the trigonal phase R-3m at a temperature $\approx$ 457 K [1], corresponding to behaviour of dielectric and optical properties. The trigonal phase exists in a very narrow temperature interval in comparison with isostructural $M_3H(XO_4)_2$ crystals [2]. The obtained structural data confirmed the previously proposed mechanism of conduction in crystals of this family: the appearance of a high protonic conductivity is associated with the formation of a qualitatively new system of hydrogen bonds - the dynamically disordered hydrogen bond network, in which both the proton positions in hydrogen bonds and the bond orientations are dynamically disordered. The network of hydrogen bonds thus formed enables protons to move over vacant crystallographically equivalent positions, which leads to anomalously high hydrogen diffusion coefficients and to superionic conductivity. Also it was received the information about solid state reactions (the crystalline state remains), occurring in investigated crystals with an increase in the temperature. The temperature increase above the trigonal phase leads to formation of K_2SO_4 phases in the samples under study. The heating and cooling of the samples lead to formation of $K_2S_2O_7$ phases also. It is necessary to notice, that according to the powder data there are absent diffraction peaks corresponding to $KHSO_4$ compound, which could be formed in $K_3H(SO_4)_2$ samples in the process of solid state reactions, as it is supposed under the literary data. The formation of a multiphase state is confirmed by X-ray diffraction data, scanning electronic microscopy and the energy dispersive X-ray spectroscopy.

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Keywords: crystal and powder X-ray diffraction structure analysis, phase transitions and structure, superionic conductivity

FA2-MS16-P38

$Y_4H_8Si_3O_{16}$: A naturally occuring defect silicate of the KDP-structure type. Thomas Malcherek[a], Jochen Schlüter[a], Boriana Mihailova[a], Tomas A. Husdal[b]. [a]*Mineralogie, Universität Hamburg, Grindelallee 48, D-20146 Hamburg.* [b]*Høglia 81, N-8027 Bodø, Norway.* E-mail: thomas.malcherek@uni-hamburg.de

A new type of rare earth (RE) silicate with idealized composition $(Y,Ln)_4H_8Si_3O_{16}$ (Ln = Gd, Tb, Dy, Ho, Er, Yb) (YSO) has been identified in a granitic pegmatite of the Stetind quarry, Tysfjord, Northern Norway. The space group symmetry is *I-42d* and the crystal structure closely corresponds to the KDP-structure type. KH_2PO_4 (KDP) is a well known ferroelectric [1], distinguished by the ordering of hydrogen bonds. Thus in the paraelectric phase of KDP, hydrogen is equally distributed across two equivalent positions along the hydrogen bond, while only one of these positions is occupied in the fully ordered ferroelectric state. In YSO a trivalent rare earth cation substitutes for the monovalent cation of KDP and Si^{4+} substitutes for P^{5+}. Provided the number of hydrogen atoms is constant, one positive charge has to be compensated, which is achieved by Si-vacancies in YSO. X-ray diffraction data has been collected on several single crystals of YSO. The structure refinements on average yield Si-occupancies of 75±5%. The presence of heavy RE elements on the Y-site has been modelled using the Yb scattering factor curve, resulting in Yb/Y ratios of 1/4. Similar compositions are obtained by electron microprobe analysis, also indicating the presence of other heavy RE cations. Raman microspectroscopy performed on the crystals used for the X-ray structure analysis, confirms the presence of OH-stretching modes. The crystal chemistry of the new compound and possible similarities to KDP in terms of hydrogen bonding are discussed.

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Keywords: hydrogen bonding of minerals, rare-earth compounds, ferroelectrics and related materials

FA2-MS16-P39

Evolution of the Shape of Nanothin Selenium Crystals during their Growth in Amorphous Films. Malkov Andrey[b], Malkov Vyacheslav[a], Strekalovsky Victor[a], Malkov Oleg[b], Puchin Vladimir[c]. [a]*Institute of High-Temperature Electrochemistry, Ural Division RAS,* [b]*"ROSNA" Scientific and Production Center,* [c]*Institute of Metal Physics, UD RAS, Ekaterinburg, Russia.* E-mail: mvb@ihte.uran.ru

The method of transmission electron microscopy was used to study the evolution of a rotational distortion of the lattice and the shape of nanothin (80÷100 nm) crystals of hexagonal selenium growing in amorphous films at crystallization temperatures of 180÷120°C.

