[a]*Faculty of Engineering, Hiroshima Institute of Technology.* [b]*Faculty of Information Sciences, Hiroshima City University.* [c]*Institute for Materials Research, Tohoku University, Japan.* E-mail: hosokawa@cc.it-hiroshima.ac.jp

From an X-ray diffraction [1], the lattice constant of diluted magnetic semiconductor $Zn_{1-x}Mn_xTe$ linearly changes with varying *x* (Vegard's law), while an XAFS results [2] showed almost unchanged Mn-Te and Zn-Te bond lengths (Pauling's rule). This discrepancy led to a question of how the large the large $MnTe_4$ tetrahedra can be squeezed into the small $ZnTe_4$ lattice.

X-ray fluorescence holography (XFH) is a new technique that allows one to investigate a three-dimensional local image around a specific element. The sample was irradiated by intense X-rays of certain energies beyond the Mn K absorption edge at BL37XU/SPring-8 in order to obtain the Mn K_α fluorescence hologram [3]. A three-dimensional atomic image around the Mn central atoms was derived from the hologram using Barton's algorithm. The nearest- and third-nearest-neighbour Te atoms were clearly visualized. However, the second-nearest-neighbour Zn or Mn atoms are barely visible in this image due probably to a highly distorted cation Zn(Mn) sub-lattice.

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Keywords: three-dimensional image reconstruction, X-ray fluorescence spectroscopy, magnetic semiconductors

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Investigation of $LaMn_{2-x}Fe_xSi_2$ ($0 \le x \le 1.2$) by Magnetic Measurements and Neutron Diffraction

Yalcın Elerman[a], Ayhan Elmali[a], Ilker Dincer[a], Helmut Ehrenberg[b], Hartmut Fuess[b], Aziz Daoud-Aladine[c], [a]*Engineering Physics, Ankara University, TR-06100 Besevler-Ankara, Turkey.* [b]*Institute for Materials Science, Darmstadt University of Technology, Petersenstrasse 23, D-64287 Darmstadt, Germany.* [c]*Laboratory for Neutron Scattering, ETHZ & PSI, CH-5232 Villigen, Switzerland.* E-mail: elerman@ankara.edu.tr

The various magnetic structures and phase transitions in the $LaMn_{2-x}Fe_xSi_2$ system have been thoroughly studied by X-ray powder diffraction, magnetic measurements and powder neutron diffraction. The substitution of Fe for Mn leads to a decrease in the lattice parameters and the magnetic interactions in the Mn sublattice cross over from a ferromagnetic character to an antiferromagnetic one. The magnetic structures of the $LaMn_{2-x}Fe_xSi_2$ compounds with $x = 0.2$, 0.475, 0.5, 0.7 and 1.0 have been determined between 2 and 450 K by neutron diffraction. A typical $SmMn_2Ge_2$-like magnetic behavior is observed for the $x = 0.475$ sample. The magnetic phase transition from ferromagnetism to antiferromagnetism for this sample occurs at the *intra*layer Mn-Mn distance $d_{Mn-Mn} = 2.89$ Å. This value exceeds the well known corresponding threshold value $d_{Mn-Mn} = 2.87$ Å in the pure Mn RMn_2X_2 compounds [1-2]. The results are summarized in the $LaMn_{2-x}Fe_xSi_2$ magnetic phase diagram [3].

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Keywords: rare-earth manganese silicides, layered structure, neutron diffraction

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Structural Reasons for the Giant Oxygen Isotope Effect in $Re_{0.5}Sr_{0.5}MnO_3$ Perovskites

Anatoly Balagurov[a], Ivan Bobrikov[a], Vladimir Pomjakushin[b], Natalia Babushkina[c], Oleg Gorbenko[d], Anrej Kaul[d], [a]*FLNP JINR, Dubna, Russia.* [b]*LNS ETH&PSI, Villigen, Switzerland.* [c]*"Kurchatov Institute", Moscow, Russia.* [d]*Moscow State University, Moscow, Russia.* E-mail: bala@nf.jinr.ru

The giant oxygen isotope effect (a metal-insulator transition induced by ^{16}O for ^{18}O substitution) has been recently discovered in $Sm_{1-x}Sr_xMnO_3$ compound for *x* close to 0.5 [1]. We performed a neutron diffraction study for elucidating structural reasons of this transition. Both crystal and magnetic structures have been determined for several compositions with Re=Sm and $(Nd_{1-y}Tb_y)$, y=0.228 and 0.456. These particular (Nd/Tb) ratios were chosen to model the average ionic radii of Sm and $(Sm_{0.5}Nd_{0.5})$ compositions respectively. In all studied samples the coexistence of ferromagnetic-metallic (FMM) and antiferromagnetic-insulating (AFMI) phases has been found at low temperature. From structural point of view both phases have the same *Pnma*-type structure but with strong difference in lattice parameters. The $d(x^2\text{-}y^2)$ orbital ordering in A-type AFMI phase leads to the huge shortening of Mn-O1 distances (≈1.2%) (as well as of *b* lattice parameter) and stimulates strong intragranular strains, which stabilize phase separated state. The same situation, though with different type of magnetic and orbital ordering in AFMI phase, has been found in LPCM-*y* type manganites, which also exhibit the giant oxygen isotope effect [2].

