced by Combustion Synthesis”
Tomsk scientific center, SB RAS

17:30 – 18:00 **Poster Session Preparation**

18:00 – 21:00 **Poster Session & Dinner**

Day 3 (3 Oct)

Session V: Invited Reports
Chair: Kawazoe Y.

9:30 – 10:00 **Istomin V. A.**
“Phase Equilibria Pore Water – Gas Phase – Bulk Gas Hydrates or Ice”
Gaszprom VNIIGAZ Jsc.

10:00 – 10:30 **Manakov A. Yu.**
“Solubility of Hydrogen in Ice Ih”
Nikolaev Institute of Inorganic Chemistry, SB RAS

10:30 – 11:00 **Bondarev E. A.**
“Possibility of Natural Gas Underground Storage in Hydrate State”
Institute of Oil and Gas Problems, SB RAS

11:00 – 11:30 **Coffee Break**

Session VI: Invited Reports
Chair: Masumoto H.

11:30 – 12:00 **Kato H.**
“Nanoporous Metals by Dealoyying in Metallic Melt and Their Application for Energy Devices”
Institute for Materials Research, Tohoku University

12:00 – 12:30 **Fujita T.**
“Dealloyed Nanoporous Metals for Green Application”
WPI-AIMR Tohoku University

12:30 – 13:00 **Belosludov R.**
“Nanoporous Materials for Energy Storage: Theoretical Aspects”
Institute for Materials Research, Tohoku University

13:00 – 14:00 **Lunch**

Session VII: Oral Reports

Chair: Istomin V. A.

14:00 – 14:20 **Belosludov V. R.**
“Hydrogen Clatrate Hydrate: Equation of State and Self-Preservation Effect”
Nikolaev Institute of Inorganic Chemistry, SB RAS

14:20 – 14:40 **Semenov A. P.**
“Kinetic Inhibition of Hydrate Formation by Water-Soluble Polymer Reagents”
Gubkin Russian State University of Oil and Gas

14:40 – 15:00 **Subbotin O. S.**
“Theoretical Modeling of Gas Hydrate Equilibria for the Gas Mixtures Containing CO_2, N_2, and CH_4”
Nikolaev Institute of Inorganic Chemistry, SB RAS

15:00 – 15:20 **Pilnik A. A.**
“A New Method of Intensifying the Process of Hydrate Formation”
Kutateladze Institute of Thermophysics, SB RAS

15:30 – 16:00 **Coffee Break**

Session VIII: Young Oral Reports

Chair: Bozhko Yu. Yu.

16:00 – 16:15 **Lazurenko D. V.**
“Structure and Properties of $Ti-Al_3Ti$ Composites Obtained by SPS of Ti and Al Foils of Different Thicknesses Enclosed in Titanium Shells”
Novosibirsk State Technical University

16:15 – 16:30 **Syrokvashin M. M.**
“X-Ray Studies of Thermoelectric Materials Based on Transition Metal Solid Solutions”
Institute of Inorganic Chemistry, SB RAS

16:30 – 16:45 **Medvedev D.**
“Influence of Acceptor Doping on the Physicochemical and Transport Properties of Materials Based on $BaCeO_3$ and $BaZrO_3$”
Institute of High Temperature Electrochemistry, UB RAS

16:45 – 17:00 **Fedorenko A. D.**
“X-Ray Study of the Electronic Structure of Transition Metal Complexes With Nitroxyl Ligands – Molecular Magnets”
Institute of Inorganic Chemistry, SB RAS

Day 4 (4 Oct)

Session IX: Invited Reports

Chair: Bardakhanov S. P.

9:30 – 10:00 **Kawazoe Y.**
“Theoretical Study on Task Specific Ionic Liquid for Metal Extraction From Garbage Caused by Tsunami”
New Industry Creation Hatchery Center, Tohoku University

10:00 – 10:30 **Fedorov A. S.**
“Application of Ab Initio Calculations for Investigation of The Lithium and Hydrogen Bahavior Inside Perspective Absorbents”
Kirenskii Institute of Physics, SB RAS

10:30 – 11:00 **Kuo J.-L.**
“Structures and Dynamics of Supercool and Nano-Confined Water: From Empirical to Ab-Initio Molecular Dynamics”
Institute of Atomic and Molecular Science, Academia Sinica

11:00 – 11:30 **Coffee Break**

Session X: Invited Reports

Chair: Kato H.

11:30 – 12:00 **Markovich D.**
“Transfer Prosesses in Compact Fuel Cells”
Novosibirsk State University

12:00 – 12:30 **Kulkova S.**
“Influence of Impurities on Hydrogen Sorption and Diffusion in Ti-Based Alloys”
Institute of Strength Physics and Materials Science, SB RAS

12:30 – 13:00 **Bardakhanov S. P.**
“Electron Beam Technology of Nanopowder Production for Possible Application in Functional Materials”
Khristianovich Institute of Theoretical and Applied Mechanics, SB RAS

13:00 – 14:00 **Lunch**

Session XI: Oral Reports

Chair: Maguire J. F.

14:00 – 14:20 **Zhanpeisov N. U.**
“Theoretical DFT Study on Structure and Chemical Activity of Complex Modified Catalysts”
Institute for Excellence in Higher Education & Department of Chemistry, Graduate School of Science, Tohoku University

14:20 – 14:40 **Filippov N.**
“Electrokinetic Devices Based on Silicon Microchannel Membranes”
Rzhanov Institute of Semiconductor Physics, SB RAS

14:40 – 15:00 **Artemkina S.B.**
“Highly-Dispersed 1D and 2D Chalcogenides and Decoration of Their Surfaces by Metal Nanoparticles”
Nikolaev Institute of Inorganic Chemistry, SB RAS

15:00 – 15:20 **Seriy S.**
“Modern Ab-Initio Calculations Based on Tomas-Fermi-Dirac Theory With Quantum, Correlation and Multi-Shells Corrections”
R.E. Alekseev Nizhny Novgorod State Technical University

15:30 – 16:00 **Coffee Break**

Session XI: Young Oral Reports

Chair: Bozhko Yu. Yu.

16:00 – 16:15 **Semushkina G. I.**
“Electronic Structure Analysis of Organic Semiconductor Based on H_2PC”
Institute of Inorganic Chemistry, SB RAS

16:15 – 16:30 **Bakulin A. V.**
“Initial Oxidation of Low-Index $TiAl_3$ Surfaces”
Institute of Strength Physics and Materials Science, SB RAS

16:30 – 16:45 **Medvedev D.**
“Structural, Electrical and Thermo-Mechanical Properties of Ca-Substituted Pr_2NiO_4”
Institute of High Temperature Electrochemistry, UB RAS

16:45 – 17:00 **Shevtsova L. I.**
“Structure and Properties of “nickel Aluminide – Nickel” Composite Materials Obtained by SPS Method”
Novosibirsk State Technical University, Russia

Day 5 (5 Oct)

Session XII: Invited Reports
Chair: Chen Y.

9:30 – 10:00 **Malinovsky V. K.**
“Anomaly of Water Viscosity Behavior Near the 273K Temperature”
Institute of Automation and Electrometry, SB RAS

10:00 – 10:30 **Das G. P.**
“First-Principles Design of Nanostructured Materials for Efficient Storage of Hydrogen”
Indian Association for the Cultivation of Science, India

10:30 – 11:00 **Inerbaev T. M.**
“Theoretical Modeling of Materials for Hydrogen Energy Applications”
L.N. Gumilyov Eurasian National University

11:00 – 11:30 **Coffee Break**

Session XIII: Invited Reports
Chair: Inerbaev T. M.

11:30 – 12:00 **Fedin V. P.**
“Porous Coordination Polymers: from Synthesis and Structure to Functional Properties”
Nikolaev Institute of Inorganic Chemistry, SB RAS

12:00 – 12:30 **Koptyug I. V.**
“Parahydrogen Induced Polarization in Catalysis and Medicine”
International Tomography Center, SB RAS

12:30 – 13:00 **Masumoto H.**
“Preparation of Metal-Ceramics Nano-Composite Films for Multi-Functional Properties”
Frontier Research Institute for Interdisciplinary Sciences

13:00 – 14:00 **Lunch**

Session XIV: Oral Reports
Chair: Belosludov R.

14:00 – 14:20 **Dudina D. V.**
"Microstructural Features of Dense and Porous Materials Produced in Systems Experiencing Partial Chemical Transformations During Spark Plasma Sintering"
Lavrentyev Institute of Hydrodynamics, SB RAS

14:20 – 14:40 **Safonov A.**
"Synthesis and Optical Properties of Silver Thin Film Coated by Flouropolymer"
Kutateladze Institute of Thermophysics, SB RAS

14:40 – 15:00 **Seung-Geun Yu**
"Three-Dimensional Bicontinuous Porous Graphite Generated in Low Temperature Metallic Liquid"
Dept. of Materials Science, Grad. School of Engineering, Tohoku University

15:00 – 15:20 **Chen J.**
"Preparation of Sr-Ti-O Films on Polycrystalline AlN Substrates Using Laser CVD"
Institute for Materials Research, Tohoku University

15:30 – 16:00 **Coffee Break**

Session XV: Young Oral Reports
Chair: Bozhko Yu. Yu.

16:00 – 16:15 **Maliutina Iu. N.**
"Combination of Explosive Welding and Spark Plasma Sintering for Reliable Joints Produsing Between Dissimilar Materials"
Novosibirsk State Technical University

16:15 – 16:30 **Ukhina A. V.**
"Interaction Between Nickel and Diamond Particles During Sintering of Powder Mixtures"
Institute of Solid State Chemistry and Mechanochemistry, SB RAS

16:30 – 16:45 **Ermakova E.**
"SiCN Films: Synthesis, Optical and Mechanical Properties"
Nikolaev Institute of Inorganic Chemistry, SB RAS

17:30 – 18:00 **Closing & Award**

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Reports

Invited Speakers

SOLID-STATE THIN FILM LITHIUM BATTERY BY CHEMICAL VAPOR DEPOSITION

Goto T.*, Katsui H.

Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

All-solid-state Li-ion battery with high energy densities has much attention due to heavy usage and safety issue. Thin film technoplgy such as sputtering and PLD (pulsed laser ablation) can be a candidate processing for fabricating cell components of electrodes and electolytes. $LiCoO_3$, a candidate material as a cathode, has layered rock-salt structure in which Li, cobalt (Co) and oxygen (O) atoms form a layer-by layer structure in the direction of the c-axis. The electrochemical properties of $LiCoO_2$ films are expected to depend on the crystalline orientation; the (003) plane parallel to the substrate blocks Li-ion current, whereas (003) inclined from the substrate enables the smooth migration of Li ions. Hetero-epitaxial growth is a powerful method to fabricate films oriented to a specific plane. Epitaxial $LiCoO_2$ films with well-defined structures and orientations provide a promising pathway to study the anisotropic nature of $LiCoO_2$.

Li-ion-conducting solid electrolytes require high ion conductivity and electrochemical stability against the Li metal anode. Garnet-type $Li_7La_3Zr_2O_{12}$ ia a candidate as solid electrolyte material. Although $Li_7La_3Zr_2O_{12}$ films were prepared on $SrTiO_3$ (100) and sapphire (0001) single crystals by pulsed laser deposition (PLD), and on garnet $Gd_3Gd_5O_{12}$ single crystals by PLD, there are no reports on the fabrication of $Li_7La_3Zr_2O_{12}$ films on poly-crystalline substrates.

We have developed laser CVD which enables one to increase deposition rate several 10-100 times and to modify the orientation, microstructure and orientation. In the present study, the $LiCoO_2$ film as a cathode and $Li_7La_3Zr_2O_{12}$ film as an electrolyte were prepared by thermal and laser CVD, and the orientation, morphology and deposition rates were investigated.

Dipivaloylmethanato-lithium (Li(DPM)) and tridipivaloylmethanato-cobalt ($Co(DPM)_3$) were used as precursors to prepare $LiCoO_2$ films. The deposition temperature of thermal CVD was 923 K. Diode laser was used for laser CVD. Hetero-epitaxial (104) and (018) $LiCoO_2$ films on (100) and (110) MgO single crystals were obtained by thermal CVD. The epitaxial in-plane orientation relationships of the (104) $LiCoO_2$ films on (100)MgO and of the (018) $LiCoO_2$ films on (110) MgO were [010] $LiCoO_2$ // [011]MgO and [100] $LiCoO_2$ // [110] MgO, respectively. The deposition rates of (104)- and (018)-oriented films were 11 μm h^{-1} and 9 μm h^{-1},which were almost 100 times greater than those reported by PLD. The laser CVD can prepare more densely faceted $LiCoO_2$ films at deposition rates of 30 μm h^{-1} at 1225 K. $Li_7La_3Zr_2O_{12}$ films were prepared on poly-crystalline Al_2O_3. $La(DPM)_3$ and $Zr(DPM)_4$ were used as precursors for La and Zr. With increasing deposition temperature from 973 to 1223 K, a pyrochloretype $La_2Zr_2O_7$ film having the (111) orientation, tetragonal $Li_7La_3Zr_2O_{12}$ film, cubic $Li_7La_3Zr_2O_{12}$ film and pyrochlore-type $La_2Zr_2O_7$ film with (100) orientation were obtained. The deposition rates of the $Li_7La_3Zr_2O_{12}$ film were about 20 μm h^{-1} by thermal CVD, which were one to two orders of magnitude greater than those by PLD. By using laser CVD the deposition rate increased to 50-150μm h^{-1}.

*Contact: goto@imr.tohoku.ac.jp

MULTI-SCALE MODELING OF MATERIALS FOR ENERGY APPLICATIONS

Maguire J.F.*[1], Prichard J.[1], Petsev D.[2], Brenner E.[2]

[1]Scientifiiic Simulation Systems Inc, 10 West Second Street, Dayton, Ohio, USA
[2] University of New Mexico, Dept. of Nuclear Engineering, Albuquerque, USA

The development of statistical mechanical models with *a priori* predictive capability for real forms of matter presents many challenges in both analytic theory and numerical simulation. In numerical simulation (Monte Carlo or Molecular Dynamics) the usual scheme involves applying an empirical potential which has been optimized to produce the required properties; from a scientific viewpoint this is intrinsically unsatisfactory in that “post hoc ergo propter hoc”; agreement between prediction and experiment is usually reasonably good but tells you little that you did not already know! The fundamental problem is, of course, that electrons are fermions and obey the Pauli exclusion principle. This gives rise to exceedingly strong repulsive forces at short range which, in turn, necessitate discrete time scales in the femtosecond regime if energy stability is to be obtained. With the advent of larger computers it is now possible to address low wave vector phenomena but only for relatively short time.

In this paper we shall illustrate how recent discoveries in basic physics [1] may be coupled with large-scale density functional calculations to enable *ab-inito* computer simulation of materials for much longer times than is possible with the standard approaches. When combined with density functional approaches [2] to chemical reactions the realm of computer simulation may be extended into areas where it is of use in practical applications; examples in chemical reaction mechanisms at surfaces and interfaces in energy storage and photovoltaics and at semiconductor interfaces will be presented.

[1] R.S. Saksena, L.V. Woodcock and J.F. Maguire, Molecular Physics **102**, 3, 259-266 (2004)

[2] M.E. Fleharty, F. van Swol, and D.N. Petsev, J. Colloid and Interface Science **449**, 408-415 (2015)

*Contact: JohnMaguire@SciSimSystems.com

WEB BASED NANO MATERIALS DESIGN PLATFORM

Lee K.-R.*

Computational Science Center, Korea Institute of Science and Technology, Seoul, Korea

Owing to the rapid increase in computing power and successful development of the computation methodology, molecular level simulation has driven new paradigm of materials research. This new trend is now strongly supported by various government funding as we observe in Materials Genome Initiative of the U.S., WPI-MANA and Strategic Element Research Program in Japan, and Creative Materials Discovery in Korea. In order to support this new strategy of the materials research, we has been developing web-based virtual fab for materials design based on combination of various process and property simulation methods. In the present talk, the concept of platform will be introduced with brief demonstration of the materials design platforms. Challenging issues for the progress of the platform will be discussed.

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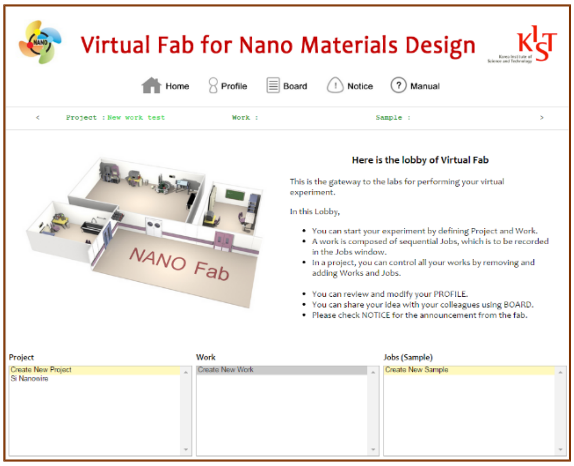


Project : New work test   Work :   Sample :

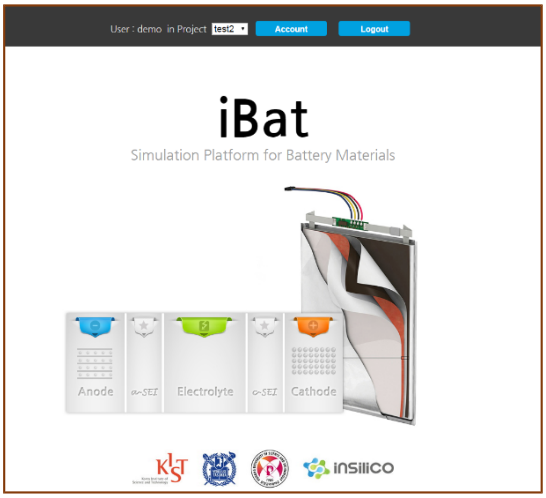
Here is the lobby of Virtual Fab

This is the gateway to the labs for performing your virtual experiment.

In this Lobby,

- You can start your experiment by defining Project and Work.
- A work is composed of sequential Jobs, which is to be recorded in the Jobs window.
- In a project, you can control all your works by removing and adding Works and Jobs.

- You can review and modify your PROFILE.
- You can share your idea with your colleagues using BOARD.
- Please check NOTICE for the announcement from the fab.



DESIGN OF NOVEL HIGH CAPACITY ANODE MATERIALS FOR Li- ION BATTERIES BASED ON NANOSTRUCTURED SIC-GRAPHENE COMPOSITES

Yakovlev V.N.[1], Pozdnyakov G.A.[2], Galkin P.S.[1], Saprykin A.I.[1]*

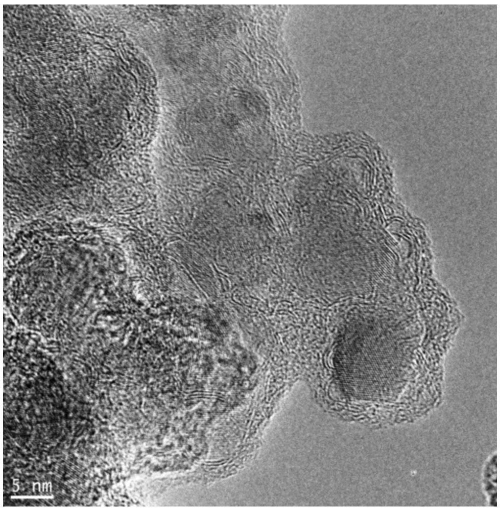
[1] *Nikolaev Institute of Inorganic Chemistry SB RAS, Novosibirsk, Russia*
[2] *Khristianovich Institute of Theoretical and Applied Mechanics, Novosibirsk, Russia*

Thanks to high performances of lithium-ion (Li-ion) batteries, their production sharply increased in recent years. Li-ion batteries are of special interest for automotive industry where viability of the technology, capable to solve strong requirements of consumers is still called in question. Key parameters for automobile Li-ion batteries – specific energy and power (both gravimetric and volume), a cycling, speed of charging, safety, working temperature range, production cost. Despite significant progress in this field, in production and operation technologies of Li-ion batteries yet are available many questions demands the solution.