It was found that the lattice of nanothin selenium crystals growing in amorphous films at crystallization temperatures of 180÷150°C undergoes a nonuniform elastic rotational distortion around the [001] direction (180÷160°C) or in two mutually perpendicular directions, namely, around [001] and the perpendicular direction of the maximum growth rate (150°C). Nanothin selenium crystals growing in this range of crystallization temperatures have a rectilinear rhombic shape (Fig.1a,b).

At crystallization temperatures of 140÷120°C the lattice of nanothin selenium crystals undegoes a nonuniform elastoplastic rotational distortion around three mutually perpendicular directions [1]. In addition to the aforementioned directions, the lattice of nanothin selenium crystals undergoes a nonuniform rotational distortion around a direction, which is not in the film plane and is perpendicular to the first two directions. It is called an azimuthal distortion. The nanothin selenium crystals, which grow at crystallization temperatures of 140÷120°C, have a distorted curvilinear rhombic shape (Fig.1c,d). The sign of distortion of the shape of a nanothin selenium crystal always coincides with the sign of the azimuthal distortion of its lattice (Fig.1c,d). It can be concluded from this fact that the azimuthal distortion of the lattice of a nanothin selenium crystal determines the azimuthal distortion of its shape.

Fig. 1. Evolution of the shape of nanothin selenium crystals: rhomboid crystals of a rectilinear shape (a, b); nanothin crystals of a curvilinear shape (c, d), ×10 000

A model for the avolution of the shape of nanothin selenium crystals has been proposed. This model is based on the assumption that the evolution of the real structure of nanothin

selenium crystals has a decisive effect on the avolution of their shape as the crystals grow in amorphous films.

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Keywords: selenium-1, crystals-2, crystal shape-3

FA2-MS16-P40

Structural Peculiarities of Sillenites. <u>Tatyana I. Mel'nikova</u>[a], Galina M. Kuz'micheva[a], Victor B. Rybakov[b], Nadezhda B. Bolotina[c], A. Cousson[d].
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The phases with general formula $Bi_{24}M_2O_{40}$ or $Bi_{24}(M,M')_2O_{40}$ have sillenite structure (γ-Bi_2O_3, sp.gr. *I23*, *z*=13) and interesting physical properties such as photoconductivity, piezo-and electrooptical effects and other. Numerous literature data show that properties depend on the M and M' cations in the tetrahedral sites and their formal charges (FC). *The aim* of this paper is to determine structural peculiarities of the phases with sillenite structure.
The samples of initial compositions ($Bi_{24}[M_2]O_{40}$ (M=Si, Ge, Ti, Mn, Fe, V, (V+Sm)) and $Bi_{24}[Si_{2-y}M_y]O_{40}$ (M=Mn, V) have been grown by hydrothermal method (*t*=400ºC±10ºC, *p*=150MPa) by spontaneous crystallization as cubes and tetrahedral or combination of cubes and tetrahedral. The structure and composition have been found using results of single crystal X-ray (CAD-4 diffractometer–AgK_{α}, SHELXL-97 program and Xcalibur diffractometer–MoK_{α}, JANA2000 program; graphite monochromator) and neutron (5C2, Orphee reactor, λ=0.828Å) studies. Besides, IR-spectroscopy results and crystallochemical analysis have been used.
The phases with $Bi_{24}[M_2]O_{40}$ initial composition can describe by some models (sp.gr. *I23*) with different point defects:
1. $Bi_{24}[M^{4+}_2]O_{40}$: M^{4+} = Si, Ge, Ti, Mn (r(M) = 0.26÷0.42Å, r(M)-ionic radii; *000* - coordinates for M). These phases are known as "ideal" sillenites.
2. $Bi_{24}[M^{3+}_{2-x}[]_x](Bi_i)O_{40-\delta}$ (M^{3+} = B [1], r(B)= 0.11Å; Fe and Ga [2], r(M)= 0.47÷0.49Å; ~*0.02 0.02 0.02* -coordinates for Bi_i) or $Bi_{24}[M^{3+}_{2-x}[]_x]O_{40-\delta}$ (M^{3+} = Fe, Bi [2]).
3. $Bi_{24}[M^{5+}_{2-x}[]_x]O_{40}$ (M^{5+}= P and As [3]; r(M) = 0.17÷0.33Å) or $Bi_{24}[(V^{5+}O)_4(BiO)_4]O_{32}$ (*000* – coordinates for V and Bi; two sites for O atoms) [4], $Bi_{24}[Bi_xV^{5+}_y[]_{2-x-y}]O_{40}(O_i)$ (*1/2 0 0* – coordinates for O_i) [2], $(Bi_{24-x}[]_x)[Bi_{2-y}V^{5+}_y]O_{40}$, $[Bi_{24-w}Sm_w][Bi_{2-y}V^{5+}_y]O_{40}$ (r(V) = 0.36 Å, r(Sm) = 0.96 Å).
The structures of solid solutions with $Bi_{24}[Si_{2-y}M_y]O_{40}$ (M=Mn, V) initial composition are related to the first model. Their real compositions may be exhibited following ways:
1. $Bi_{24}[Bi^{3+}_{2-y}M_y]O_{40}$ (M=Mn^{4+}) (sp. gr. *P23*)
2. $Bi_{24}[Si^{4+}_{2-y}M_y]O_{40}$ (M=Mn^{4+}, Mn^{4+}+Mn^{5+})(sp. gr. *P23*)
3. $Bi_{24}[Si^{4+}_{2-x-y}Bi^{3+}_xM_y]O_{40}$ (M=Mn^{4+}, V^{4+}+V^{5+}, V^{5+}) (sp. gr. *I23* and sp. gr. *P23*).
The different space group (sp. gr. *I23* or sp. gr. *P23*) of crystals (a structure dissymmetrization) is attributed to the kinetic phase transition of order-disorder type. The causes are associated with a presence of several atoms in M position of sillenite structure and preparation conditions simultaneously.