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Keywords: manganites, neutron diffraction, isotope effect

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X-ray Study of the Native Solid Hydrocarbons Transformation

Olga V. Kovaleva[a], U.M. Korolev[b], [a] *Institute of Geology, Komi Science Centre, Uralian Branch of RAS, Syktyvkar, Komi Republic, Russia.* [b]*Institute of Petrochemical Synthesis of RAS, Moscow, Russia.* E-mail: OlgaKovaleva@geo.komisc.ru

The subject of our investigation the native hydrocarbons (bitumens), which we defines as organic compounds with a primarily hydrocarbon basis. In the structural relation bitumens are characterized by the supermolecular organization with the sizes of elements from tens nanometers up to micron. The X-ray method opens new possible in the diagnostics of complex systems, using as numerical index a graphitization degree (Sg), which allows to diagnose as well as follow the dynamics and transformation mechanism of bitumens in the carbonization series: asphalt – asphaltite – kerite – anthraxolite – graphite.

The purpose of the research work is to study X-ray transformation of bitumens on the supermolecular level. The X-ray spectrum of bitumens of different transformation stages consist of two basic reflection 0.48 and 0.38 nm corresponding to the hydrocarbon polynaphtenic phase (N_f) and an amorphous graphite-like phase (G_f). The concentration of the latter increase with the growth of the catagenetic transformations degree. That is a final transformation product of natural bitumen is graphite. This testify to the single ransformation mechanism of natural bitumens. Thus, the X-ray methods allow to determine the genetic type of native organic substances and establish the catagenetic transformation level of the organic substances.

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Keywords: X-ray diffraction and structure, hydrocarbons, nanostructures

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The Influence of Synthesis Conditions on the Packing of the Spherical Particles of Silica in a Supramolecular Structure

Dmitry V. Kamashev, *Institute of Geology, Komi Science Centre, Uralian Branch, Russian Academy of Science, Syktyvkar, Russia.* E-mail: kamashev@geo.komisc.ru

As a result of the conducted experiments on the synthesis and precipitation of monodisperse spherical silica particles (100-800 nm) in different conditions we have determined a direct relationship between the packing type of particles and pH, water concentration, ammonium ions, size and precipitation speed of the globules.

In fact, at high pH values we have spherical silica particles surrounded by a dense shell of gegenions that results in their electrostatic repulsion. As a result, during precipitating of particles on the surface of a supramolecular crystal, their position in the structure is conditioned by the repulsion of precipitating particles from the surface analogous to charged globules in the structure. It results in maximal filling of space. The situation is changed at low pH values and low sizes (less 400 nm) of particles which results in reducing their surface and the greater reduction of the concentration of gegenions, and as a consequence, of the force of their electrostatic repulsion. Forming here hydrogen bonds prevent the precipitation of the particles in the most favorable positions which results in reducing the filling ratio of the particles.

In the framework of the experiment conducted by us, the packing type of spheric particles in opal matrixes depends on the sol pH and silica sphere sizes. At pH 7.5–8.0 a primitive cubic packing of particles is realized. The increase of pH up to 8.5-9.0 results in the formation of hexagonal packing with a corresponding increase of particle sizes. At a higher pH values the closest packing formed which is characteristic for natural noble opal.

Keywords: amorphous materials, supramolecular crystals, spherical silica particles

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Quantitative Analysis of Poorly Crystalline Fe_2O_3 Specimens

Tomas Grygar[a], Petr Bezdicka[a], Veronika Simova[a], Oldrich Schneeweiss[b], Radek Zboril[c], [a]*Institute of Inorganic Chemistry AS CR, Rez, Czech Republic.* [b]*Institute of Physics of Materials AS CR, Brno, Czech Republic.* [c]*Palacky University, Olomouc, Czech Republic.* E-mail: grygar@iic.cas.cz

We analyzed amorphous and nanocrystalline natural and synthetic ferric oxides by X-ray diffraction (XRD), Mossbauer and UV-Vis spectroscopies, voltammetry of microparticles, and thermoanalytical methods. The quantitative analytical methods were tested with intermediates of the thermal conversion of ferrihydrite to nanocrystalline hematite.