In the Li-ion batteries, both anode and cathode materials are equally important. While new cathode materials show significant progress last time, in all commercial batteries the negative electrode (anode) is made of carbon materials (particularly, of graphite) which appeared very convenient matrix for Li intercalation. The volume of carbon materials in the course of intercalation-deintercalation of Li^+ changes slightly. Theoretical specific capacity of the graphite-based anode is relatively low (372 mAh/g in case of LiC_6 formation), it stimulates searches of new more effective anode materials.

The use of composite materials based on nano silicon (n-Si) or silicon carbide (n-SiC) with conductive carbon additives (carbon black, graphite, graphene) as a material for the anode allows to obtain high specific capacity (from 1000 to 2000 mAh/g) in the initial cycles, but rapidly (20 to - 30 cycle) degraded to the level of 200 - 300 mAh/g. Materials retain high specific capacity during prolonged cycling can be obtained, if the nanoparticles of n-Si or N-SiC coated by carbon (or graphene) layers as an electrically conductive material.

Resently we proposed new method for the synthesis of nano-sized silicon powders from monosilane (SiH_4) in argon by adiabatic compression [1]. By changing the gas mixture composition it is possible to change of conditions of SiH_4 thermal decomposition, resulting in the diferent silicon-containd nanoparticle formation. The proposed method allows us set the composition, structure and morphology of the obtained nanoparticles. To realize the thermal decomposition of reacting gas mixture by adiabatic compression origilal experimental device has been created. The device is equipped by a measuring complex allowing to control temperature and pressure during the prosses of synthesis of nanoparticles, to record the electric field and to carry out optical measurements.



Experimentally shown that during adiabatic compression of the gas mixture of monosilane in argon and acetylene resulting to the initiation of reaction of monosilane and acetylene decomposition with following formation of nano-sized particles of silicon carbide coated by carbon layers in form of graphite or graphene (n- SiC@C).

As an example in figure a transmission electron microscopy (TEM) photo of the product obtained by adiabatic compression of the mixture of 10% SiH_4 in argon with addition of C_2H_2 is shown. It can be seen that the resulting nanoparticles have SiC core (size ~10 nm) coated by carbon layers of 3-5 nm in the form of graphene. First experiments showed that the anode of Li-ion based on such composites can reversibly intercalate lithium with the discharge capacity up to 1000 mAh/g at a current loading of 100 - 250 mA/g which significantly exceeds a specific capacity of carbon graphite materials (~ 350 mAh/g). Proposed method for producing of nanopowders of SiC@C can be scaled and realized in production lines.

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FIRST-PRINCIPLES MODELLING OF FORMATION AND EFFECT OF NdO_X PHASE IN GRAINBOUNDARY OF Nd-Fe-B

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The development of advanced rare-earth permanent magnet, such as Nd-Fe-B, draws great attention in recent years due to its important application as the energy materials. One of the focuses is the relation between coercivity and microstructure at the grain boundaries of magnets. A disordered fcc-NdO_x phase is observed and believed to take an important role in coercivity generation [1,2]. To have a thorough understanding on the formation mechanism of this particular oxide and its relation to the surface coercivity, ground state analysis for whole oxygen concentration in Nd-O has been performed by combing the LSDA+U and the Cluster Expansion Method (CEM). Systematic calculations revealed that a sequent fcc-based structures formed by introducing oxygen vacancies into fcc-based NdO is stable in almost all 0-50% oxygen concentration range, whereas in a series hcp-based structures developed from hP5-Nd_2O_3, no stable structure is observed [3], which coincides with the experimental measurement very well. Further analysis of formation energies and relevant changes in electronic structures of single oxygen vacancy in various structures revealed the insight of such fcc-based phase formation, and further explained the relation between the phase stability and coercivity.urthermoew, the stability and binding properties of the Cu-doped Cu-fcc-NdO_x structures which was reported to be favorite for increasing coercivity are also investigated, a possibility of stable solid solution of (Nd, Cu)O is revealed.

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COMPUTATIONAL MATERIALS DESIGN ON HIGH-PERFORMANCE GAS SEPARATION MATERIALS

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Propylene is an important commercial petrochemical, produced on a large scale. Its production requires separation from propylene and propane mixtures, but this is intrinsically difficult due to the similar physical and chemical properties of these molecules. Energy-intensive, costly cryogenic distillation has been used for over 70 years for propylene / propane separation. In general, adsorptive separation is an energy- and cost-effective alternative to distillation, and a few organic materials have shown potential for propylene / propane separations through either an equilibrium-based, a kinetic-based or a gate-opening mechanism. In the present study, we chose zeolitic imidazolate frameworks (ZIFs) as a gas separation material and discussed the potential barriers of diffusion process estimated by using Nudged Elastic Band (NEB) method.

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PHASE EQUILIBRIA PORE WATER – GAS PHASE - BULK GAS HYDRATES OR ICE

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At present, natural gas hydrates are in the focus of research activity all over the world as one of the important unconventional hydrocarbon resources. At on shore condition gas hydrates deposits are connected with permafrost and/or under permafrost zones. Now in Russia the new gas and gas-condensate low-temperature fields is stated for recovery (over-senomanian gas fields at Western Siberia, oil-gas-condensate fields at south part of Sakha Republic as well as upper horizons of Tambey fields at Yamal peninsula). The thermodynamic conditions of such deposits are very close to three phase equilibrium line: “natural gas - pore residual water - gas hydrate”. So we are not exclude the existence of gas hydrate component in equilibrium with water and compressed gas inside the productive horizons at these fields.

The phase equilibria of “pore water - bulk ice” and “pore water – gas - bulk gas-hydrate” depending on pressure, temperature, water content in the porous samples and gas hydrate-former are discussed. The term “bulk” means that solid particles of hydrate or ice are not too small (at least more than several microns), so the chemical potential of such particles practically equal to chemical potential of a bulk solid phase. The consideration of these equilibriums is possible if we only know the chemical potential of pore water (in comparison with bulk liquid water phase). Such equilibriums are thermodynamically stable. In comparison the equilibriums like “pore water – pore ice” (or “pore water – gas – pore hydrate”) with very small solid particles inside porous media are metastable. For description of the last metastable equilibriums we need additionally to know the chemical potential of solid ice particle (or hydrate particle) inside porous space depending on its size. Below we are considered only the stable equilibriums by using experimental data on chemical potential of pore water in the samples of porous media.

The rapid experimental technique for determination of equilibrium water content in porous media in contact with ice (unfrozen water) or gas hydrates (nonclathrated water) is developed. The method is based on experimental data of pore water potential via water content on the samples and some thermodynamic calculations. The water potential of soil (or artificial porous media) is determined by device WP4–T, developed by Decagon Devices (USA) at the range of positive in Celsius temperatures (above and below room temperature). The main purpose of the report is to demonstrate how the experimental data on water potential Ψ (as well as a difference of chemical potential between pore water and bulk water) via water content in porous media (natural soils and artificial media) may be used for thermodynamic calculations of unfrozen and nonclathrated water content as a function of pressure and temperature. As for unfrozen water content in porous media the method is work in a wide range of negative on Celsius temperatures between zero and minus 30 °C. As for nonclathrated water content the method is work both at negative and positive temperatures.

Comparison of calculated values of unfrozen and nonclathrated water contents with the experimental data for natural clay sediments are presented. A good agreement of equilibrium water content, proposed by calculation method and direct experimental method (known in geocryology as “contact method”) for frozen as well as hydrate bearing clay sediments. Also this technique may be used for prediction of pore water phase behavior at the artificial porous media (like porous glasses).

Proposed technique for calculations of water content in the samples in equilibrium with ice or gas hydrate depending temperature and pressure give us possibilities for further prognosis of the physico-chemical and mechanical properties of frozen (or hydrate-containing) soils.

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SOLUBILITY OF HYDROGEN IN ICE Ih

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The development of new materials that are capable of multiple and reversible sorption/desorption of hydrogen and can be used to store this gas is topical and practically significant research area. At present, clathrate hydrates of hydrogen and double clathrate hydrates of hydrogen with various auxiliary components are intensively studied as materials for hydrogen storage. Studies in the field of technologies of light gas (helium, hydrogen) separation from gas mixtures are of substantial interest, too.

We performed experimental studies of the solubility of hydrogen in ice Ih (usual low-pressure ice) at temperature -1 - -2°C and pressures up to 8 MPa. At a pressure equal to 1.90 and 8.04 MPa, hydrogen solubility in the ice was found to be 0.15 and 1.32 cm^3/g, respectively (hydrogen volume was reduced to the normal conditions). Comparison with the literature data [1-3] shows a reasonable correspondence between our results and the results of [1]. The solubility values reported in [2] and especially in [3] are substantially higher. If we assume that Henry's law can be used for the data fitting, linear approximation of our data and the data presented in [1] gave the expression S=0.024(64)+0.1183(21)*P. Here S is the solubility of hydrogen in ice, cm^3/g of ice (gas volume was reduced to normal conditions), P is hydrogen pressure, MPa. This expression can be recommended to calculate the solubility of hydrogen in ice at a pressure up to 80 MPa and a temperature close to the ice melting point. The work was supported by the Government of Russian Federation under project No. 14.B25.31.0030 (leading scientist Y. Kawazoe, S. S. Kutateladze Institute of Thermal Physics SB RAS).

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POSSIBILITY OF NATURAL GAS UNDERGROUND STORAGE IN HYDRATE STATE

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One of the promising ways of gas hydrates industrial applications (beyond water desalination, extracting pure components from mixtures, gas transportation and many others) is natural gas storage. Such possibility is based on larger mass content of gas in hydrate state as compared with its free state, pressure and temperature being equal. Besides, some researchers suggest to conserve CO_2 and some toxic gases in hydrate state to insure high level of safety at comparatively lower energy consumption.

Nowadays underground gas storages are build in the depleted gas reservoirs or aquifers which are situated near gas pipe lines or large units of gas consumption. They are used to meet season variations of gas cosumption, that is, gas is injected into storage during periods of low demand and is withdrawn during periods of peak demand.. It is especially important for the Northern regions where the variations of gas consumption between year seasons are especially great.

One of the alternatives to common gas storages is that of hydrates compounds formed when natural gas is cooled in the presence of water. The advantage being that as much as 181 standard cubic meters of natural gas could be stored in a single cubic meter of hydrate. The above figure depends on natural gas content. Another advantages are lower volume and increased stability of storage, partly due to immobilization of all free water into hydrate state.

An approach to predict a possibility of natural gas underground storage in hydrate state in corresponding geological structures (under permafrost aquifers) has been proposed. It is based on the mathematical model of non-isothermal multiphase real gas and water flow in porous media. The model takes into account transformation of gas and water into hydrate at certain temperature which depends on gas flow pressure. The model is able to predict the dynamics of hydrate and water saturation as well as pressure and temperature fields in a chosen reservoir with given porosity, permeability and initial values of pressure, temperature and water saturation. An implicit finite-difference scheme is used to approximate the original boundary-value problem. The finite-difference equations have been solved using iteration and sweeping algorithms. Results of calculations showed that possibility of creation of such gas hydrate storages significantly depends on capacity and hydrodynamic characteristics of the aquifers.

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NANOPOROUS METALS BY DEALOYYING IN METALLIC MELT AND THEIR APPLICATION FOR ENERGY DEVICES

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Nanoporous metals have drawn considerable attention for their highly functional properties due to its unique 3D open cell structures. They are usually produced by selective dissolution of elements from a multicomponent alloy (known as the dealloying method in aqueous solutions). Thus, the corrosion or etching is the mechanism of the dealloying technique. This method is based on differences in the electrode potential of each element present in the alloy, therefore, porous structure can be mainly obtained for noble metals of which potential is higher than the standard hydrogen electrode. In this paper, an alternative dealloying technique for developing porous structure even in the base and half metals having low electrode potential is newly introduced. [1] The molten metal is employed in place of the acid/alkali aqueous solutions for dealloying process. The chemical interaction among the elements indicated by the mixing enthalpy is the dominant factor as the same as the standard electrode potential of the metals in the aqueous solution. For example, strong attractive interaction between Mg and Cu, and strong repulsive interaction between Mg and Ti at elevated temperature enable us to perform dissolving Cu from Ti-Cu solid alloy in the Mg melt, which resulted in the formation of a hcp-Ti/hcp-Mg bicontinuous composite. In many acid solutions, pure Ti is passive, while Mg is highly active. This great difference in corrosion behavior enables selective removal of hcp-Mg from the hcp-Ti/hcp-Mg composite, resulting in the open nanoporous Ti metal. [1] Using this technique, we have succeeded in preparing porous metals, Zr, V, Nb[2], Ta, Cr[3], Mo, W, Fe[3], C, Si[4] and alloys, β-Ti[5], Fe-Cr[3], Ni-Cr. In this talk, preparation and energy device application of nanoporous Nb and Si will be discussed.

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DEALLOYED NANOPOROUS METALS FOR GREEN APPLICATION

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Nanoporous metal (NPM) produced by dealloying is an emergent multifunctional material. The simple dealloying technique produces a self-organized and self-supporting three-dimensional nano-architecture offering a variety of attractive applications. NPM is now a new form of ‘Gold rush’. In this presentation, some examples will be introduced for green application.

First, we characterized the microstructure of nanoporous gold using spherical-aberration-corrected transmission electron microscopy (Cs-corrected TEM). The arrangement of near-surface atoms was also measured accurately by Cs-corrected high-resolution TEM (HRTEM), which provides phase-contrast images with high displacement sensitivity. In addition to the static observation in inert vacuum environment, we also characterized the surface atomic structure evolution during CO oxidation in a reactive atmosphere using a newly dedicated environmental HRTEM [1-3].

Second, we have developed an innovative fabrication technique based on using Japanese “Washi” paper as a template for a slurry of metal powder and binder, which is then consolidated into a microporous sheet through sintering. Subsequent selective etching (dealloying) through immersion in acid solution creates additional nanopores, allowing either a bi-modal or tri-modal porous structure. This method is used to create a tri-modal nanoporous Au electrode, as a well as a hierarchical NiMn electrode that achieves high electrochemical capacitance and a rapid rate of oxygen evolution in water splitting. The proposed method is not only easily adapted to large scale production, but also has the potential to be used with a wide range of metals and alloys [4].

Other applications may be introduced.

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NANOPOROUS MATERIALS FOR ENERGY STORAGE: THEORETICAL ASPECTS

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In order to design materials with desirable characteristics it is important to have a good understanding of the atomic-scale chemical and physical properties of materials. Therefore, in parallel to experimental efforts, the detailed theoretical analysis the adsorption of targeted molecules into selected nanoporous materials is important in order to accelerate the realization of novel materials. The metal−organic framework (MOF) material as new functional adsorbents with novel topologies and exceptional host-guest properties has been selected due to scientific interest in their application for storage and separation [1]. Due to the regularity of MOF structures, in a computer simulation we are easily able to build structural models of MOFs that are very helpful to find new materials with desired characteristics [2].

The adsorption of several gas molecules on urotropine $Zn_4(dmf)(ndc)_4(ur)_2$ has been investigated. The synthesis of MOF with the urotropine moiety can improve the selective adsorption of C_2H_2 and CO_2 gases. Thus, it has been found that the inclusion of the urotropine ligand into the MOF framework enhances the adsorption of acetylene and carbon dioxide. This is in agreement with experimental data that showed a large difference in absorption energies between the C_2H_2, CO_2 and CO molecules [3]. Recently, the specific nanoporous material that selectively adsorbs CO with adaptable pores has been studied using first-principles calculations. The high selectivity of CO has been achieved from a mixture with nitrogen by both the local interaction between CO and accessible Cu^{2+} metal sites and the modification of nanopore size [4].

The interpenetration effect on thermodynamic stability of MOF structures with high pore size has been also studied. We have selected the well-known binuclear carboxylate complexes having an octahedral geometry ($Zn_2(R)_4L_2$). The biphenyl connected to the Zn metals through pyridine molecules and terphenyldicarboxylate (TPDC) are selected as *L* and *R* ligands, respectively. The calculated interaction energies between two frameworks have shown that the interpenetrating structure is energetically more favorable due to attractive interaction between the MOF ligands. The close distances between TPDC of different frameworks can leads to interweaving between two frameworks. The substitution of biphenyl by porphyrin moieties can prevent such adhesion due to the increasing distance between TPDC and results in weaker interaction between two interpenetrating frameworks.

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THEORETICAL STUDY ON TASK SPECIFIC IONIC LIQUID FOR METAL EXTRACTION FROM GARBAGE CAUSED BY TSUNAMI

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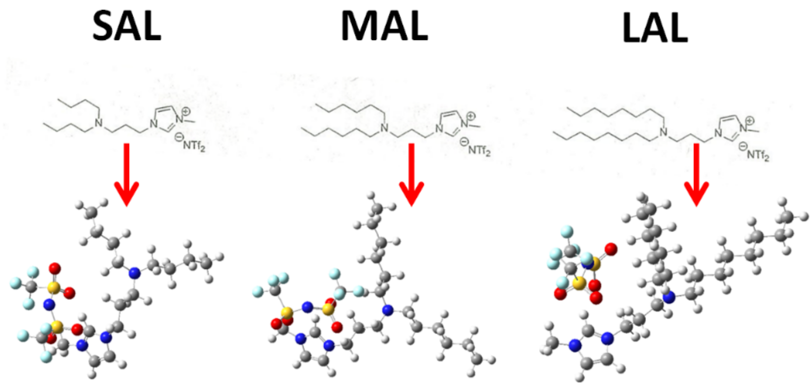
After 4 years from the big tsunami attaked Tohoku area in Japan, still there remain a large amount of garvages. They have been collected to limited areas and classified as stones, steels, woods, etc., and among them there are a large amount of electronic circuit boards, which contain expensive metals should be reused. We have been trying to extract such metals by using ionic liquid experimentally and theoretically. The ionic liquid is functionalized by attached ligands for extraction of specific metal element, and is called "task specific ionic liquids (TSIL)".

Since the properties of TSIL varies strongly as a function of temperature and not easy to understand experimentally, especially temperature dependence of viscosity and hydrophobicity are difficult. We have developed a new theoretical method based on molecular dynamics and hydrodynamics to determine theoretically the viscosity in TSIL, and successfully applied to compute for several TSIL.



Up to the present Rh has been the worst to be extracted efficiently from garvage in industry. We studied the properties of Rh and proposed a new TSIL, which atomic structure is shown on the right and is expected to be suitable for Rh extraction compared to existing industrial methods.

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APPLICATION OF AB INITIO CALCULATIONS FOR INVESTIGATION OF THE LITHIUM AND HYDROGEN BAHAVIOR INSIDE PERSPECTIVE ABSORBENTS

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Intensive development of alternative energy technologies requires a focused development of new materials for high-performance electrical batteries and hydrogen accumulators. The cost of experimental study of such materials is growing all the time, so the theoretical modeling of these materials using the quantum chemistry methods allows to avoid the costly experiments and reduce time of the study. Herewith the accuracy of these theoretical studies, especially ab initio methods, is usually quite high. In this study we carried out a modeling of essential properties of advanced materials for their using as anodes in Li-ion batteries, as well as hydrogen-storage matter. For that DFT-PBE calculations were carried out using the VASP5.2 package [1], which used PAW (projector augmented wave) method and plane wave basis set.

The absorption energy and diffusion rates of lithium atoms inside graphite-like boron carbide (BC3) crystal were calculated.. It was shown that Li may effectively intercalate this structure with the maximum lithium concentration corresponding to Li_2BC_3 stoichiometry, which is threefold in comparison to Li in graphite. The potential barrier values for Li diffusion are about 0.19 eV only, so that Li atoms inside BC3 structure can move easily. These findings suggest that BC3 is very perspective new anode material for Li-ion batteries. Also Li absorption inside both crystalline and amorphous silicon was studied for different temperatures. With help of the developed method for the amorphous Si structure modeling it was shown the Li diffusion in amorphous Si was substantially accelerated in comparison with the crystalline Si. The calculated values can help also in the production of new Li-ion batteries. Also it were investigated the stability of magnesium hydride (MgH*x*) (*x*= 0.5-2) both pure material and this with impurities (Sc,Ti). It was shown the phase of partly saturated MgH_x hydrides (x<2) must decompose into the phase of pure Mg and the phase of MgH_2 that is accompanied by a sharp decreasing of the H diffusion rate. Also it was shown the frequency of the H ion jumps inside MgH2 with Ti impurities is higher by $\sim 2.5\square 10^{6}$ times in the vicinity of Ti atoms in comparison with pure MgH2 case. This means that the hydrogen diffusion in manganese hydride with small admixtures of titanium atoms must be considerably eased that is key to developing the Mg-based hydrogen batteries.

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STRUCTURES AND DYNAMICS OF SUPERCOOL AND NANO-CONFINED WATER: FROM EMPIRICAL TO AB INITIO MOLECULAR DYNAMICS

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Peculiar structure and dynamics of confined and interfacial water are linked to many fundamental questions in biology, chemistry and physics, but detailed understanding of these properties of water is limited due to the lack of precise experimental measurements. At the same time, new phenomena often require further theoretical and computational developments. In this talk, I will present our recent implementation on volume-temperature replica exchange MD [1] method to understand thermal and transport anomalies of water down to supercool region [2]. Based on these understandings, we are working toward understanding how confinement can modulate these properties of water. In more applied directions, we have been studying interfacial water on GaN surfaces using empirical to ab initio MD methods to address a wide range of applications ranging from working principles behind ultra-sonic devices [3-5] to photo-catalytic water splitting processes [6-8].

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TRANSFER PROSESSES IN COMPACT FUEL CELLS

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Portable fuel cells (FC) are perspective power sources for portable electronic devices, especially in field applications, when permanent electric power supply is absent. There exist a number of low temperature FC types which are perspective for portable applications. Among them polymer electrolyte membrane FCs, direct methanol FCs, metal-air FCs (MAFCs), metal hydride FCs, direct borohydride FCs (DBFCs) are actively developed now by multiple technology companies. The need for weight and size reduction of portable fuel cells leads to their exploitation at extremely high power densities. Thought there are specific problems in developing of each type of FCs, all of them have one common problem – the enhancement of heat and mass transfer. In this lecture we consider how different problems of thermal physics as well as adjacent problems of FC's performance optimization can be resolved by means of modeling and experimental investigation. As model examples the DBFCs and the MAFCs in development of which the Institute of Thermophysics SB RAS has a long time experience, will be discussed. Design and development of the FCs with high power densities requires the detailed mathematical modeling and numerical simulations of heat and mass transfer particularly in the critical thermal regimes with the high internal heat generation. Popular methods of thermo-technical calculations are based on the averaged correlations and cannot capture the effects of strong non-uniformity of the internal temperature field which strongly affects chemical kinetics of electrochemical reactions, which can result in significant modeling errors. To avoid this, the model for the numerical simulation of the local conjugate heat-mass transport and electrochemical reactions was developed in Institute of Thermophysics SB RAS. Realized model describes the 3D unsteady evolution of the fluid flow and temperature fields and local current generation inside the fuel cell. For the gas-diffusion cathodes with water-based electrolyte the water evaporation and the evaporation cooling are incorporated in the model. The developed software can simulate the work of fuel cells with liquid and solid (porous) electrolyte, as well as with fuel being the anode (as in MAFCs). Different examples of numerical simulations are presented. The necessity to include in the model the processes of water evaporation and convective motion of fluid electrolyte for the adequate modeling of FCs performance is shown. Different experimental methods including PIV measurements of convection, bubble diagnostics and controlling in fluid electrolytes, optimization and flaw detection of porous electrodes in DBFCs and metal anodes in MAFCs also discussed and their usability in improving of FC's performance is demonstrated on concrete examples.

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INFLUENCE OF IMPURITIES ON HYDROGEN SORPTION AND DIFFUSION IN Ti-BASED ALLOYS

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The metal hydrides hydrogen storage technology is an important aspect of the development of alternative clean energy sources. An important factor of hydrogen storage materials is fast and reversible hydrogen uptake and release under moderate conditions in combination with low cost. Among Ti-based alloys with B2-structure TiFe alloy is the most promising candidate for hydrogen storage material. In spite of this alloy has fast reaction kinetics its poor activation performance resulting in significant deterioration of hydrogen sorption properties. Several attempts to enhance the rate of the initial activation were made by the partial substitution of the constituent elements by other transition metals such as Ni, Mo, Cr, Co, Cu, Mn, Pd, Zr, V as well as by mish-metals. In the present work, the influence of substitutional impurities on the absorption and diffusion characteristics of hydrogen in TiFe is discussed. The calculations of the minimum energy paths and the transition states for the H diffusion in alloy were performed by the climbing image nudged elastic band (CI-NEB) method. Structural and electronic factors which influence strongly on the hydrogen diffusion barriers in TiFe alloy are analyzed. On other hand even small concentration of H reduces the mechanical strength and may limit some industrial applications of advanced materials. In this connection we consider the influence of the interstitial (B, C) and substitutional (Co, Ni, Pd, Al) impurities on H sorption properties at TiFe grain boundary $\Sigma5$ (310) and corresponding surface as well as on grain boundary cohesion. In order to understand the grain boundary cohesion of materials it is necessary to calculate the Griffith work, because local electronic structure or interatomic interactions contribute indirectly to the fracture properties. It was found that H decreases the surface energies more significantly than the grain boundary energy, which results in decrease of the Griffith work and indicates also the decrease of the strength of the grain boundary. The segregation of H at the GB makes intergranular fracture much easier because the bonding between metal atoms, which are neighbors of H, is weakened. In contrast to H other interstitial impurities (B or C) lead to opposite effect on the Griffith work. Our estimation of the Griffith work for the alloy containing both B and H atoms gives its increase in comparison with undoped alloy but the effect of carbon on the GB strengthening during hydrogenation seems to be negligible. The contributions of the chemical and elastic mechanisms to the binding energies and Griffith work are discussed also. Thus, the analysis of the electronic properties allows us to establish the microscopic nature of the chemical bonding of interstitial impurities at the internal and external interfaces. We demonstrate that such calculations can be a bridge between microscopic features and macroscopic material properties.

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ELECTRON BEAM TECHNOLOGY OF NANOPOWDER PRODUCTION FOR POSSIBLE APPLICATION IN FUNCTIONAL MATERIALS

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Nanopowder production is associated with a number of technological challenges. The most common of existing production methods involve chemicals which can be dangerous and environmentally harmful. At the heart of our process is a method of obtaining powders by the evaporation of the raw material on industrial electron accelerator with power up to 100 kWt and energy 1.4 MeV followed by the cooling the high-temperature vapor and condensation of substance into very small particles (nanoparticles) which then become highly dispersed (nano-size) powders. From fundamental view it can be related with the generation of high-temperature aerosol. The method is universal for a wide range of simple materials, nanopowder is produced in one stage, the technology allows to control the key parameters of finished products and is environmentally friendly. Advantages of the technology result in the advantages of the final products: particles size which ranges from 15 to 200nm can be controlled; small range of particle sizes; since the technology does not involve chemicals, the purity of the product is determined only by the purity of raw materials; the possibility to modify the surface of the particles; the combination of these factors allows the simultaneous control of the four parameters to produce nanopowders that ideally suit to the needs of each application. The nanopowders were tested in various areas, including functional materials.

Up to the moment the following substances had been produced: OXIDES – SiO_2, SiO, MgO, Al_2O_3, TiO_2, Y_2O_3, Gd_2O_3, Cu_2O, iron oxides, oxides of tungsten (in particular, WO_3) and molybdenum (various types), Bi_2O_3, ZnO, METALS - W, Ta, Mo, Co, Al, Fe, Ni, Ag, Cu, Bi and some others, in different atmospheres; SEMICONDUCTORS - Si in nitrogen and argon, nanoparticles and nanowires, and others; NITRIDES - AlN, TiN, including in the form of nanorods; CARBIDES –SiC, including in the form of nanowires, WC; carbon fullerenes and carbon single-wall and multi-wall nanotubes; the core-shell inorganic composite nanoparticles; and other substances in various gas atmospheres.

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ANOMALY OF WATER VISCOSITY BEHAVIOR NEAR THE 273K TEMPERATURE

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It is well known that low-viscosity liquids can be characterized by the Arrhenius temperature dependence of viscosity in the temperature area of the liquid state. However, glass-forming liquids are observed to have a slower dynamics of molecules in comparison to the thermal activation law. Therefore, the nature of the temperature dependence of viscosity is complex. The first peculiarity appears at the temperature (T_a) at which the viscosity starts to display a non-Arrhenius behavior. It can be obviously assumed that the liquid structure changes at T_a, which crystallization and makes the liquid transform to the glassy state. Does this temperature T_a exist in water?

It this study, we simulate a cell containing 6591 water rigid molecules. This cell was constructed by using the LAMMPS molecular dynamics software [1] and the TIP4P/2005 [2] potential with the NPT ensemble. The viscosity is calculated on the basis of the velocity profile of water molecules in two parallel multidirectional streams in the cell [3] by using NVT ensemble.

The results show that the viscosity in the 0ºC-25ºC temperature region is in good agreement with the experimental data, but the value of T_a of water is 0ºC. Below this temperature, the viscosity starts to display a non-Arrhenius behavior. The study of the water structure in the temperature region [240K; 400K] shows that all water molecules are connected by hydrogen bonds and more than 75% of them have at least one “short” hydrogen bond (shorter than the average length of the hydrogen bond). Molecules with “short” hydrogen bonds form instantaneous clusters with sizes ranging from 2 to ~100 molecules. It is found that the number of clusters containing more than 20 molecules grows with a decrease in temperature. These clusters may be the reason for the change in the viscosity behavior at temperatures below 0ºC.

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FIRST-PRINCIPLES DESIGN OF NANOSTRUCTURED MATERIALS FOR EFFICIENT STORAGE OF HYDROGEN

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Carbon, Boron Nitride and Magnesium based nanostructures have been investigated for efficient storage of hydrogen, because of their significant hydrogen adsorption capacity. The higher surface to volume ratios of the nanostructured materials lead to improved adsorption and desorption kinetics for hydrogen storage. First principles density functional theory (DFT) is a viable approach to explore the kinetics of hydrogen by investigating its interaction energy in these nanostructured systems.

We first discuss Mg-based nanomaterials that show impressive gravimetric efficiencies (~7.7 wt %), apart from their low cost and abundant availability. Adsorption in atomic form leads to the chemisorption of hydrogen into the interstitial positions of the Mg atoms within Mg nanoclusters [1] or surfaces. Practical usage of these systems has been hindered because of high desorption enthalpy (~ 0.8 eV/H_2 molecule), which results in an undesirable desorption temperature (> 200^0C) close to the bulk counterpart. However, adsorption in molecular form leads to the physisorption of hydrogen surrounding the Mg nanoclusters [2] or Mg(0001) surfaces. On Mg nanoclusters and Mg(0001) surfaces, the naturally occurring H_2 molecule does not dissociate spontaneously into H-H atom pair, unless some external energy is supplied for its dissociation. This makes molecular adsorption of hydrogen (physisorption) on Mg-nanostructures energetically favorable as compared to the atomic adsorption (chemisorption). In this talk, we shall discuss our DFT based results on the structure, stability and desorption kinetics of H_2 molecules physisorbed on neutral as well as charged Mg_n nanoclusters.

Next we shall discuss another interesting system for Hydrogen storage is hexagonal Boron Nitride (h-BN) sheet, which is isostructural to graphene. On full hydrogenation, this sheet (BHNH) becomes slightly corrugated. By substituting one alkali metal atom, such as Li, in place of H on the BHNH sheet (‘chair’ configuration), it is found that Li becomes cationic and acts as an anchor to adsorb hydrogen molecules via anti-Kubas interaction [3]. The details of the structure, stability and H-storage efficiency of this planar nanostructure will be discussed in this talk. Thus by performing self-consistent DFT calculations along with *ab initio* molecular dynamics, we have tried to establish the suitability of Mg and h-BN based nanomaterials for hydrogen storage.

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THEORETICAL MODELING OF MATERIALS FOR HYDROGEN ENERGY APPLICATIONS

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A growing demand for energy coupled with increasing pollution is forcing us to seek environmentally clean alternative energy resources to substitute fossil fuels. As the sun is our largest and free energy resource available, it could be considered the ultimate renewable energy resource. Among the limited methods for solar energy conversion and utilization, solar water splitting has been considered as the most effective and cleanest way to produce hydrogen. The hydrogen produced can then be used by fuel cells to generate electricity, where water constitutes the only emission. Both problems of hydrogen production and utilization need new materials for successful realization.

Here we discuss different aspects of photoelectrochemical water splitting process that include (i) the non-equilibrium photo-excited charge dynamics in anode material to describe the charge transfer that triggers the photocatalytic event (such as water oxidation or reduction half-reaction) [1,2] and (ii) thermodynamics of oxygen evolution half-reaction on the surface of anode material [3]. Non-equilibrium photo-excited charge dynamics is *ab initio* modeled by the reduced density matrix method in the basis of Kohn−Sham orbitals. Solution for non-equilibrium density of electrons is used for determining the dynamics of formation of charge transfer state on the surface, computing surface photo-voltage, and rates of energy and charge transfer. To design a new material for solid oxide fuel cells we perform versatile computer modeling of Ag atoms interaction with $LaMnO_3$ surfaces. Silver atoms adsorption energies, migration barriers and catalytic effect on the oxygen reduction and dissociation are discussed [4].

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POROUS COORDINATION POLYMERS: FROM SYNTHESIS AND STRUCTURE TO FUNCTIONAL PROPERTIES

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Porous coordination polymers/metal-organic frameworks (PCPs/MOFs) are considered to be promising for the development of the most recent problems in highly selective separation, heterogeneous catalysis, luminescent materials design and others.

Herein we report the synthesis, structure and functional properties of new microporous Li- and Zn-based carboxylates with permanent porosity, interesting guest-dependent luminescence properties and remarkable gas selective sorption properties. Single-crystal to single-crystal formation of different host–guest systems is also investigated. Novel 3D lithium-organic frameworks with rigid carboxylate linkers were obtained. The framework $[Li_{11}(H_2O)_5(Html)_6]$ (H_3tml − 1,2,4-benzenetricarboxylic) is based on undecanuclear Li carboxylate complex. Assembly of these units leads to open structure with pore diameter 7 Å. This impressive unique $\{Li_{11}\}$ fragment is an interesting example of rare lithium polynuclear complexes. Furthermore, the compound is capable of reversible guest exchange process. The photoluminescence properties of this porous compound were shown to depend on the nature of the guest molecules, providing the opportunity for the selective detection of dangerous explosive aromatic molecules.

A unique example of a biporous MOF, $[Zn_4(ndc)_4(ur)_2]$ (ndc = 2,6-naphthalenedicarboxylate, ur = urotropin), with two distinct isolated 1D channels with different chemical interface is considered. The co-existence of different channels by itself broads the host-guest chemistry of such compounds so as the channels dimensions allow the size-selective guest uptake, and the distinctions between chemical behavior of the channels surfaces allows not only size-selective sorption but governed by chemical affinity as well. Such a circumstance makes biporous MOFs prominent for separation purposes. The first example of step-by-step activation of a biporous MOF *via* formation of the intermediate coordination polymer is also considered.

We report the impregnation of the mesoporous MIL-101 structure by nonvolatile strong mineral/organic acids or salts. Such a simple approach affords solid materials with potent proton-conducting properties at moderate temperatures, which is critically important for the proper function of on-board automobile fuel cells. The proton conductivities of H_2SO_4@MIL-101 and H_3PO_4@MIL-101 at $T = 150$ ºC and low humidity outperform any other MOF-based material and could be compared with the best proton conductors. The acid molecules reside in the pores of the host framework and are not removed either by heating or upon any associated changes of the sample hydration while handled in a humid atmosphere.

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PARAHYDROGEN INDUCED POLARIZATION IN CATALYSIS AND MEDICINE

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When parahydrogen (nuclear spin isomer of H_2) is used in catalytic hydrogenations instead of normal H_2, the NMR signals of reaction products and intermediates can be enhanced by 3-4 orders of magnitude and more owing to the phenomenon of parahydrogen-induced polarization (PHIP). It has been shown previously that PHIP can be used to detect reaction products and short-lived intermediates during activation of H_2 by transition metal complexes and clusters in solution even when their concentrations are too low for conventional NMR. The objective of our research is to extend the scope of PHIP applications to heterogeneous H_2 activation processes over solid materials (e.g., heterogeneous hydrogenation catalysts). Potential applications include the in situ studies of H_2 storage and chemical conversion processes, and the production of hyperpolarized fluids for novel MRI applications including the advanced in vivo studies.

We demonstrate that transition metal complexes immobilized on solid supports (silica, alumina, MOFs, polymers) are able to produce strong PHIP effects when parahydrogen is used in hydrogenation of unsaturated hydrocarbons. [1], [2] For materials comprising transition metal nanoparticles (MNPs) supported on porous materials (e.g., Pt/Al_2O_3, Pd/TiO_2), the PHIP effects were found to be sensitive to the MNP size and shape, the nature of the metal and support as well as the strength of their interaction, and the type of substrate used in the reaction. We also demonstrated PHIP effects for several metal oxides and unsupported metals used as hydrogenation catalysts. [3] This provides access to the mechanistic information on the activation of H_2 and hydrogenation of unsaturated compounds over such materials. Further potential extensions of the technique include the use of metal-free materials for activating H_2. [4] In addition to applying PHIP to the studies of materials and the mechanisms of hydrogenation processes, several NMR imaging (MRI) applications of PHIP have been already demonstrated in the literature, including MRI of catalytic reactions in operating model (micro)reactors [5] and biomedical NMR and MRI studies.

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PREPARATION OF METAL-CERAMICS NANO-COMPOSITE FILMS FOR MULTI-FUNCTIONAL PROPERTIES

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Development of the multi-functional film materials such as magnetic-dielectric for wide and high frequency range has been required for a high integration, high functionality and energy saving of the next-generation device. In this research, the nano-composite films which have magnetic nano-particles dispersed in the ceramic matrix were prepared by two kinds of sputtering method. High frequency soft magnetic materials which can be used in all direction, electromagnetic-wave shielding films with heat-resistance at wide and high frequency range, and magnetoelectric multi-functional material at high frequency of GHz-range were synthesized.

The rf-magnetron sputtering system was used to prepare metal (Co) ceramics (TiN, AlN) films. The composite films were deposited onto Si, quartz and Pt/Si substrates with Ar gas at room temperature. The film composition and structure were determined by EPMA-WDS and XRD, relatively. Magnetic property was measured by Vibrate sample magnetometer (VSM) with fields up to 1 kOe. The permeability (μ) was measured by the shielded loop coil method at the frequency from 1 MHz to 3 GHz. Magnetic domain structure of films was observed by Magnetic force microscopy (MFM).

The Co particle size in Co-TiN nano-composite films keeps around 4 nmΦ with the thickness from 510 nm to 920 nm by Scherrer Formula calculation. Typical soft magnetic hysteresis loops of Co-TiN composite films are obtained. The 920 nm film has an in-plane uniaxial magnetic anisotropy (H_k), which results in hard and easy axes of magnetization. The film has the Hk of about 25 Oe, and coercivity as low as 5 Oe. The magnetization at 5 kOe of all films is around 8 kG. The high μ of films is obtained in the films with the thickness from 340 nm to 920 nm. The resonance frequency of all the films is around 1.5 GHz. Moreover, the films show the high magnetic loss absorption around 1.5 GHz, which is promising for using in various noise-suppress applications.

The Co particle size in Co-AlN nano-composite films were 3-5 nm in diameter. The in-plane magnetization curve of 80 at.%Co-AlN film is completely independent along the direction of applied field, which indicates that the film is magnetically isotropic for all in-plane direction. The clear and sharp peak of μ' is observed at fr in the vicinity of 1.2 GHz. It is practically available that the resonance frequency of magnetically isotropic Co-Al-N film can be widely changed the frequency range from 2.4 to 10 GHz.