The XRD measurement with the addition of a known amount of reference material (Si) is not applicable when the mean coherence is only a few nm. Moessbauer spectroscopy and voltammetry of microparticles of such poorly ordered solids should be supported by the results of other methods, but under optimal conditions they are expected to "see" both amorphous and crystalline components with a comparable sensitivity permitting their determination. However, the minimal particle size of the target compounds is not known for Mossbauer spectroscopy and voltammetry of microparticles, and it seems to be equal or even larger than mean coherence length enabling XRD measurement. Diffuse reflectance spectroscopy can only be used to qualitative analysis, because the spectra of ferrihydrite and almost amorphous Fe_2O_3 are hardly interpretable.

The results indicate a lack of the knowledge on a local structure of 2-line ferrihydrite and XRD amorphous ferric oxides.

Keywords: amorphous materials, nanocrystalline materials, iron oxides

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Revisitation of the Structural Models for Ferrihydrites

Gabriele Navarra, Maria F. Casula, Gabriella Pinna, *Department of Chemical Sciences, University of Cagliari, Cagliari, Italy.* E-mail: navarra@unica.it

Ferrihydrite is a generic term for various poorly ordered Fe(III) oxyhydroxides. They are also characterized by small particle size, as evident from X-ray diffraction patterns. They in fact consist of a number of broad peaks varying from 2 to 6; the extreme forms are referred to as 2-line and 6-line ferrihydrite, while the 4-line one is better known as feroxyhyte. The lack of experimental details causes concern about the uniqueness of structural interpretation of XRD data.

In spite of this [1,2], several models have been proposed: however, the agreements with the experiments were reached assuming a mixture of two or three crystalline structures which made use of sets of rather unreasonable atomic occupancies. Besides, some Fe-Fe distances obtained from EXAFS analysis are not consistent with those interpretations.

We present here structural models for the three forms of ferrihydrites in which the oxygen atoms have unitary weights and the iron atoms, with half weights according to the oxide stoichiometry, are set in all the available octahedral sites.

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Keywords: ferrihydrite, disordered systems, xrd

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Crystal Structure of New Lanthanide Diphosphates

Francesco Capitelli[a], Brahim El Bali[b], Juan F. Piniella[c], [a]*IC-CNR, Bari, Italy.* [b]*Dépt. de Chimie, Faculté des Sciences Dhar Mehraz, BP 1796 Atlas, 30000 Fès, Morocco.* [c]*Dept. of Geology, Universitat Autònoma de Barcelona, Bellaterra, Spain.* E-mail: francesco.capitelli@ic.cnr.it

In the context of a general study on synthetic phosphates [1-2], the crystal structures of three new lanthanide diphosphates are presented: $KLnP_2O_7{\cdot}2H_2O$, where *Ln* is Gd, Tb and Yb. Suitable monocrystals were grown after the synthesis carried out using equimolar proportions of $K_4P_2O_7$ (dissolved in HCl) and $LnCl_3{\cdot}6H_2O$ as reagents. The structures, solved by X-ray diffraction methods (SIR97) and refined by full-matrix least squares (SHELXL-97), resulted to be isostructural within space group $P2_1/c$. In table 1 are presented the unit-cell parameters, the volumes and the final R_1 ($I \geq 2\sigma(I)$) values. The three-dimensional frameworks are made by zig-zag chains of KO_9 polyhedra down *c*, sharing edges with discrete LnO_7 polyhedra and P_2O_7 units; intricate hydrogen bonding networks complete the arrays.

Table 1

Ln	***a(Å)***	***b(Å)***	***c(Å)***	***β(°)***	**V*(Å³)***	**R_1(%)**
Gd	7.7522(2)	10.6732(8)	10.1375(7)	93.308(5)	837.39(9)	4.31
Tb	7.7380(6)	10.6360(8)	10.1060(7)	93.283(6)	830.37(11)	3.85
Yb	7.6791(3)	10.4992(7)	9.9554(9)	93.214(6)	801.39(10)	5.42

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Keywords: diphosphate, lanthanide, X-ray single crystal diffractometry

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Roman Ceramics in the Transylvanian Basin (Romania)

Ion Niculae Robu[a], L. Robu[a], A. Pescaru[b] , G. Verdes[c], A. Ursoi[c], [a]*Geological Institute of Romania, Caransebes str. 1, 012271-Bucuresti, Romania.* [b]*Museum of Dacic and Roman Civilization, Decebal str. 2, Deva, Romania.* [c]*Gold Museum, Independentei str. 3, Brad, Romania.* E-mail: inrobu@yahoo.com

Some ceramic objects, as pots, have been found in some graves, emplacement in the Muncelu-Ruda zone from the Apuseni Mountains, Transylvania Region. They are associated with high burnt bones, quartz crystals, burnt ore, silver coins and funeral monuments, belonging to Roman Period (II-III).

Some fragments of pots belonging to different pots have been investigated for their mineralogical properties: thinness, color, porosity, engobe, and technique of moulding-fashioning of the ceramic paste.

The investigated fragments are characterized by different porosity (high-low), variation of burning degree intensity, its effect being recognized in both wells of the pots as very parallel different red-brownish tints of strip. The structural aspects consist in the parallel