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Oral Presentations

ELECTROCHEMICAL PROPERTIES OF Ca DOPED PRASEODYMIUM NICKELATE OXIDE CATHODES IN CONTACT WITH $Ce_{0.8}Sm_{0.2}O_{1.9}$ ELECTROLYTE

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Solid oxide fuel cells (SOFCs) have the potential to be one of the cleanest and most efficient energy technologies for directly converting chemical fuels to electricity. The production of economically competitive SOFC systems requires development of the materials and the fabrication processes to enhance the system performance, lifetime and reduce its cost. The minimization of resistance to the oxygen reduction reaction (ORR) at the cathode, which contribute the most to performance degradation and efficiency loss in the existing SOFCs, is a fundamental step for the real application of SOFCs on a large scale [1]. The development of a cathode that is stable against CO_2 present in the atmosphere still remains a challenge. Cathode materials with a perovskite structure such as $La_{1-x}Sr_xCo_yFe_{1-y}O_{3-\delta}$ and $Ba_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$, commonly used in intermediate temperature SOFCs contain strontium and barium, which form carbonates in CO_2 containing air, blocking the access of oxygen to the catalytic surface and significantly decreasing the cathode performance over time [2]. Pr_2NiO_4 have attracted much attention as promising cathode materials for the intermediate temperature SOFCs, as far as it possesses a sufficiently low ASR value [3], but it is not thermodynamically stable at working SOFC's conditions. Doping with Sr dramatically improves thermal stability of Pr_2NiO_4, but can be a reason for cathode degradation in CO_2 containing atmosphere.

The present work focuses on the electrochemical performance of the bilayer cathodes with $Pr_{2-x}Ca_xNiO_{4+\delta}$ (x=0-0.5) functional layer and $LaNi_{0.6}Fe_{0.4}O_{3-\delta}$ current collector in contact with a $Ce_{0.8}Sm_{0.2}O_{1.9}$ electrolyte. The effect of the sintering temperature and Ca content on the polarization resistance of the electrodes has been studied by an impedance spectroscopy method in comparison with $Pr_{1.7}Sr_{0.3}NiO_{4+\delta}$ electrode.

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IONIC CONDUCTION IN SINGLE-CRYSTALLINE $BaTiO_3$ AND $BaTi_2O_5$

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$BaTi_2O_5$ is a lead-free ferroelectric material with the Curie temperature (T_c) of 748K. The piezoelectric constant (e_{22}) estimated by the first principle study is 2.02 C/m^2, which is comparable with that of $BaTiO_3$ (e_{33} = 5.3 C/m^2). It is, however, difficult to polarize $BaTi_2O_5$ due to the high leakage current. $BaTiO_3$ was reported as an oxygen ion conductor. Glower et al. reported the predominant ionic conduction in $BaTiO_3$ at T = 373K–573K by measuring the electromotive force of concentration cells [1]. We have synthesized single crystals of $BaTi_2O_5$ and investigated their electrical conductivity and permittivity by impedance measurements. Impedance spectroscopy is a useful method to reveal the ionic conduction. In this study, the ionic conduction in single-crystalline $BaTiO_3$ and $BaTi_2O_5$ was studied by impedance measurements over a wide frequency (10^{-2} Hz–10^6 Hz) and temperature (298K–973K) range.

Single-crystalline $BaTiO_3$ was purchased from MTI Corp., USA (5×5×1 mm^3). $BaCO_3$ (99.99%, Sr = 6.67 ppm) and TiO_2 (99.99%) were source materials for the synthesis of single-crystalline $BaTi_2O_5$ by a floating zone (FZ) method in the O_2 atmosphere. Blocking electrodes were prepared using gold paste, which was applied on both faces of $BaTiO_3$ and $BaTi_2O_5$, and fired at 1073K for 3.6 ks. Their electrical conductivity and permittivity were examined by impedance spectroscopy (Solartron 1260 and 1296) at $f = 10^{-2}$ Hz–10^6 Hz and T = 298K–973K. The samples were kept for 3.6×10^3 s prior to impedance measurements to be equilibrated to ambient temperature. Impedance specta were fitted to equivalent circuits using ZView software.

The T_c of single-crystalline $BaTiO_3$ and $BaTi_2O_5$ were 400 K and 750 K, respectively, which were consistent with the literature. The dielectric loss (tanδ) of $BaTiO_3$ increased drastically above 650 K, while the tanδ of $BaTi_2O_5$ increased above 900 K. Complex impedance plane plots of $BaTiO_3$ and $BaTi_2O_5$ showed a spike at low frequencies at T = 548K–648K and T = 573 K–673K, respectively. The low-frequency spike indicated the ionic conduction. Impedance spectra of $BaTiO_3$ were fitted to an eqivalent circuit consisiting of two parallel RC elements in series and the Warburg impedance. The electrical conductivity (σ) of $BaTiO_3$ was two orders of magnitude higher than that of $BaTi_2O_5$. The activation energy (E_a) of the σ of $BaTiO_3$ was 1.8 eV at T = 648K–740K, which was 0.8 eV higher than that at T = 473K–648K. The E_a of $BaTi_2O_5$ were 0.9 eV in the ferroelectric phase and 1.5 eV in the paraelectric phase, respectively.

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MOLECULAR DYNAMICS SIMULATION OF IONIC CONDUCTIVITY IN YTTRIA-STABILIZED ZIRCONIA: THE ROLE OF PHASE COMPOSITION

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Yttria-stabilized zirconia, $[ZrO_2]_{1-x}[Y_2O_3]_x$, is a well-known material, which is widely used as electrolyte in solid oxide fuel cells because of its good ionic conductivity. The ability of this material to conduct oxygen ions results from the doping of ZrO_2 by another oxide, such as Y_2O_3. As the Zr^{4+} ions are replaced in the cationic sub-lattice by Y^{3+} ions, vacancies emerge in the anionic sub-lattice due to the electroneutrality condition.

Molecular dynamics (MD) simulations were carried out to study ionic transport in cubic and tetragonal $[ZrO_2]_{1-x}[Y_2O_3]_x$ solid oxide (yttria-stabilized zirconia, YSZ) at 1373 K, 1673 K, and 1973 K for samples containing up to 12 mol.% of Y_2O_3. Calculated oxygen diffusion coefficients were averaged over twenty random cation distributions for each YSZ composition to ensure correct evaluation of the dependence of diffusivity on yttria content. The data obtained from MD simulations were used in conjunction with experimental phase diagram (Figure 1) to estimate the oxygen transport performance of YSZ samples, including those containing more than one phase. For heterogeneous samples (T+C) the quantities of coexisting phases were obtained from the phase diagram using the lever rule.

The dependencies of oxygen diffusion coefficients on yttria content for cubic and tetragonal YSZ were essentially similar. The phase diagram-based approach used in the present work for evaluating the conductivity of heterogeneous YSZ samples demonstrated a significant improvement over single-phase predictions (Figure 2).

The oxygen diffusion activation energies were calculated for all the configurations (Figure 3). Simulation results are in good agreement with available experimental data. The comparison of calculated diffusion activations energies of cubic and tetragonal phases for YSZ samples containing from 4 to 7 mol.% Y_2O_3 suggests that the mechanisms of diffusion in both polymorphs are essentially similar.

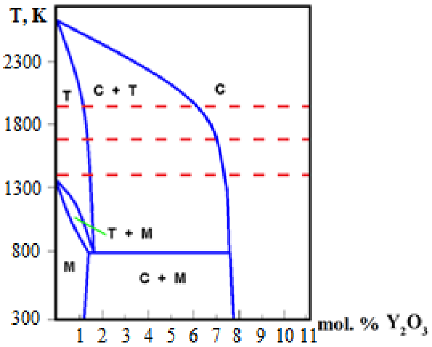

Figure 1. Phase diagram of yttria-stabilized zirconia. C – cubic phase, T – tetragonal phase, M – monoclinic phase.

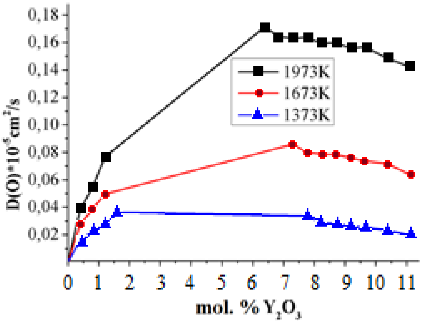

Figure 2. Diffusivities dependence of yttria content.

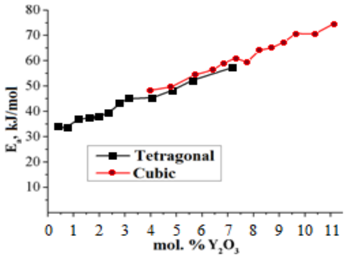

Figure 3. The activation energies of cubic and tetragonal YSZ.

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POROUS NICKEL-ALUMINIDES AS KEY ELEMENTS OF POROUS RADIANT BURNERS

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Premixed gas combustion in porous radiant burners is an efficient method of thermal power generation. In comparison with conventional open-flame burners, the porous burners exhibit higher radiative-energy efficiency and comparatively low NOx emission. The principle of operation of a porous radiant burner relies on burning of a gaseous fuel - air mixture inside a porous medium made from a heat-resistant material. The porous material (matrix) during combustion heats up to 1000 - 1800 K and radiates in the IR region. Porous matrices are commonly made from ceramics based on alumina, zirconia or silicon carbide. Significant disadvantages of ceramic material are brittle fracture under the influence of a temperature gradient as well as its low thermal conductivity. These issues constrain the possible regimes of porous radiant burner operation. An alternative way is the use of metallic materials. Due to their plasticity and high thermal conductivity, porous metals are resistant to thermal and mechanical stresses, that allow quick start and tuning of combustion modes to provide high efficiency of the burners. Promising porous materials for gas-burner applications are intermetallic NiAl-alloys capable of operating in oxidizing media at the temperatures up to 1800 K. Combustion synthesis provides a comparatively simple way of producing NiAl-materials. Using the heat of an exothermal reaction between the components of a specially prepared powder mixture, it is possible to sinter a porous medium with predetermined geometry, composition and structure in a single technological process.

Using the combustion synthesis technique, a wide range of porous nickel-aluminum matrices (phase composition: Ni_3Al+NiAl) for porous radiant burners were developed – spherical (diameter: 30-200 mm), cylindrical (diameter: 15-300 mm, length up to 1000 mm or more), planar (side of the rectangle up to 500 mm or more). Range of wall thicknesses of synthesized items was 3 - 30 mm. Porosity structure of the matrices might be adjusted in wide range (Fig.1): average frame element 10-1000 μm, average gas transport channel 2 – 500 μm.

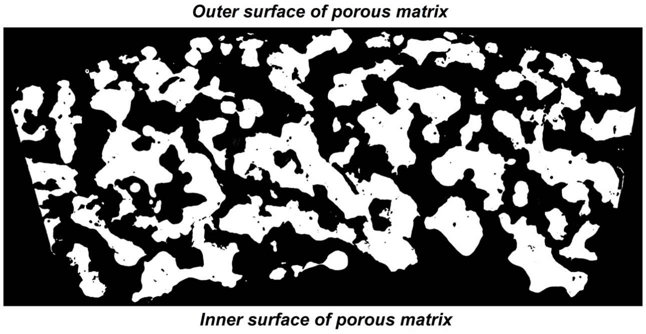

Figure 1. Example of porous structure of the NiAl matrix – cross section of spherical matrix with wall thickness 5 mm. Black region – pore space, white region – Ni-Al material.

Our experiments on methane-air combustion inside synthesized porous matrices (spherical or cylindrical) have shown that up to 70% of combustion energy transformed into the infrared flux [1]. Total power density of 60 W/cm^2 was obtained for burners in this case. Analysis of combustion products showed low level of NOx exhaust (33÷36 mg/m^3).

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HYDROGEN CLATRATE HYDRATE: EQUATION OF STATE AND SELF-PRESERVATION EFFECT

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The thermodynamic properties of the hydrogen clathrate hydrate with cubic structure II and hexagonal ice I_h have been investigated using both lattice dynamics and molecular dynamics methods with the aim of predicting the existence of the self-preservation phenomenon in the hydrogen hydrate. The statistical thermodynamics model with modifications describing host lattice relaxation, guest-guest interactions and the quantum nature of guest behavior in clathrate hydrates has been applied to calculate the thermal expansion of the volume for both systems. It has been shown that hydrate phase immersed in the ice phase are stable below the three-phase ice–hydrate–gas equilibrium pressure. The calculations show that the hydrate remains in a stable region within the phase diagram because the thermal expansion of the hydrate phase is limited by the thermal expansion of ice. The differences in thermal expansion should lead to the self-preservation effect with the application of additional pressure on the hydrate phase. From a practical point of view this effect can be used for the storage and transport of hydrogen in the hydrate form.

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KINETIC INHIBITION OF HYDRATE FORMATION BY WATER-SOLUBLE POLYMER REAGENTS

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Kinetic hydrate inhibitors are widely used in oil and gas industry for preventing gas hydrates from plugging oil and gas production wells and pipelines. To assess the possibility of using specific reagents in oil and gas industry laboratory studies are conducted. The most widely used method is based on the use of units of the “rocking cell” type, which make it possible to study the kinetics of hydrate formation for different hydrate-forming systems under different conditions.

In this paper the commercially available kinetic hydrate inhibitors Luvicap 55W and Luvicap EG were studied. Samples of these reagents were supplied by BASF. The high-molecular weight compounds (HMC) that were used in the experiments were obtained from these reagents by vacuum distillation of the solvent and lyophylic drying of the solid residue. Distilled water was used to prepare aqueous solutions of the HMCs. As the model gases we used methane forming hydrate CS-I and gas mixture 95.6 % CH_4 +4.4 % C_3H_8 (% mol.) forming hydrate CS-II. All experiments were conducted in the pressure range 4 – 12 MPa, in the temperature range 273.2 – 295.2 K, in the presence of 0.5 % (wt.) Luvicap EG or Luvicap 55W in aqueous phase.

Experiments on the kinetic inhibition of hydrate formation were conducted on the six-cell unit Sapphire Rocking Cell RCS6 (made by PSL Systemtechnik). The apparatus consists of a thermostatic bath in which six sapphire cells are placed. Each cell has a volume of 22 cm^3 and can operate at a maximum pressure of 20 MPa. The cells are placed on a mobile axes that can be rocked at angles between 0° and ±45° and with frequencies of 0 – 0.33 s^{-1}. Each cell is equipped with a temperature sensor Pt100 and a pressure sensor Tecsis p3276b. We used the method of cooling at a constant rate (1 K/h) to evaluate the efficiency of kinetic inhibition.

The results of our experiments say that initial pressure doesn’t effect on the maximum supercooling degree before hydrate onset in system with and without kinetic inhibitor. When present at a concentration of 0.5 wt. %, reagents Luvicap 55W and Luvicap EG can inhibit the formation of CS-I hydrates when the degree of supercooling is no greater than 6 – 7 K and CS-II hydrates when the degree of supercooling is no greater than 13 – 14 K.

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THEORETICAL MODELING OF GAS HYDRATE EQUILIBRIA FOR THE GAS MIXTURES CONTAINING CO_2, N_2, AND CH_4

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Over a wide pressure-temperature range, we have perform atomistic-level theoretical modeling of structural, dynamical, and thermodynamic properties of various hydrates with differing structures, using our original approach. It is shown that carbon dioxide content in hydrate exceeds its content in the gas mixture.

The formation pressures of double hydrates have been calculated as a function of the methane content in the gas mixture at temperatures corresponding to equilibria 'ice – gas–hydrate' and 'water – gas–hydrate'. It was found that at decreasing temperature the influence of the gas mixture composition on the hydrate formation pressure weakens. Calculations of the hydrate composition in dependence on the gas phase composition have been performed. It was shown that the formation pressure of double methane – carbon dioxide hydrates is the linear function of methane (carbon dioxide) content in the hydrate.

It is demonstrated that carbon dioxide can replace methane in the hydrate phase at temperatures and pressure typical for the permafrost zone, i.e. at temperatures below 0°C and low pressure. It is shown also that the replacement can occur at conditions of ocean continental slopes, i.e., at temperatures above zero degrees and pressures above 300 atm.

The authors are thankful for support to the supercomputer center HITACHI SR11000-K2/51 of the Institute for Materials Research of Tohoku University (Sendai, Japan) and to NEDO (New Energy and Industrial Technology Development Organization) organization.

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A NEW METHOD OF INTENSIFYING THE PROCESS OF HYDRATE FORMATION

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The high-speed hydrodynamic processes occurring at explosive boiling, accompanying the mixing of liquids with different boiling temperatures, were studied experimentally. The scientific and practical importance of studying the problem of explosive boiling is evident, because understanding the thermohydrodynamic processes and studying kinetics of the decay of a metastable state can contribute to the creation of the new high-intensity technologies in various industries.

The hydrodynamic processes, occurring at injection of a jet of cryogenic liquid into water, were recorded at a high speed; at that, the structure and stages of this process were revealed. It can be seen in the frames that active turbulent mixing is observed at the external boundary of a vapor cylindrical bubble, and this should be taken into account at developing the mathematical model of the process.

The technology of liquid nitrogen supply through the original injector was developed. The construction of this injector and principle of its operation were patented (RF patent No.2507438).

The experimental results prove the achievement of pressure jumps required for gas hydrate formation. The maximal obtained pressure was 53 bar. At that, the rate of pressure increase was 567 bar/s. The results obtained are aimed at investigating the new method of gas hydrate production based on the shock-wave technique.

The work was carried out with the financial support of RF Government grant for promotion of scientific research conducted under the guidance of leading scientists № 14.B25.31.0030 (the leading scientist – Y. Kawazoe, FSBES The Kutateladze Institute of Thermophysics, SB RAS).

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THEORETICAL DFT STUDY ON STRUCTURE AND CHEMICAL ACTIVITY OF COMPLEX MODIFIED CATALYSTS

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Transition metal oxides, modified zeolites as well as transition metals are of particular interest because of their well-defined framework structures, the wealth of experimental studies and their technological and industrial importance as catalysts, adsorbents, supports, etc. Metal-organic framework (MOF) materials with their well-defined porous and channel structures have tremendous potential in chemistry and physics as well as in variety applications in catalysis fields. They can be used as gas storage and gas separation materials, molecular sieves, sensors and many others.

In present talk we would like to bolster advantages of the cluster approach (being relatively very simple but complementary to other periodic slab model calculations) in proper modeling of extended systems as well as in understanding of the molecular level interactions (or transformations) at the exposed crystalline surfaces. At first, an insight is given to clear the origin of bands appeared at CO stretching vibrations and active site nature of Pt/zeolite catalysts. Next, by modification of alternate metal oxide connectors with increased basicity linked to organic linkers into extended metal-organic framework (MOF) networks, some solution is given to stabilize and store hydrogen molecule(s) in new IRMOF structures. This approach has been then applied to mimic a finite-size carbon K4 structure (three-fold coordinated and three-dimensional) created by cutting a piece from a large crystalline structure. Our DFT calculations indicate possible ways to create, stabilize, and characterize this new carbon K4 structure with its decagonal rings and very high symmetry.

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ELECTROKINETIC DEVICES BASED ON SILICON MICROCHANNEL MEMBRANES

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Electrokinetic phenomena are widely used in modern nano/microfluidics. Electroosmotic pump and electrophoretic transport have its advantages on smaller scale devices due to ability to manipulate micrometer and even nanometer size objects [1, 2]. Streaming potential/current effect is applied in various sensing devices [3, 4].

We use silicon microchannel membrane as base element of different microfluidic devices. These membranes are produced by technology developed in our group [5]. The production technology includes such main operations as photolithography, electrochemical etching of silicon and silicon surface oxidation. This technology allows membranes to be obtained with ordered array of channels 2.5 to 30 microns in width and square cross section.

Electroosmotic pump and streaming potential sensor are opposite effect devices. They have been designed in the same way – silicon microchannel membrane covered by silica with two platinum electrodes placed near opposite sides of the membrane. If potential difference is applied to electrodes, electrolyte flow appears through the channels of the membrane and we get a pump. There is one main disadvantage of using electroosmotic pump as bubbles are formed due to electrolysis of water. We have designed a pump with performance depending on orientation of asymmetric membrane and suggested to use alternating current supply to avoid bubbles formation.

On the other hand, if we force electrolyte to flow through channels of the device - potential difference arises on the electrodes. Furthermore, this voltage depends on flow rate through the membrane - so we have a flow rate sensor. Preliminary fabricated device has shown quite linear dependence of voltage on pressure difference, suitable response time and sufficient sensitivity.

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HIGHLY-DISPERSED 1D AND 2D CHALCOGENIDES AND DECORATION OF THEIR SURFACES BY METAL NANOPARTICLES

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In the last few years preparation of nanosized one- and two-dimensional inorganic materials attracted wide attention due to their improved electronic, optical, catalytic properties etc. To note, there are many scientific reports demonstrating them as new materials for solving hot energy problems. [1-2] Two-dimensional layered chalcogenides showed as high-effective catalysts for water splitting (hydrogen evolution reaction), good anode and cathode materials in Li-ion batteries, etc.

Decorating the surface with nanoparticles of different types is an effective way to functionalize a material and to bring new and enhanced properties for many areas such as energy storage, catalysis and surface enhanced Raman spectroscopy devices. Composites based on highly-dispersed compounds can be prepared by so called *in situ (1)* and *ex situ (2)* processes, where the deposition of nanoparticles occurs in the presence of the dispersed compound (1) or the pre-synthesized colloid of nanoparticles are mixed with dispersed compound (2). In this report we present a short review of how composites of this type can be prepared and how they can solve hot energy problems. Here we also report our own results which we achieved in the preparation of compounds of this type. Using liquid-phase techniques for exfoliation of bulk compounds and *in situ* deposition of nanoparticles, we prepared a number of composites based on 2D materials, in particular, few-layer graphene, graphene oxide, transition metal dichalcogenides (MoS_2, $MoSe_2$, WS_2, WSe_2, etc), and 1D VS_4 [3] with metal nanoparticles (Ag, Au, Pt, Pd, Co, Fe, Ni), and the prepared composites were investigated by a set of methods. We present also layered transition metal trichalcogenides (NbS_3, $NbSe_3$, TaS_3) as another example of dispersed matrices for synthesizing new composites. We have shown that these crystal compounds form colloidal dispersions in polar media, and carried out study of colloid properties of these dispersions [4].

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MODERN AB-INITIO CALCULATIONS BASED ON TOMAS-FERMI-DIRAC THEORY WITH QUANTUM, CORRELATION AND MULTI-SHELLS CORRECTIONS

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Thomas-Fermi theory (TFT) is an approximate method, which is widely used to describe the properties of matter at various hierarchical levels (atomic nucleus , atom, molecule , solid , etc.). Special development achieved using THF to the theory of extreme states of matter appearing under high pressures, high temperatures or strong external fields. Relevant sections of physics and related sciences (astrophysics, quantum chemistry, a number of applied sciences) and determine the scope of TFT. Popularity TFT is related to its relative simplicity, clarity and versatility [1].

The latter means that result of the calculation by TFT applies immediately to all chemical elements: the transition from element to element is as simple scale transformation. These features make it highly convenient tool for qualitative and, in many cases, and quantitative analysis. TFT was originally proposed by Thomas and Fermi to describe the electron shell of a heavy atom, which is characterized by a relatively uniform distribution of the electron density. TFT is the semi-classical (WKB) limit in relation to self-consistent Hartree field equations, and therefore modification of this model are associated with a more detailed account of the correlation, exchange, quantum and multi-shell effects.

Initial approximate nature of TFT has a dual nature. Remain outside the model, firstly, correlation effects, reflecting the inaccuracy of the Hartree method and the associated self-consistent difference (average) true interaction from the true physical interaction . Secondly, in THF quantum effects are not considered responsible approximate nature of the semi-classical description of the atom. The report examines the theory of these effects, allowing to find the limits of applicability of TFT in its original form and generalize the model beyond the scope of its applicability .

The presence of correlation corrections caused by difference of self-consistent Hartree field of the actual field inside the atom. These corrections are the result of the anti-symmetry of the electron wave functions and are interpreted as the exchange correlation effects. Additionally, appear also the effects of the power correlation. We begin by considering the effects of correlation, which in turn are divided into two classes. This is primarily the effects of statistical correlation (exchange effects), describing the effect of the Pauli principle on the interaction of particles. Electrons with parallel spins are hold at a greater distance from each other than in the singlet state, and the radius of such a correlation coincides with the de Broglie wavelength of an electron.In TFD introduced accounting Dirac correlation effects [1], this expansion has been called the theory of Thomas-Fermi-Dirac (TTFD). The report shows that the total energy of the electrons can be expressed in terms of the spatial dependence of the electron density according to the Thomas-Fermi-Dirac theory.

Quantum corrections arise from the use of the semiclassical formalism and reflect the presence of non-local electron density communication to the potential in consequence of the “uncertainty principle”.

Multi-shell effects reflect irregularities physical quantities due to the discrete energy spectrum, but in the case of the continuous spectrum of these effects may occur as a result of interference of de Broglie waves and allow the model to take into account the shells structure of the atom [1].

Software implementation of TTFD and calculations (for example, rare gas atoms) taking into account quantum, correlation and muilti-shell corrections showed that the this corrections really lead to a rapprochement and converge TTFD results with experimental data, and also the results obtained by the Hartree-Fock approximation. Total energy calculations by TTFD, Hartree-Fock and experimental data are shown in the summary table in the presentation of the report.

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MICROSTRUCTURAL FEATURES OF DENSE AND POROUS MATERIALS PRODUCED IN SYSTEMS EXPERIENCING PARTIAL CHEMICAL TRANSFORMATIONS DURING SPARK PLASMA SINTERING

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The main advantages of Spark Plasma Sintering (SPS) are rapid heating of powder compacts, fast and efficient consolidation along with controllable grain growth, and flexibility of materials design in terms of chemical composition and architecture. In this presentation, we will review our current activities in the area of materials synthesis and consolidation by SPS in partially reacted systems. In the first part of this talk, the SPS behavior and phase formation of the Ni-15 at.% W alloy will be discussed. We have found that the phase composition and microstructure of the sintered compacts depend on the phase composition of the initial Ni-W alloy. Moreover, the character of the interaction between the surface of the compact and the protective graphite foil during SPS is different for a Ni-W powder mixture and a Ni(W) solid solution produced by mechanical alloying. The microstructure of regions formed as a result of diffusion of tungsten into nickel and carbon into Ni(W) during SPS have been thoroughly analyzed. Based on these results, we will discuss the formation of gradient structures at different length scales as a feature inherent to the SPS-consolidated materials. In the second part, we will show the possibilities of producing multiphase porous metallic materials by conducting partial chemical transformations during low-pressure or pressure-less SPS. A material redistribution effect within the volume of the compact at the scale of the particle size will be demonstrated using a mixture of Fe and Al powders with micron-sized spherical particles, which also appears to be suitable for studying SPS mechanisms by analyzing the contact formation between dissimilar materials. Examples presented in this work show that different metastable phase compositions can be obtained in the SPS-consolidated materials as a result of diffusion or incomplete chemical reactions. Densification and chemical reactions do not always coincide making it possible to densify partially reacted systems or obtain porous multiphase structures.

Studies of the phase formation in Ni-W-based materials during Spark Plasma Sintering are conducted within the framework of the Collaborative Project of Fundamental Research between the National Academy of Sciences of Belarus and the Siberian Branch of the Russian Academy of Sciences, Russian Federation, 2015-2017 (Project N5).

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SYNTHESIS AND OPTICAL PROPERTIES OF SILVER THIN FILM COATED BY FLOUROPOLYMER

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Nanomaterials based on noble metalls have unique properties interested for different application. Electronic structure of silver nanoparticles determine particular optical property, named Surface Plasmon Resonance (SPR). Plasmon resonance is the nonliner response on visible range light, resulting to intensity absorbing and scattering. It is important phenomene for biomedecine, nonlinear optics and solar energetics [1-3]. The character of reasonance peak may be contolled by nanostructure shape, size and concentration. The important role plays the matrix material surrounding the metal nanoparticles. In this work the use of silver nanoparticles deposited in the fluoropolymer matrix was offered. Fluoropolymer influences on optical properties of particles, forbids its coagulation and protects from active environment.

In this work the composites of silver nanoparticles with fluoropolymer (PTFE) was synthezed in two-step process. At the first stage silver nanoparticles were deposited on various substrates (glass, fused silica and silicon) by vacuum gas-jet method. By varying temperature and pressure of vapor source the spherical nanoparticles with different size and surface concentration were obtained. At the second stage silver nanoparticles thin film was covered with PTFE by Hot Wire CVD (HWCVD). PTFE film did not influence on particles geometry and had thickness around 40 nm.

The surface morphology of obtained material was studied by the method of the scanning electron microscopy. The average size of particles changed from 10 to 50 nm depending on synthesis conditions. The optical properties of synthezed samples were examined by absorption spectroscopy. The position of resonance peak shifted from 470 to 660 nm with increasing of particles size. After PTFE covering the minimum position was shifted to short wavelanght range. The results of this research are of interest in the production of coatings for solar cells, sensors and other electronic devices.

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THREE-DIMENSIONAL BICONTINUOUS POROUS GRAPHITE GENERATED IN LOW TEMPERATURE METALLIC LIQUID

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Recently, electrode materials for electrochemical devices, such as Li ion batteries, fuel cells, and electric double-layer capacitors have been extensively studied to improve their device performance. Carbon black (CB) is commonly used for electrode materials, and has a variety of advantages, such as high specific surface area, productivity, and relatively low cost. Nevertheless, the device performance of CB for electrode materials in electrochemical devices has not met expectations because CB has problems such as high electrical resistivity and low durability owing to its low crystallinity. Our research group recently developed a novel dealloying technique using metallic melts as the dealloying medium in place of the acid/alkali aqueous solution of the conventional dealloying method. With this method, three-dimensional bicontinuous porous (3Dbp) metals and metalloids with meso–macro pores, such as Ti, Nb, Si, Fe, Cr, and ferritic stainless steel, which have not been prepared by the conventional method, have been successfully fabricated. This novel dealloying method is expected to produce 3Dbp-carbon with meso–macro pores, and thus 3Dbp-graphite with high specific surface area after the following graphitization process

3Dbp-graphite can be prepared by dealloying Mn from Mn-C alloy in Bi melt. Binary Mn-C alloy ingots with nominal composition of $Mn_{85}C_{15}$ (at.%) were prepared by high frequency induction melting using pure Mn, C elements under the Ar atmosphere. The ingot was broken into powders by hammer and used as a precursor. Pure Bi in a carbon crucible was heated inductively at a constant temperature of 1073K in a He atmosphere. The precursor was immersed in the Bi melt for 10 min. After this dealloying process, the specimens were etched by the nitric acid aqueous solution to remove Bi, Bi-Mn phases adhered to specimens for 4 hours at room temperature. XRD, SEM, EPMA, BET and TEM results showed that 3Dbp-graphite constructs a three-dimensional connected structure. The Mn of precursor and Bi are found to be well removed. The specific surface area of 3Dbp-graphite was 184.8 m^2g^{-1}. The crystallinity of 3Dbp-graphite was increased after graphitization at 2773K for 2 hours. The specific surface area of 3Dbp-graphite moderately decreased from 184.8 to 117.6 m^2g^{-1} with graphitization at 2773 K. Nevertheless, the total pore volume is almost the same value (~0.8 cm^3g^{-1}) as those of the other graphitization condition. This indicates that the 3Dbp-graphite is a good candidate for many electrochemical device by electrode material.

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PREPARATION OF Sr–Ti–O FILMS ON POLYCRYSTALLINE AlN SUBSTRATES USING LASER CVD

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Compounds in Sr–Ti–O system have been attracting much attention since their various applications. $SrTiO_3$ is a promising candidate for the usage of electric devices because of its high dielectric constant. It is also known as a wide-gap photocatalytic material (band gap: 3.2 eV). TiO_2 has been widely studied as an efficient photocatalyst. $SrTiO_3$ / TiO_2 nanocomposite is expected to be widely used since their enhanced photocatalytic property and chemical stability. We prepared Sr–Ti–O films on polycrystalline AlN substrate by laser CVD. Effects of Ti mole fraction in vapor (R_{Ti}) and deposition temperature (T_{dep}) on the phase composition, orientation, microstructure and deposition rate of the films were investigated.

Sr–Ti–O films were prepared on AlN substrates. An Nd:YAG laser (wavelength: 1064 nm, output: 10–150 W) was employed. The substrate was heated on a heating stage at a pre-heating temperature of 873 K. The $Ti(O\textit{i}Pr)_2(dpm)_2$ and $Sr(dpm)_2$ were used as precursors. The vaporization temperatures were held at 453–473 K and 573 K, respectively. Ar and O_2 were used as the carrier and reaction gases, respectively. The gas flow rates of Ar were 50 sccm for each precursor. The gas flow rate of O_2 was 100 sccm. The total pressure in the CVD chamber was held at 800 Pa. The deposition was conducted for 600 s.

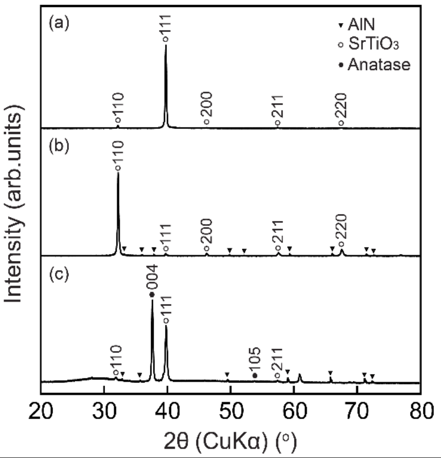

Fig. 1 XRD patterns of Sr–Ti–O films prepared at various T_{dep} and R_{Ti}: (a) 950 K and 50 mol%, (b) 900 K and 67 mol%, and (c) 910 K and 80 mol%.

Figure 1 shows the XRD patterns of $SrTiO_3$ films prepared at various T_{dep} and R_{Ti}. At T_{dep} = 950 K and R_{Ti} = 50 mol% (Fig. 1(a)), a $SrTiO_3$ film with significant (111) orientation was obtained. At T_{dep} = 900 K and R_{Ti} = 67 mol% (Fig. 1(b)), an $SrTiO_3$ film with significant (110) orientation was obtained. At T_{dep} = 910 K and R_{Ti} = 80 mol% (Fig. 1(c)), a mixture of (111)-oriented $SrTiO_3$ and (001)-oriented anatase TiO_2 film was obtained.

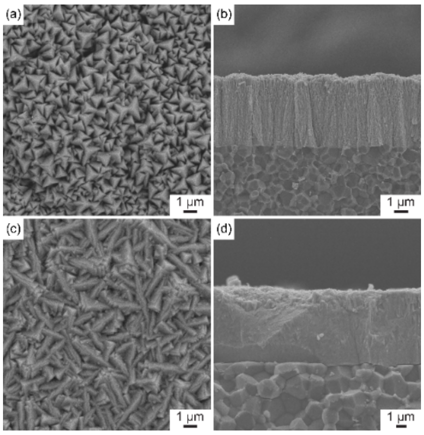

Fig. 2 SEM images of (a, b) (111)-oriented and (c, d) (110)-oriented $SrTiO_3$ films.

Figure 2 shows the surface and cross-sectional SEM images of (a, b) (111)-oriented $SrTiO_3$ film prepared at T_{dep} = 960 K and R_{Ti} = 50 mol%, and (c, d) (110)-oriented $SrTiO_3$ film prepared at T_{dep} = 900 K and R_{Ti} = 67 mol%. The (111)-oriented $SrTiO_3$ film shows a surface with pyramidal grains and a cross-section with columnar grains (Fig. 2(a, b)). The (110)-oriented $SrTiO_3$ film shows columnar structured grains with elongated roof-like caps and a dense cross-section (Fig. 2(c, d)).

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Young Reports

SIGNIFICANCE OF THE DISPERSE MEDIUM IN THE NUCLEATION PROCESS OF METHANE HYDRATE IN WATER-IN-OIL EMULSIONS

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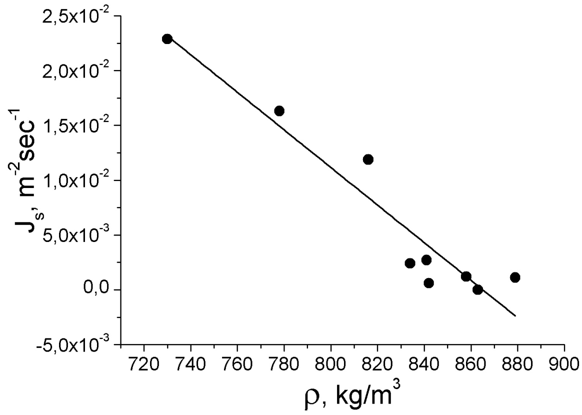

One of the reasons for permanent interest to gas hydrates is the prevention of gas hydrate plug formation in pipelines used in the oil and gas industries [1]. Nucleation theory, in application to gas hydrates, was considered in detail in [2, 3]. It is also known that, in some cases, crude oil contains natural kinetic inhibitors and anti-agglomerants (asphaltenes, resins, naphthenic acids) [4, 5]. Analysis of published data shows that systematic studies of hydrate nucleation processes in water-in-oil emulsions have not been carried out to date. In this work, we present the first results of our studies of the process of methane hydrate nucleation in the water-in-crude oil (or model liquid) emulsions [6, 7]

The figure demonstrates that the nucleation rates tend to decrease with an increase in the density of oil taken as continuous phase for emulsions. However, it is not revealed a direct correlation between the content of asphaltenes and resins and nucleation rates. It appears most probable that the observed regularities are related to the limitation of methane diffusion to water surface. In general, the results obtained herein point out to hindered nucleation of the methane hydrate and ice in the corresponding emulsions and to the individual character of the disperse medium.

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PHASE EQUILIBRIUM FOR CLATHRATE HYDRATE FORMED IN METHANE + WATER + ETHYLENE CARBONATE SYSTEM

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The equilibrium conditions of methane hydrate in the presence of additive of ethylene carbonate ($C_3H_4O_3$) in aqueous solutions were experimentally measured in this study. Three-phase equilibrium conditions V-Lw-H (liquid water-vapor-hydrate) were determined by the isochoric method. The hydrate formation/dissociation experiments were performed in a Gas Hydrate Autoclave GHA350. New experimental results are reported for pressures ranging from 4 to 16 MPa and for mass fraction of ethylene carbonate ranging from 0.05 to 0.25 (0.011 to 0.064 for mole fraction). It is demonstrated that the ethylene carbonate additive has a inhibition effect on the formation of methane hydrate. The structure of methane hydrate with this additive was determined using the Clausius-Clapeyron equation. The effect of ethylene carbonate on methane hydrate formation conditions was compared with that of cyclopentanone (C_5H_8O). Ethylene carbonate has the structural formula close to cyclopentanone. The difference between them is that in the molecule of ethylene carbonate carbonyl carbon connected with two oxygen atoms, whereas in the molecule cyclopentanone carbonyl carbon connected with two carbon atoms. Despite similarity of cycle dimensions and structure, these compounds behave in the opposite way. Cyclopentanone is a thermodynamic hydrate promoter [1] whereas ethylene carbonate acts as thermodynamic inhibitor. There is considerable interest in further study of the issue related to the opposite effects of the two compounds similar in structure on the phase equilibrium conditions of methane clathrate hydrates.

This work was supported by the Ministry of Education and Science of the Russian Federation (Target funding, project 13.1926.2014/K).

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POROUS NICKEL-ALUMINIDES AS METAL SUPPORT FOR SOLID OXIDE FUEL CELLS

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Solid oxide fuel cell (SOFC) is an electrochemical device converting energy of chemical interaction into electricity. A single cell consists from at least three functional layers, which provide the electrochemical processes. These include a porous anode, a gas-tight electrolyte and a porous cathode. For medium-temperature SOFC, operating in the temperature range 600-800 ºC, as the anode is commonly used porous Ni-YSZ cermet, YSZ is used as the electrolyte and complex oxides $LaSrMnO_3$, $LaSrCoO_3$, $LaSrCoFeO_3$ are used as cathode. In addition, one of the above mentioned layers must provide the cell with mechanical strength and to act as a support base for other layers. There are modification with anode, electrolyte and cathode-supported SOFC. But ceramics are capable of brittle fracture under impact of thermal or mechanical shocks. Therefore there is alternative configuration, when all functional layers are applied on porous metal support. This configuration is called metal-supported SOFC (MS-SOFC). Through the plasticity and high thermal conductivity MS-SOFC potentially adapted to quick start, thermal cycling and mechanical shocks. Prospective candidates are alloys based on nickel-aluminum intermetallics, which are able to operate in an oxidizing environment up to 1100 ^{0}C. Nevertheless, to protect a metal-support against corrosion, the deposition of functional layers is possible only in vacuum or inert atmosphere. Special deposition techniques such as vacuum deposition or thermal spray are used for that reason. Deposition rate for above-mentioned techniques are about 10 μm per hour. Therefore roughness of the support surface should be as low as possible. This is achieved through the use of materials with fine porous structure.

We developed a wide range of porous Ni-Al plane supports produced by combustion synthesis. The main idea is to perform synthesis in thermal explosion mode of combustion synthesis [1]. Here a porous sample is placed between heat sink plates and then are heated up to a temperature of thermal explosion (about 600 ^{0}C). An exothermal reaction between the components of a specially prepared powder mixture take place at this temperature. Using this approach it is possible to sinter a porous medium with predetermined geometry and porous structure. Subsequent annealing of the materials at 800-1000ºC allows to stabilize a phase composition without loss of obtained structure parameters. The parameters of developed Ni-Al materials are: chemical composition – $NiAl+Ni_3Al$ (from 10 to 31 mass % of aluminum); porosity – 0.4 ÷ 0.6; thickness – < 0.4 mm; gas transport channels – 2 ÷ 7 μm; bending strength – 100 ÷ 200 MPa.

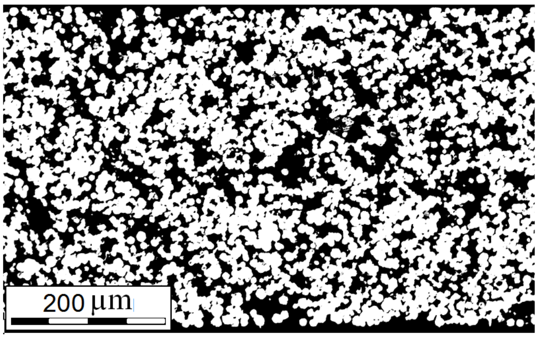

Figure 1. Example of porous structure of the Ni-Al support – cross section of plate with thickness 0.4 mm. Black region – pore space, white region – Ni-Al material.

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POROUS PENETRABLE SIALON CERAMICS PRODUCED BY COMBUSTION SYNTHESIS

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Sialon ceramics are attractive engineering materials due to their durability under chemical impact at elevated temperatures. Therefore sialons prospectively be used as hazardous-medium filters, porous gas burners and catalyst-supporting media. These applications involve the use of porous penetrable materials. Sialons can be obtained using the energy-efficient method of combustion synthesis (CS). Here the ceramic is synthesized via propagation of a combustion wave throughout a powder sample placed in a nitrogen.

Our efforts are focused on the study of combustion synthesis of porous oxynitrides ceramics. To vary porous parameters of the products we used powder samples with a two-level structure – a macroporous structure formed by large powdered aggregates whose microporous structure is formed by fine reaction powders [1]. Structuring of the reaction systems was performed via foaming of water-based slurry of reacting powders and using burnable pore-forming agents. The porosity parameters of the synthesized materials are: porosity 40 ÷ 75%, average size of the frame elements 240 μm ÷ 3.5 mm, average size of permeable channel 9 ÷ 390 μm and percentage of closed porosity 16 ÷ 60% (figure 1). Our investigations have shown that combustion synthesis under conditions of forced nitrogen filtration, where the reaction gas is blown through the combustion-wave zone, intensifies the synthesis due to a directed heat and mass transfer. The macroscopic synthesis parameters are by 10 % better than those obtained without forcing the reaction-gas flow. Synthesis in forced filtration mode allows us to obtain sialon ceramics with the product yield 0.99 (on the example of $Si_2Al_4O_4N_4$ system).

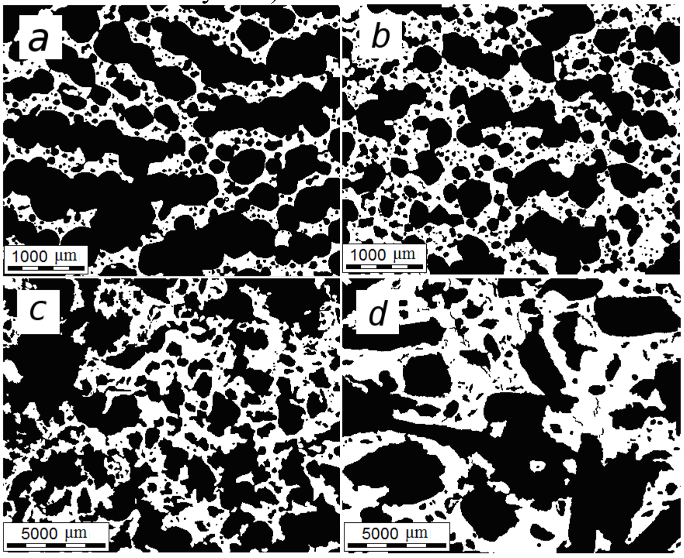

Fig. 1. Structures of the combustion synthesized products (black – pore space, white - ceramic). Without burnable pore-forming agents: part *a* - porosity 0.75, part *b* - porosity 0.58. With burnable pore-forming agents: part *c* – only arbitrary shape agent, part *d* – with 30 voll.% of elongated agent.

This work was supported by Russian Foundation for Basic Research (Grant # 14-03-31474 mol_a)

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STRUCTURE AND PROPERTIES OF TI-AL_3TI COMPOSITES OBTAINED BY SPS OF TI AND AL FOILS OF DIFFERENT THICKNESSES ENCLOSED IN TITANIUM SHELLS

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Over the last decades attention of many researches is focused on the problem of formation of metal-intermetallic lamellar (MIL) composites based on Ti and Al due to their outstanding combination of properties [1]. The traditional method of fabrication of MIL composites consists in reactive sintering of metallic plates under the pressure at a temperature near the aluminum melting point (660 °C) [2]. Our previous research revealed that spark plasma sintering (SPS) at higher temperatures (830 and 1050 °C) can be an efficient technology of MIL composites formation as well [3]. This study is devoted to estimation of influence of thicknesses of initial metallic foils on the structure and properties of MIL materials.

Al foils with a thickness of 100 μm and Ti foils with thicknesses ranged between 25 and 200 μm were enclosed in titanium shells to prevent aluminum leakage from the reaction zone. Composites were prepared by SPS at a temperature of 830 °C during 10 minutes. It was found during structural investigations that SPS allowed fabricating high-quality Ti – Al_3Ti composites containing thin transition layers consisted of Al_2Ti, AlTi and $AlTi_3$ intermetallic phases and a Ti(Al) solid solution at the interfaces. Depending on a thickness of starting titanium layers, the volume fraction of the intermatallic component varied from 45.5 to 76.5 %. In the case of using 25 μm titanium layers, titanium was fully expended for the formation titanium tri-aluminide and the lamellar structure was not formed. The average microhardness of the intermetallic phase was about 550 HV, while the titanium microhardness did not exceed 260 HV. Compression tests revealed that the strengths of composites did not depend significantly on the volume fraction of intermetallic component and a scheme of loading (in the direction perpendicular or along the layers). An average compression hardness of multilayered materials was about 770 MPa.

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X-RAY STUDIES OF THERMOELECTRIC MATERIALS BASED ON TRANSITION METAL SOLID SOLUTIONS

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Invention of a highly efficient thermoelectric materials is one of the important direction of modern materials science. Substances with direct conversion «thermal» energy into «electric power» seem to be perspective. These systems could have a broad range of applications on the mobile power supply systems and the concept of a «smart home» [1,2].

One of the directions on finding of new thermoelectric materials is the study of systems, in which metal-dielectric transition is observed. The systems of such kind could be solid solutions based on the transition metal sulfides possess high values specific of thermoelectric: $CuCr_{1-x}V_xS_2$ (x=0-0.40) и $Mn_{1-x}M_xS$ (M=Co, V) [3-5].

Electrophysical properties of such functional matrials is primarily determined by features of its electronic structure. In this connection, current work involves a comprehensive study of features interrelationship of the cation-substituted sulfides $CuCr_{1-x}V_xS_2$ (x=0-0.40) and $Mn_{1-x}Ln_xS$ (x=0;0.01;0.05; Ln=Dy, Tm, Yb) electronic structure (using X-ray spectroscopy) and its thermoelectris properties.

X-ray emission spectra (CuLα, $CrK\beta_{2,5}$, VLα, MnLα, $SK\beta_{1,3}$ LnL*vv')* provides information about the electronic structure of valance band (XES). X-ray absorption spoectra (K-absorbtion spectra of Cu, Cr, V, Mn, S; L-spectra of lanthanides) provides information about conduction band electronic structure of investigated solid solutions (XAS). XAS and XES spectra (CuLα, $CrK\beta_{2,5}$, VLα, MnLα, $SK\beta_{1,3}$ LnLβ…) were figered in unified energy scale in order to investigate electronic structure. The results X-ray spectra analysis were compared with quantum chemical calculations in the FDMNES and BAND software packages.

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INFLUENCE OF ACCEPTOR DOPING ON THE PHYSICOCHEMICAL AND TRANSPORT PROPERTIES OF MATERIALS BASED ON $BaCeO_3$ AND $BaZrO_3$

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The mixed systems based on $BaCeO_3$–$BaZrO_3$ are considered as promising and perspective electrolytes for solid oxide fuel cells due to their good chemical stability and acceptable ionic conductivity. It is well known that the nature and concentration of dopants affect the target properties of such materials. For example, the stability can be achieved mainly by the variation of Zr/Ce ratio in $BaCeO_3$–$BaZrO_3$ systems, whereas ionic conductivity depends on the type and concentration of acceptor dopant(s). This work aims at identifying the influence of acceptor dopant on the crystal, microstructure, thermal and electrical properties of $BaCe_{0.5}Zr_{0.3}Ln_{0.2}O_{3-\delta}$ (Ln = Yb, Y, Gd, Sm, Nd).

The ceramic samples were prepared by a modified version of citrate-nitrate combustion synthesis followed by synthesis at 1150 °C for 5 h and sintering at 1450 °C for 5 h. The relative density of all ceramics obtained was higher than 95% from the theoretical value. The phase composition, microstructure, thermal and electrical properties were studied by X-ray diffraction (XRD) analysis, scanning electron microscopy (SEM), dilatometry and 4-probe DC method of conductivity measurements, respectively.

According to XRD data, all the samples are single-phase and belong to the perovskite structure. For ceramic samples with Ln = Yb and Y the structure was identified as rhombohedral distorted perovskite (sp. gr. R3c), whereas the samples with Ln = Gd, Sm and Nd were identified as cubic perovskite (sp. gr. Pm3m). SEM analysis confirms well-developed structure and no presence of impurity phases on the grain and grain boundary of the samples. The dilatometry data shows that the value of avarge thermal expansion coefficient increases (from $7.6\cdot10^{-6}$ to $10.7\cdot10^{-6}$ K^{-1}) with increasing ionic radius of Ln^{3+}. The values of the total conductivity of $BaCe_{0.5}Zr_{0.3}Ln_{0.2}O_{3-\delta}$ (Ln=Yb, Y, Gd, Sm, Nd) ceramics in air at 900°C are equal 46, 46, 26, 37 and 36 $mS\cdot cm^{-1}$, respectively. The ionic conductivity of $BaCe_{0.5}Zr_{0.3}Ln_{0.2}O_{3-\delta}$ ceramics tends to decrease with the transition from Y^{3+} to La^{3+}, showing the predominant influence of Zr-ions on the transport properties of mixed cerate-zirconate materials; at the same time, the contribution of p-type electronic conductivity increases.

On the base of electrical measurements, Y^{3+} can be considered as most suitable dopant for mixed $BaCeO_3$–$BaZrO_3$ system due to the achievement of the best combination of target properties.

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X-RAY STUDY OF THE ELECTRONIC STRUCTURE OF TRANSITION METAL COMPLEXES WITH NITROXYL LIGANDS - MOLECULAR MAGNETS

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Obtaining appears promising functional molecular magnets in which magnetic activity combined with other physicochemical properties: photochemical, optical, electrical conductivity, adsorption on the substrate surface without changing the characteristics. In this connection, great interest in coordination transition 3d-metal compounds with stable nitroxyl ligands. Variation of ligands and metal ions in the complexes opens up the possibility of controlling the characteristics of molecular magnets.

The study of the electron density distribution and the possible channels of delocalization of the electron density in the respective complexes are actual. In this respect, it is the study of the actual nature of the electron density distribution, and the possible channels of delocalization of the electron density in the respective complexes. Magnetic properties of the transition metal complexes with polyvalent chelate ligands, having in its composition nitroxyl group ($\mathrm{N}\overset{\bullet}{—}\mathrm{O}$), are determined by the nature of the electronic interactions of paramagnetic centers Cu^{2+} and $\mathrm{N}\overset{\bullet}{—}\mathrm{O}$.

The use of X-ray spectroscopy for the study of transition metal complexes with nitroxyl radicals makes possible to determine the charge states of atoms in the molecule and the spin density localized on the respective atoms, which will evaluate the magnetic characteristics. Satellite lines in the XPS spectra of transition metals can be effectively used to determine the spin state of the metal atom in the nitroxyl heterospin complexes. It is shown that the main role in the formation of XPS N1s, O1s and C1s spectra of complexes plays a charge state. The spin state of the atoms does not significantly affect the structure of the XPS spectra of atoms. According to the charge transfer model it is shown that the main peak in the XPS $\mathrm{Cu}2p_{3/2}$-spectra of copper complexes with nitroxyl ligand corresponds to the $|2p^{5}3d^{10}\underline{L}>$ configuration, and satellite lines can be attributed to the $|2p^{5}3d^{9}L>$ configuration. Magnitude of the multiplet splitting for $|2p^{5}3d^{10}\underline{L}>$ configuration is proportional to the spin density.

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ELECTRONIC STRUCTURE ANALYSIS OF ORGANIC SEMICONDUCTOR BASED ON H_2PC

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Organic semiconductors have drawn in the last few years increasing interest as alternative semiconductor material. Thin films of phthalocyanines are widely used in modern macromolecular electronics as circuit elements. In particular, thin films of corresponding compounds are used as organic light emitting diodes (Organic light emitting diodes – OLEDs). A typical OLED has a layered structure in which is hole transport layer, a layer for blocking electrons, the active layer (emission layer), a blocking layer holes, electron transport layer in addition to the electrodes. Phthalocyanines can have both hole and electron conductivity depending on nature of central macrocycle and peripheral substituents in the ligand composition. This property allows them to be used as conductive layers in the OLED. The effeciency of the OLED layers is determined primarily by the characteristics of the electron spectrum of the higher occupied molecular orbital (HOMO) and lower unoccupied molecular orbitals (LUMO).

In this work, we present a combined analysis of the energy spectrum and partial atomic structure of HOMO and LUMO by x-ray (XES, XANES) and x-ray electron spectroscopy (XPS) on the example of the universal model phthalocyanine - H_2Pc. Experimental result are compared with theoretical spectra obtained by calculating density functional theory (DFT) and time-dependent functional theory (TDDFT). The calculations have been performed with the Jaguar 6.0 program in the DFT Z+1 approximation and with ADF 2013 program in TDDFT taking into account excited states.

Thus, the combined use of experimental and theoretical methods has allowed us to determine the order of occupied and unoccupied levels, the binding energy of HOMO and LUMO, partial composition of MO and the presence of interaction between the individual atoms of the compounds. It is shown that the HOMO (-1,5±0.3 eV) includes $2p_\pi$ - AO of carbon atoms (Cα). The next HOMO with a significant contribution of nitrogen atoms is located deeper by 2.1 eV and characterizes nitrogen $2p_\pi$ - AOs $N\alpha_{(1,2)}$.. A multipurpose analysis of the fine structure of absorption spectra showed that the main contribution to it is made by nitrogen $2p_\pi$ - AOs of the $N\alpha_{(1,2)}$ group atoms with the energy positions of –2.3 eV. Found that the good agreement between the experimental partial density distribution in HOMO and LUMO with the theoretical one is observed for the DFT calculation in the Z+1 approximation and for the TDDFT approach with functional LB94.

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INITIAL OXIDATION OF LOW-INDEX $TiAl_3$ SURFACES

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The Ti-Al alloys are very attractive for technological applications in aerospace, automobile, marine industries and in other fields because of their excellent mechanical properties. The main drawback of Ti-Al alloys is known to be their low oxidation resistance at elevate temperatures that limits their applications. This is due to the easy formation of both TiO_2 and Al_2O_3 mixed layers which prevent the formation of dense and protective alumina film. Experimentally was shown that the growth of protective α-Al_2O_3 layers can depends strongly on the composition of surface layer, reactivity of alloying metals and also on the presence of other point defects. In this connection a surface segregation may influence considerably the composition of the surface layer and oxidation mechanism. For example, $TiAl_3$ alloy has the highest corrosion resistance among Ti-Al alloys. In order to understand on the microscopic level the formation of oxide layers on Ti-Al surfaces, first of all it is necessary to study the O adsorption on the surface as the initial stage of the oxidation. In this work we present the results of the first principles investigation of oxygen adsorption on low-index $TiAl_3$ surfaces. Oxygen adsorption in several high symmetry positions on the $TiAl_3$ surface with (001), (100) and (110) orientations is considered. It is shown that the H-position above Al subsurface atom is found to be preferred for O adsorption on both Al and TiAl terminations of non-stoichiometric (001) surface. Analysis of electronic structure shows that the preference of this position results from strong hybridization of *s*,*p*-states of oxygen with states of both metals. It should be noted that the similar trend was found on TiAl(001) surface in our previous work. On $TiAl_3$(110) oxygen prefers to be adsorbed in short bridge site irrespective of surface termination whereas in case of stoichiometric (100) surface the most preferential position is bridge-site between Ti and Al atoms. In latter case the value of adsorption energy in the three-fold coordinated F-site in which oxygen atom is surrounded by two Al atoms and one Ti atom, is smaller only by 0.28 eV than in the bridge-site. The mechanism of chemical bonding of O atom with differently oriented $TiAl_3$ surfaces is discussed. The investigations of influence of oxygen concentration on atomic and electronic structure of alloy surfaces are performed. The formation of oxide layers on the low-index $TiAl_3$ surfaces is analyzed.

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STRUCTURAL, ELECTRICAL AND THERMO-MECHANICAL PROPERTIES OF Ca-SUBSTITUTED Pr_2NiO_4

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Rare-earth nickelates Ln_2NiO_4 (Ln = La, Nd and Pr) have attracted much attention as promising cathode materials for the Intermediate Temperature Solid Oxide Fuel Cells (IT-SOFC). Among them Pr_2NiO_4 have been found possess the lowest ASR value [1], but it is not thermodynamically stable at working SOFC's conditions and decomposes into $Pr_4Ni_3O_9$ and $PrO_{1.71}$ at 800 °C. Doping with Sr dramatically improves thermal stability of Pr_2NiO_4, chemical compatibility with yttria stabilized zirconia (YSZ) and electrochemical performance [2]. The aim of this work is to investigate the influence of Ca-doping level on the structural, electrical and thermo-mechanical properties of $Pr_{1-x}Ca_xNiO_{4+\delta}$ to evaluate a perspective of their usage as cathode materials in contact with CeO_2 and $BaCeO_3$ based electrolytes.

Solid solutions $Pr_{2-x}Ca_xNiO_{4+\delta}$ ($x = 0.0$- 0.7) were synthesized by a three-step solid state reaction method. Ca-doping changed the Pr_2NiO_4 structure from orthorhombic (*Fmmm* space group) to tetragonal one (*I4/mmm* space group) with decreasing of *a* and *c* lattice cell's parameters with an increase in calcium content; the solubility limit was found to be equal to 0.5. The total conductivity measurements were performed by DC four-probe method in the temperature range 300-900 °C and revealed a conductivity growth in the Ca solubility limit due to the extrinsic defects, secondary phase CaO appeared in the synthesized materials at $x>0.5$ caused decreasing the conductivity. The thermal expansion coefficient (TEC) displayed a non-linear dependence on Ca content with maximum at $x=0.4$ (15.7×10^{-6} K^{-1}). By XRD method was shown that Ca-doping increased the chemical stability of Pr_2NiO_4 in composites with $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ electrolyte. Chemically stable $Pr_{1.5}Ca_{0.5}NiO_{4+\delta}$ material with relatively low TEC value (14.5×10^{-6} K^{-1}) and total conductivity value equal to 135 S/cm can be recommended as cathode material for IT-SOFC's applications individually or in composites with $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ electrolyte.

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STRUCTURE AND PROPERTIES OF “NICKEL ALUMINIDE – NICKEL” COMPOSITE MATERIALS OBTAINED BY SPS METHOD

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Ni_3Al intermetallic is considered as a promising material for constructional applications due to the outstanding complex of mechanical properties [1]. The most important drawback of this intermetallic material is increased brittleness at low temperatures that restricts possibility of treatment of this material using forming and cutting technologies. It was established experimentally that spark plasma sintering (SPS) can be the efficient process which allows obtaining high-quality products from intermetallic powders. Nevertheless, this technology does not significantly increase the plasticity of the intermetallics. One of the solutions of aforementioned problem is based on creating nickel aluminide – nickel composites by adding ductile nickel particles to a brittle intermetallic powder.

The powder of carbonyl nickel (PNK UT3) and Ni_3Al powder produced by self-propagating high-temperature synthesis (SHS) of pure Ni and Al powders were used as the initial materials. For the formation of fine structure preliminar mechanical activation of the reaction mixture was carried in the AGO-2 planetary ball mill for 3 minutes. The centrifugal acceleration of balls was 40 g. SPS was carried out according the regime described elsewhere [2]. Analysis of the results obtained showed that addition of ductile nickel particles to powder mixtures positively affected the density and strength properties of the sintered composities. The relative density of sintered composites exceeded 98 % (Table 1). The highest bending strength level (2690 MPa) possessed a sample obtained by mixing 70 % of Ni_3Al obtained by SHS with 30 % of Ni followed by SPS at 1100 °C. This value was higher then strength of pure intermetallic sintered under the same conditions by factor of 3.3.

Composition of powder mixtures and properties of sintered materials.

Type of powder mixture	Density of sintered composite, g/cm^3	Relative density of sintered composite, %	Bending strength, MPa
70 % Ni_3Al – 30 % Ni	7.78	98.3	2690
Ni_3Al	7.27	96.9	800

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COMBINATION OF EXPLOSIVE WELDING AND SPARK PLASMA SINTERING FOR RELIABLE JOINTS PRODUSING BETWEEN DISSIMILAR MATERIALS

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Development of modern technologies of joints formation between dissimilar metallic materials makes high demands on quality and properties of welds. The problem is particularly acute for welding of materials between each other brittle intermetallic compounds are formed. Consequently conventional fusion welding techniques are unsuitable. Explosive welding is an alternative solution of above noted problem. It is a prospective technology produces weld joints by severe plastic deformation proceeding between collided plates. In the last time with increasing frequency for joining of dissimilar materials thin barrier layers are used for elements diffusion prevention. Spark plasma sintering (SPS) technology is a relatively novel method based on combination of hot pressing and current impulse generation. Sintering process proceeds at high speed and low temperature resulting effectively restrain grain growth and materials producing with high dense and fine crystalline structure. As SPS technology is regularly used for powder compacts manufacturing it also attractive for joining of dissimilar materials. The temperature at the welding interface is precisely controlled by machine and there is no any evidence of plastic deformation in the process of sintering. Combination of above described both technologies is effective solution in the production of high strength and defects free composite materials allowing expansion of nomenclature of welded materials.

In current research work titanium and nickel alloy based composite materials were formed in the following way. At the first stage by explosive welding 4-layered composite materials were obtained. Nickel alloy was used as the base plate to which thin layers (~ 100 μm) of copper, tantalum and commercially pure titanium were explosively welded. Produced after explosive welding composites were cutted on the templates of square section. To the exterior titanium layer by SPS on the Labox 1575 machine titanium alloy VT20 was welded. Produced composites were analysed by optical metllography and electron microscopy. Conducted researches have revealed defects free interface between all layers with lowest strength of copper layer.

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INTERACTION BETWEEN NICKEL AND DIAMOND PARTICLES DURING SINTERING OF POWDER MIXTURES

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The interaction at the nickel/diamond interface is extremely important for many applications, such as epitaxial growth of diamond films on nickel substrates, catalytic etching of diamond surfaces, and design of diamond-metal composites as heat sink materials. In this work, we present a detailed microstructural analysis of the nickel/diamond interfaces formed during sintering of powder mixtures at temperatures well below the melting point of nickel or the nickel-graphite eutectic. We observed the formation and analyzed the development of the nickel/diamond interface in compacts partially densified by Spark Plasma Sintering, hot pressing and conventional sintering of powder mixtures. In the sintered compacts, the fracture of the nickel-diamond inter-particle joints was cohesive and resulted in the formation of nickel-containing patches on the diamond facets. The number of joints was greater in the Spark Plasma Sintered compact than in the conventionally sintered compact, their microstructural features remaining similar. The joints were more uniformly distributed over the surface of diamond particles in the Spark Plasma Sintered compact compared with the conventionally sintered compact. The microstructure of the patches adhered to the diamond surface, their geometry and orientation relative to the edges of the diamond crystals suggested that the formation and development of the interface involved contact melting followed by crystallization of the melt upon cooling according to certain directions of the diamond crystalline lattice. A viable explanation of the formation of liquid at such a low temperature is contact melting of a metastable eutectic between nickel and diamond [1]. The composition of the gaseous atmosphere, in which sintering of nickel-diamond materials is conducted, plays a decisive role in the formation and evolution of the microstructure of the inter-particle joints.

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SiCN FILMS: SYNTHESIS, OPTICAL AND MECHANICAL PROPERTIES

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Amorphous silicon carbonitride SiC_xN_y films have some superior properties for electronic devices, such as wide band gap and low value of dielectric constant. In addition, their high temperature stability, transmittance and hardness make them a high-promising material for production of different types of coatings. Use of organosilicon precursors in PECVD processes appeared to be a useful technique for the synthesis that allows to prepare SiC_xN_y films of various chemical and phase composition. Use of different additional gases makes possible to vary physical and chemical properties significantly.

Trimethylphenylsilane (TMPhS), bis(trimethylsilyl)phenylamine (BTMSPhA) and bis(trimethylsilyl)ethylamine (BTMSEA) were synthesized and characterized as CVD precursors. The temperature dependence of vapour pressure and thermal stability were measured by tensimetry. The vapour pressure of the precursors was enough to use them at room temperature ($EtN(SiMe_3)_2$ – 2,4 Torr, $PhSiMe_3$ – 5,1 Torr, $PhN(SiMe_3)_2$ – 0,2 Torr). SiC_xN_y films were deposited by PECVD technique from TMPhS, BTMSPhA or BTMSEA in mixture with NH_3 or He at the temperature range of 100-700 °C. The influence of reactive mixture and deposition temperature on the structure and functional properties of the deposited films were investigated.

The change in initial reactive mixture allowed to prepare films with various composition from SiC_x and SiC_xN_y to SiN_y (FTIR, EDX). It was revealed by Raman spectroscopy that high-temperature SiC_x and SiC_xN_y films contain graphite clusters. The addition of excess of ammonia resulted "SiN_x"-like film deposition with carbon content less than 10 at.%. The films of intermediate composition contained both Si-C and Si-N bonds that could indicate the presence of mixture of SiC and Si_3N_4 phases, or phase with C-Si-N fragments. It is worth mentioning that STEM and SAED analysis showed only the continuous amorphous state. By controlling the amount of Si-C and Si-N bonds and graphite concentration it is possible to tune the transparency, optical bandgap, hardness and Young's modulus significantly. The best combination of high hardness and transmittance was obtained for the film deposited from BTMSEA at 600 °C (H = 23 GPa and transmittance rival to SiO_2).

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Poster Presentations

ACOUSTO-OPTIC LOW FREQUENCY RESONANCE-LIKE VIBRATION BEHAVIOUR IN THE HDA ICE

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In this study we present the research of acousto-optic resonance-like behaviour of vibration modes in high density amorphous ice (HDA). The stable cubic model of HDA ice containing 512 rigid water molecules was constructed using the molecular dynamics method and modified SPC/E potential. The approach, which considers the model cell as a unit cell of the pseudo-crystal was applied (taking into consideration the periodic boundary conditions of HDA ice model cell). Combination of such kind of approach and the lattice dynamics method provides us vast variety of the dynamical characteristics of HDA ice structure in the middle of the Brillouin zone and along the Brillouin zone of pseudo-crystal.

The results of simulation let us construct the dispersion curves of HDA ice in defferent directions of cubic cell. The resonance-like behaviour of longitudinal acoustic vibration curve and lowest energy crystal-like optic vibration curve was found. Participation ratio characteristic was calculated for every vibration at each Brillouin zone point. The found growth of molecular amplitudes and number of involved molecules of vibrations close to resonance-like point of vibration modes also indicates the presence of resonance. To confirm this founding the projections of molecule displacement vectors were built.

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INFLUENCE OF DISPERSED ADDITIONS OF DIFFERENT NATURE ON FORMATION OF STRUCTURE AND PROPERTIES OF COPPER-BASED POWDER MATERIALS

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Improvment of reliability and durability of friction units, which to a great extent determine the reliability both of separate units and the entire machine, is achieved by using effective anti-friction powder materials that provide minimal friction koefficient and wear of friction surfaces. One of the methods for obtaining such materials is introduction of ultrafine and nanosized additives of different nature. Introduction of modifying refractory additives into powder non-ferrous alloys allowed to create new contact materials with high anti-friction characteristics with a satisfactory level of electrical properties [1, 2]. Introduction of modifying refractory additives into iron alloys significantly improved their tribological properties [3].

The objective of this paper is the experimental investigation of structure formation and mechanical and tribological properties of sintered tin bronze with dispersed additives of various compositions. Studies showed that introduction of 1-2% of dispersed to 0.5-1 μm fused alumina powder allowed to increase hardness of the sintered bronze to 96-110 HB, reduce the friction coefficient from 0.12 to 0.09 and improve the wear resistance of 2.2 times. When we increase content of alumina up to 5%, it results in a substantial decrease in strength (by 1.5 times at its maximum) due to structural changes in the material. Addition of nickel oxide to alumina promotes strength improvement and wear resistance increase of sintering bronze due to interaction of base material during deoxidization of nickel oxide in the course of sintering.

Introduction of 0.5% of mechanically activated in a jet mill powder Fe-10% Sn allows to increase strength and tribological properties of sintering bronze by modifying the structure and formation of intermetallic FeSn. In such event the friction coefficient of tin bronze decreases by 1.4 times, and the extreme setting pressure increases from 5 to 7 MPa.

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SIMULATION OF Ta, Mo AND Si THIN COATINGS AT TiNi(001) AND (110) SURFACES

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Intermetallic TiNi alloy exhibiting excellent mechanical properties such as the shape memory effect, superelasticity, reversible strain recovery without materials failure, etc. has widespread application in industry and medicine. In the latter case TiNi and TiNi-based alloys are used for manufacturing different implants and fixation devices. The interaction between implant material and human tissue is fundamental issue of medicine. Materials used for medical applications must provide a high biocompatibility. It is believed that the biocompatibility of TiNi is due to formation of inert titanium dioxide layers which effectively passivate alloy surface. To prevent the release of Ni and improve the biocompatibility and corrosion resistance of implants it is necessary to modify their surface properties only because surface or thin surface layers are in contact with blood and body tissue. For this goal appropriate surface treatment by ion beams or deposition of thin coatings of biotolerable chemical elements are applied. As was shown in literature elements such as Zr, Ta, Si are very promising for this purpose. However, the influence of metal and silicon coatings on the corrosion resistance is not completely understood. Moreover, the adhesion properties of different coatings have not been studied by theoretical approaches. In this study the properties of interfaces (001) and (110) between TiNi and thin coatings (Ta, Mo, Si) are investigated by *ab-initio* method within density functional theory. To describe Me/TiNi(001) and Me/TiNi(110) interfaces a symmetrical slabs model with seven layers of alloy and four-six layers of metals on both sides of alloy surfaces was used. In the case of Si/TiNi interfaces the surface cell of TiNi(2×2) was used in order to coincide with Si thin film. Our results demonstrate that the work of separation of Mo thin film is greater than that of Ta or Si irrespective of the interface orientation. It was established that in case of different metal film configuration on alloy surfaces the configuration with smaller interfacial distance demonstrates higher adhesion properties. The filling of *d*-band of Mo leads to its shift below the Fermi level that contributes to chemical bonding at interface and increase the adhesion properties of Mo thin film in comparison with Ta one. The investigation of metal-oxide interface was also performed because titanium oxides can be formed at alloy surface. It is shown that the formation of intermediate oxide layers at Me/TiNi interfaces leads to decrease of adhesion properties. Obtained results are in qualitative agreement with the experimental ones.

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ANALYSIS OF SILICON FOR SOLAR CELLS AND MICROELECTRONIC

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Requirements for methods of elemental analysis of silicon are determined by their functional purpose. In the Analytical Laboratory NIIC SB RAS are developed express techniques for survey balk analysis of silicon "solar" quality by atomic emission spectrometry with excitation spectra in the inductively coupled plasma (AES-ICP). The AES-ICP techniques based on dissolving of silicon samples 0.2-05 g in the mixture of hydrofluoric and nitric acids and analysis of dilute solutions at AES-ICP spectrometer iCAP-6500. By studying of the spectral and nonspectral influence of silicon on intensity analytical lines were selected and compromise concentration of silicon at 50 mg/ml was chosen. The developed techniques allowed to define 29 trace-elements in silicon with detection limits of $n \cdot 10^{-7}$ - $n \cdot 10^{-5}$ wt %.

To achieve the required detection limits of impurities required for the analysis of the silicon "semiconductor" quality, it is advisable to use distillation of the matrix element in the form of silicon tetrafluoride (SiF_4). The combination of pre-concentration with ICP-AES technique has allowed to determine up to 44 trace-elements with detection limits of $n \cdot 10^{-8}$ - $n \cdot 10^{-6}$ wt. % and reproducibility of 2-15 %. Developed ICP-AES technique superior to silicon analysis techniques recommended by GOST 26239.1-84 (silicon semiconductor) by the number of simultaneous determined trace-elements and by the limits of their detection.

In order to achieve lower detection limits we suggested decomposition and vapor-phase distilling of the matrix element using specially manufactured PTFE autoclaves for microwave furnace MARS 5. This technique is realized without samples contact with the acid solution, which significantly reduces the value of contamination of the concentrate to be analyzed by the common trace-elements.

The new technique of AES-ICP analysis of the silicon with vapor-phase distillation of matrix element in the microwave furnace let us to reduce the detection limits especially for spread impurities and to determine up to 30 analytes (Ag, Al, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, Hf, In, K, Li, Mn, Mo, Na, Nb, Ni, P, Rb, Sb, Sn, Sr, Ta, V, W, Zn, Zr) with detection limits of $n \cdot 10^{-8}$ - $n \cdot 10^{-6}$ wt. % and reproducibility of 2-15 %.

The developed techniques are used in the Nikolaev Institute of Inorganic Chemistry SB RAS for the trace analysis and certification of silicon for solar cells and microelectronics.

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CHEMICAL AND THERMAL COMPATIBILITY OF CATHODE MATERIALS WITH BARIUM CERATE ELECTROLYTE

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It is widely known that solid oxide fuel cells (SOFCs) are highly effective and environmentally friendly devices, capable of converting chemical energy to electricity. Due to the decrease of capital costs and the degree of total degradation during working regime, the main attention of scientists is devoted to the intermediate-temperature SOFCs working between 500 and 750°C. It is possible to decrease of working temperatures of SOFCs by using the electrolytes having higher conductivity than YSZ one, for example, materials based on $BaCeO_3$. In additional to the development of stable and conductive proton electrolytes, the selection of electrode materials is required for optimization of SOFCs output characteristics.

In this work a number of electrode materials were synthesized and their thermal and chemical compatibility with $BaCe_{0.8}Y_{0.2}O_{3-\delta}$ (BCY) electrolyte was verified. The following electrode materials have been selected: double cobaltites ($GdBaCo_2O_{5+\delta}$, $GdBaCoFeO_{5+\delta}$, simple cobaltites and cobaltite-ferrites ($Ba_{0.5}Sr_{0.5}CoO_{3-\delta}$, $nBa_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$, $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$), manganite ($La_{0.75}Sr_{0.2}MnO_{3-\delta}$), nikelate and nikelite ($LaNi_{0.6}Fe_{0.4}O_{3-\delta}$, $La_2NiO_{4+\delta}$).

In order to study chemical interaction between the electrolyte and cathode materials, selected substances were mixed in a ratio of 50:50 wt.% and annealed at 1100 °C (10 h). The phase composition of chemical interaction products was investigated by XRD. Dilatometry measurements of ceramic materials were performed using a Tesatronic TT–80 device in air in the temperature range of 100–900 °C.

Analyzing the chemical and thermal compatibility data, it can be concluded that only three cathode materials ($LaNi_{0.6}Fe_{0.4}O_{3-\delta}$, $La_2NiO_{4+\delta}$ and $Y_{0.8}Ca_{0.2}BaCo_4O_{7+\delta}$) are most suitable for $BaCe_{0.8}Y_{0.2}O_{3-\delta}$ electrolyte. However, the conclusion about the applicability of the cathode can be selected after a study of their electrical and electrochemical characteristics.

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STRUCTURAL, ELECTRICAL AND THERMO-MECHANICAL PROPERTIES OF Ca-SUBSTITUTED Pr_2NiO_4

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Rare-earth nickelates Ln_2NiO_4 (Ln = La, Nd and Pr) have attracted much attention as promising cathode materials for the Intermediate Temperature Solid Oxide Fuel Cells (IT-SOFC). Among them Pr_2NiO_4 have been found possess the lowest ASR value [1], but it is not thermodynamically stable at working SOFC's conditions and decomposes into $Pr_4Ni_3O_9$ and $PrO_{1.71}$ at 800 °C. Doping with Sr dramatically improves thermal stability of Pr_2NiO_4, chemical compatibility with yttria stabilized zirconia (YSZ) and electrochemical performance [2]. The aim of this work is to investigate the influence of Ca-doping level on the structural, electrical and thermo-mechanical properties of $Pr_{1-x}Ca_xNiO_{4+\delta}$ to evaluate a perspective of their usage as cathode materials in contact with CeO_2 and $BaCeO_3$ based electrolytes.

Solid solutions $Pr_{2-x}Ca_xNiO_{4+\delta}$ ($x = 0.0$- 0.7) were synthesized by a three-step solid state reaction method. Ca-doping changed the Pr_2NiO_4 structure from orthorhombic (*Fmmm* space group) to tetragonal one (*I4/mmm* space group) with decreasing of *a* and *c* lattice cell's parameters with an increase in calcium content; the solubility limit was found to be equal to 0.5. The total conductivity measurements were performed by DC four-probe method in the temperature range 300-900 °C and revealed a conductivity growth in the Ca solubility limit due to the extrinsic defects, secondary phase CaO appeared in the synthesized materials at $x>0.5$ caused decreasing the conductivity. The thermal expansion coefficient (TEC) displayed a non-linear dependence on Ca content with maximum at $x=0.4$ (15.7×10^{-6} K^{-1}). By XRD method was shown that Ca-doping increased the chemical stability of Pr_2NiO_4 in composites with $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ electrolyte. Chemically stable $Pr_{1.5}Ca_{0.5}NiO_{4+\delta}$ material with relatively low TEC value (14.5×10^{-6} K^{-1}) and total conductivity value equal to 135 S/cm can be recommended as cathode material for IT-SOFC's applications individually or in composites with $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ electrolyte.

This work was financially supported by RFBR (projects No 14-03-00414; 13-03-00065), Program of UD RAS (project No 15-20-3-15), the Council of the President of the Russian Federation (grant No. СП-1885.2015.1).

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IONIC CLATHRATE HYDRATES IN $(C_4H_9)_4NC_nH_{2n+1}CO_2 – H_2O$ (n = 0 ÷ 4) BINARY SYSTEMS: SYHTHESIS AND CALORIMETRIC MEASUREMENTS

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The ionic clathrate hydrates are relatives of gas hydrates and one of the subgroups of a wider class of hydrate inclusion compounds. In ionic clathrate hydrate structures water molecules and anions/cations form a water-ion cage host framework by hydrogen bonding. A counter-ion (guest) is enclosed in the cages of the water-ion host framework. Hydrates of peralkylonium salts are characteristic representatives of the ionic clathrate hydrates and very intensively studied in the last few years as potentially applicable for various fields. The property of their crystal structure to include small gas molecules allows to use them in gas separation and gas (energy) storage systems. Hydrates of some peralkylonium salts are considered as perspective for cool energy storage and transportation since they have sufficient latent heat of solid-liquid phase transition, decomposition temperatures from 0 ºC to room (in dependence on salt concentration) at ambient pressure, and they crystallize as a slurry that can be transported directly through a pipeline.

Previous study showed that tetrabutylammonium carboxylates ($(C_4H_9)_4NC_nH_{2n+1}CO_2$, n = 0 ÷ 5) form with water a large number of hydrate compounds with m. p. of 7.9 to 21.6 ºC at ambient pressure [1]. To reveal the potential applicability of the ionic clathrate hydrates of TBA carboxylates for energy/cold storage and gas separation we have measured the compositions, the melting temperatures, and the enthalpies of fusion of twelve hydrates forming in $(C_4H_9)_4NC_nH_{2n+1}CO_2 – H_2O$ (n = 0 ÷ 4) binary systems. From the obtained results the entropies of fusion were calculated. The maximum for each system values of Δ_{fus} and T_{melt} range of 197.5 J/g (for $(C_4H_9)_4NHCO_2·31.5H_2O$) to 219.0 J/g (for $(C_4H_9)_4NC_3H_7CO_2·36.2H_2O$) and of 10.4 ºC (for $(C_4H_9)_4NC_4H_9CO_2·39.7H_2O$) to 17.3 ºC (for TBAProp·$31.6H_2O$), respectively. These results indicate that ionic clathrate hydrates obtained in the present work are promising cool energy storage materials. As regards the applicability to the separation of gases the only $(C_4H_9)_4NHCO_2·31.5H_2O$ of tetragonal structure – I could be considered as potentially applicable for gas separation and storage.

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NATURAL GAS HYDRATES FORMATION/DECOMPOSITION PROCESSES IN SYSTEMS CONSISTING OF «COMMERCIAL ASPHALTENE-RESIN-PARAFFIN DEPOSITS AND WATER» BY DSC MEASUREMENTS

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Results obtained in a study of the natural gas hydrate (NGH) formation/decomposition in model systems consisting of various proportions from commercial paraffinic type asphaltene-resin-paraffin deposits (ARPD) and distilled water were considered. The synthesis and decomposition of hydrates in the systems under study were performed in a DSC calorimetric cell. The thermobaric conditions of natural gas hydrates phase transitions in paraffin deposits and water were discussed. It was found that specific features of the hydrate formation process in the systems under study reflect upon the shapes of crystallization isotherm signals. The hydrate formatio/n process favors coalescence of dispersed water drops in the samples under study and leads to formation of coarse water fragments. The experimental data we obtained were compared with the equilibrium hydrate formation conditions calculated by the Sloan procedure [1] for the NG used in the study (Fig. 1). For comparison, the same fi gure presents the results of a study of the NGH formation in systems based on distilled water (points *1*, *8–10*), published in [2]. Thus, in the presence of the ARPD, the curve of equilibrium hydrate formation conditions shifts to high pressures.

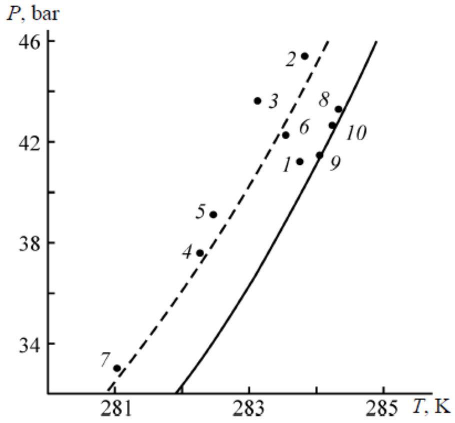

Fig. 1. Comparison of the calculated (curves) and experimental (points) conditions of hydrate formation of natural gas from the Srednevilyuiskoe oil field for various systems. (*P*) Pressure and (*T*) temperature. (*1*) Distilled water, (*2*, *5*) ARPD/H2O =40/60, (*3*, *6*) ARPD/H2O = 60/40, (*4*, *7*) ARPD/H2O = 80/20, (*8*) distilled water + sand, (*9*) water with thermal history, and (*10*) water with thermal history + sand. The solid line is the equilibrium curve for natural gas; the dashed line is the approximation of the conditions for ARPD/H2O systems.

The study was financially supported by the Ministry of Education and Science of the Russian Federation in line with the base part of a State assignment (project 1896 "Organization of research activities").

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SIMULATION OF STRUCTURE, DYNAMIC AND THERMODYNAMIC PROPERTIES OF MULTICOMPONENT GAS HYDRATES

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Within the earlier developed approach the calculations of properties of multicomponent clathrate hydrates were performed for air and air + ozone gas mixture with and without presence of tetrachloro carbon which is simplest model of freons. Air was considered as multicomponent gas mixture containing nitrogen, oxygen, argon and carbon dioxide with content satisfied real air composition. Carbon dioxide + carbon tetrachloride was fixed at level 0.032 mol% and carbon tetrachloride content varies from 0 to 0.032 mol%.

It was found that ozone can compete with other gases at stratospheric conditions at hydrate formation in presence of freons, but can not be captured from ozone layer by hydrates because of small content ($8x10^{-6}$).

The conducted investigations shows that air itself can not form clathrate hydrates at ambient pressures at the temperatures which are realized on the Earth but in the presence of freons it can form clathrate hydrates at low pressures (less then 10^4 Pa) at moderate low temperatures (-53°C). Formation conditions for mixed hydrates were found for large region of pressures and temperatures.

It was found that at ambient pressure formation of ozone containing gas hydrate with air can occure at the presence of tetrachlorocarbon at moderate temperatures. These types of hydrates can be formed at stratospheric conditions.

Our simulations show also redistribution of gases at clathrate hydrates formation. The heaviest gases are first captured by hydrates. Hydrate formation can be the cause of air purification.

The suggested approach can be useful for calculation of composition and phase diagrams for wide range of gas mixtures such as natural gas, main gas and so on.

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H_2-AR DOUBLE HYDRATES AS HYDROGEN STORAGE MATERIAL

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One possible solution of the environmental safe fuel is the usage of hydrogen. However issue of it storage still is under discussion. Hydrates formation from hydrogen was proposed as a possible hydrogen storage method by many researchers. Hydrogen storage capacity of this material is about 5 wt%, this material is cheap and has low environmental hazard. Unlike pure hydrogen hydrate that has relatively high formation pressure, formation of gas hydrates from gas mixtures allow to reduce formation pressure. In this work gas mixture of argon and hydrogen has been considered as hydrate formation base.

Formation pressure and hydrate composition dependence on temperature was calculated in a wide temperature range. With pressure increasing, the filling ratio of the large cavities by clusters of four hydrogen molecules grows gradually, also clusters of one, two, and three hydrogen molecules are can be found in the cavities but its occupation ratio drops with further pressure increasing. Argon atoms are more favorable in the small cages than hydrogen clusters. In the large cages hydrogen clusters are more preferable. Mixed argon + hydrogen clusters formation also have been considered, such clusters can be found in the large cages only at low pressure and their content do not exceed 3%. At high pressures almost all large cages are filled by hydrogen clusters of four molecules and small cages are filled by argon. In the case of low argon fraction the highest hydrogen content in this system can be reached at moderate pressures.

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Expoplace

MATERIAL DESIGN, CRYSTAL CHEMISTRY AND SINGLE CRYSTAL GROWTH OF HIGH PERFORMANCE SCINTILLATORS; GAGG, LA-GPS, EU:SRI2

Yoshikawa A. *[1,2,3] , Nikl M. [4], Kamada K.[2,3], Kurosawa S.[1,2], Yokota Y.[2], Ohashi Y.[1],
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Recent R&D works on Ce:GAGG, Ce:La-GPS and Eu:SrI_2 single crystals will be reviewed. Ce: $\{Gd,RE\}_3(Ga,Al)_5O_{12}$ (RE=Y, Lu) (Ce:GAGG) single crystals shows high light yield and high energy resolution [1]. Though the lattice constant, volume and emission wavelength changes linearly, LY has maxima at the specific ratio. This is explained as the result of suitable BGE. From the crystal chemistry point of view, in the psude-binary system between Gd_2O_3 and α-Al_2O_3, $GdAlO_3$ (perovskite) is congruent, however, $Gd_3Al_5O_{12}$ (garnet) is incongruent. Partial substitution of Ga in Al site or partial substitution of RE in Gd site is effective to make the garnet phase congruent. 3 inch diameter Ce:GAGG single crystal is available now. The study on investigate the role of Ce^{4+} become popular, co-doping effect on Ce:GAGG will be also reported.

Ce-doped gadolinium pyrosilicate (or disilicate), Ce:$Gd_2Si_2O_7$ (Ce:GPS) crystals have also high light output of 30,000 photons/MeV and FWHM energy resolution of 6.0% at 662 keV at room temperature. However, Ce:GPS crystals need to be grown with heavy Ce-doping (approximately 10 at.% regarding Gd^+ host cations to be substituted) in order to modify the phase diagram and to stabilize the crystal growth process. Such excessive Ce-concentration leads to reduced light output because of self-absorption or concentration quenching. On the other hand, recently, we found substitution of La into Gd site gives positive effect of the phase stability of this pyrosilicate. In this study, the Czochralski growth of 2inch Ce: $(La,Gd)_2Si_2O_7$ (Ce:La-GPS) crystals was examined [2]. After the crystal growth, PL, PL decay, RL, pulse height spectra and scintillation decay were measured. LY~42,000ph/MeV, ER~7 % are obtained at the x=0.01, y=0.24. The relation between the composition and properties will be reported.

Crystal growth technology is also the key to obtain high performance scintillators in your hand. Eu:SrI_2 is the typical example. Eu:SrI_2 is rediscovered by the progress of the precise atmosphare control during the crystal growth process. Eu:SrI_2 scintillator crystals with strong hygroscopic nature have been grown by the Vertical Bridgman (VB) method using a quartz ampoule. We developed a modified micro-pulling-down (μ-PD) method with a removable chamber in order to grow single crystals of halide materials at higher growth rate than the VB method. We reported the results of crystal growth and scintillation properties of halide scintillator crystals as represented by $CeBr_3$, Ce:$LaBr_3$ and Eu:SrI_2 using the modified μ-PD method. However, the modified μ-PD method couldn't grow a bulk single crystal with more than 10 mm in diameter. Therefore, we have developed a novel VB method using the μ-PD furnace with the removable chamber to grow bulk single crystals of hygroscopic halide materials. Bulk crystal growth of Eu:SrI_2 will be reported.

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LOW COST OLIVINE AFePO$_4$ AND NASICON A$_3$V$_2$(PO$_4$)$_3$ (A = Li, Na) PHOSPHATE CATHODE MATERIALS FOR NEXT GENERATION RECHARGEABLE BATTERIES

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Olivine and NASICON type's phosphates have attracted attention as novel cathode materials for rechargeable lithium and sodium ion batteries because of their structural and thermal stability during charge/discharge cycling. We carried out the synthesis of olivine AFePO$_4$ and NASICON A$_3$V$_2$(PO$_4$)$_3$ (A = Li, Na) materials of different geometries including bulk, nano-structures and carbon coated shell structured AFePO$_4$ and A$_3$V$_2$(PO$_4$)$_3$ core materials. The structural investigations are carried out using powder X-ray diffraction and Rietveld refinement, to understand the structural evolution and phase purity of the synthesized materials. The microstructural and chemical compositions of the synthesized materials are investigated using Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray (EDX). The representative SEM micrographs (Fig.1) and X-ray diffraction patterns (Fig.2) for LiFePO$_4$/carbon and Li$_3$V$_2$(PO$_4$)$_3$/carbon composite samples are shown. These results confirm the stoichiometric phase purity of the synthesized materials. We will also discuss the associated materials synthesis challenges and their correlation with vibrational properties of these materials.

Authors A.V. Ivanishchev, A.V. Churikov, A.V. Ushakov wish to thank the Russian Science Foundation (project #15-13-10006) for support of synthesis and structural characterization of materials, and Russian Foundation for Basic Research (projects #14-29-04005 and #15-53-45091) for support of electrochemical study of materials. Authors M. J. Sneha and A. Dixit thank BRNS, Department of Atomic Energy (project # 2013/37P/72/BRNS/2933) and Department of Science and Technology (project # INT/RUS/RFBR/P-190) for financial support.

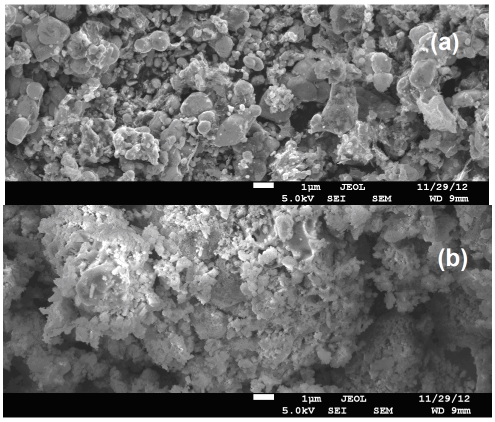

Fig. 1. SEM images of the LiFePO$_4$/carbon (a) and Li$_3$V$_2$(PO$_4$)$_3$/carbon (b) composites samples

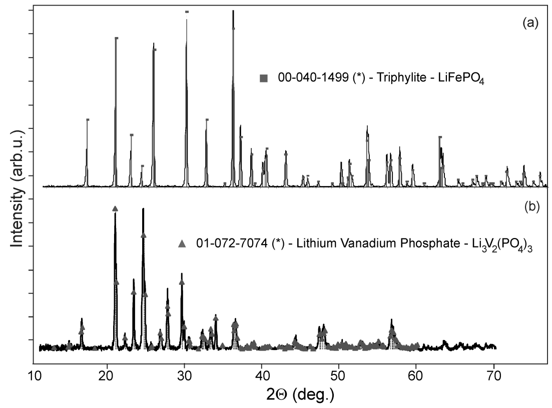

Fig. 2. X-ray diffraction patterns of the LiFePO$_4$/carbon (a) and Li$_3$V$_2$(PO$_4$)$_3$/carbon (b) composites samples

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ELECTRONIC STRUCTURE, VIBRATIONAL STUDIES AND Li^+- DIFFUSION PROPERTIES OF OLIVINE $AFePO_4$ AND NASICON $A_3V_2(PO_4)_3$ (A = Li, Na) PHOSPHATE CATHODE MATERIALS: EFFECT OF LOCAL STRUCTURE

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We carried out diffuse reflectance and Fourier Transform Infrared (FTIR) spectroscopic measurements, to probe the electronic structure and vibrational analysis of phase pure olivine $AFePO_4$ and NASICON $A_3V_2(PO_4)_3$ (A = Li, Na) phosphates materials. The intrinsic insulting properties of these structures are correlated with observed electronic structures and results are discussed in terms of their complex electronic band structure. The vibrational spectroscopic investigations suggest that local crystal structure has strong effect on observed vibrational modes. The respective shifts for $NaFePO_4$ and $Na_3V_2(PO_4)_3$ vibrational modes have been attributed to the larger Na atomic mass in these olivine and NASICON phosphate materials. We will also discuss the effect of local structure and symmetries of these materials to understand electronic properties and their impact on electrochemical performance.

Electrode impedance spectroscopy method allows performing research in the widest possible time/frequency range, which is especially valuable in the application to the lithium electrochemical systems, in which the process of ion-electron transport comprises the stages of the bulk and cross-border transport with very different characteristic times. As is known, the results of impedance spectra (Fig. 1) analysis is strongly dependent on the model used - the equivalent electrical circuit (EEC). Our choice of EEC was based on the structural, morphological and electrochemical data. The calculated values of the diffusion coefficient of lithium in the material are in the range $10^{-14} – 10^{-12}$ cm^2/s depending on the composition and the lithiation degree

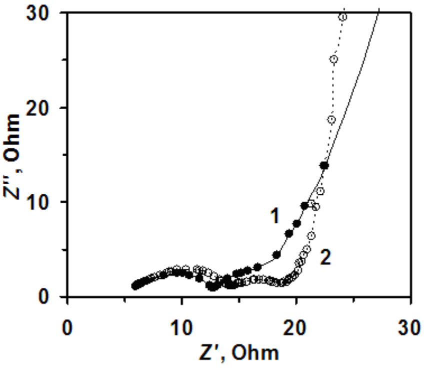

Fig. 1. The impedance spectra of the $Li_3V_2(PO_4)_3$ electrode: (1) maximum lithiated, E = 3.50V; (2) partially delithiated, E = 4.03V. Frequency range $3{\cdot}10^4 – 10^{-4}$ Hz.

Authors A.V. Ivanishchev, A.V. Churikov, A.V. Ushakov wish to thank Russian Science Foundation (project #15-13-10006) for support of synthesis and structural characterization of materials, and Russian Foundation for Basic Research (projects #14-29-04005 and #15-53-45091) for support of electrochemical study of materials. Authors M. J. Sneha and A. Dixit thank BRNS, Department of Atomic Energy (project # 2013/37P/72/BRNS/2933) and Department of Science and Technology (project # INT/RUS/RFBR/P-190) for financial support.

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ELECTROCHEMICAL BEHAVIOR OF LITHIUM-INTERCALATED ORTHOSILICATES Li_2MSiO_4 (M = Fe, Mn, Co)

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Lithium-ion batteries (LIB) nowadays are the most powerful and energy-efficient electrochemical devices; LIBs are the basis of an autonomous energetics. Therefore the improving of all LIB's components is being continued. Among promising cathode materials there are complex (lithium + transition metals) orthosilicates having general formula Li_2MSiO_4 (M = Fe, Mn, etc.). The theoretical capacity of these two compounds at the extraction of two lithium ions is about 330 mAh/g, that is significantly higher than for the most of known cathode materials. However, practical implementation of such characteristics turned out to be very difficult, mainly due to the extremely low electrical conductivity of silicate materials. The most efficient way to solve this problem is incorporation of such compounds into the conductive nanostructured composites [1,2].

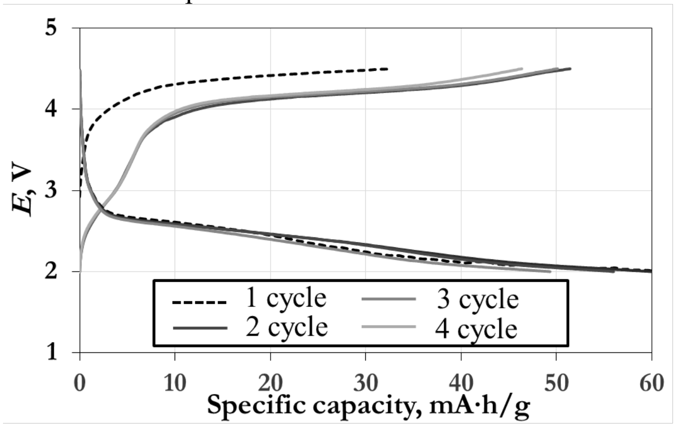

Fig.1. Charge-discharge characteristics of the Li_2FeSiO_4 electrode at the current 0.02C.

We have developed the synthetic procedure for obtaining composite material with Li_2MSiO_4 (where M = Fe, Mn, Co), while the formation of the electroactive component is commonly hampered due to low reactivity of silicon compounds. As a result, we carried out the synthesis process in stepwise manner using inexpensive and accessible reagents. In parallel with the formation of an electrically conductive matrix of the composite consisting of carbonaceous materials the chemically inactive silica SiO_2 has been involved (through the formation of metasilicate Li_2SiO_3) in the formation of the final product Li_2MSiO_4. The resulting material has stable charge-discharge characteristics and good cycling capacity (Fig. 1). Further optimization aimed to efficient management of the size and shape of the particles of the electroactive component, that will increase efficiency and capacity of cycling. Authors A.V. Ivanishchev, A.V. Churikov, A.V. Ushakov wish to thank Russian Science Foundation (project #15-13-10006) for support of synthesis and structural characterization of materials, and Russian Foundation for Basic Research (projects #14-29-04005 and #15-53-45091) for support of electrochemical study of materials. Authors M. J. Sneha and A. Dixit thank BRNS, Department of Atomic Energy (project # 2013/37P/72/BRNS/2933) and Department of Science and Technology (project # INT/RUS/RFBR/P-190) for financial support.

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