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**Keywords: sillenites, composition, structure**

FA2-MS16-P41

New phases in the Li-Cu-B-O system: $Li_3CuB_3O_7$, $Li_2Cu_9B_{12}O_{28}$ and monoclinic $Cu_3B_2O_6$. <u>Daria Mikhailova</u>[a,b], Natalia Kuratieva[a,c], Helmut Ehrenberg[a]. [a]*Institute for Complex Materials, IFW Dresden, Germany.* [b]*Institute for Materials Science, Technische Universität Darmstadt, Germany.* [c]*Institute of Inorganic Chemistry SB Russian Academy of Science, Russia.*
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Li-containing borates with 3d elements attract a large interest in the last years as potential intercalation electrode materials for Li batteries. For example, $LiFeBO_3$ with chains of distorted edge-shared FeO_5-units with Fe^{2+}, was proposed as a perspective cathode material for Li-deinsertion [1]. The advantages of such materials are an existence of 3d metals in different oxidation states and the ability of boron to form BO_3-triangles and BO_4-tetrahedra, which are connected with each other in a different manner.
The common feature of all known copper(II) borates is a Jahn-Teller distortion of Cu^{2+} coordinated polyhedra due to the electronic configuration of the d^9 ion, which can lead to an anisotropic character of the crystal structure. The information about phases in the Li-Cu-B-O system is deficient and contradictory: three compounds $Li_4CuB_2O_6$, $Li_2Cu_2B_2O_6$ and $Li_2CuB_4O_8$ were synthesized in air, but neither crystal structures nor cell parameters were reported [2].
During phase investigations in the Li-Cu-B-O system we have found some new complex borates at ambient pressure, namely $Li_3CuB_3O_7$, $Li_2Cu_9B_{12}O_{28}$ and a new polymorphic modification of $Cu_3B_2O_6$ [3]. This new $Cu_3B_2O_6$-polymorph with a pseudo-layered monoclinic structure has both BO_3-triangles and B_2O_6-units consisting of corner-sharing BO_3-triangles and BO_4-tetrahedra. In contrast to the well-known triclinic form of $Cu_3B_2O_6$ [4], layers are linked with each other by BO_4-tetrahedra. Crystal structures of $Li_3CuB_3O_7$ and $Li_2Cu_9B_{12}O_{28}$ exhibit only BO_3-triangles, which are connected with each other via corners. $Li_3CuB_3O_7$ demonstrates infinite Cu,O-chains from Cu_2O_8-units consisting of edge-sharing CuO_5-pyramids. These chains are responsible for the strong anisotropic character of the thermal expansion of the phase along the *a*-axis. In the structure of $Li_2Cu_9B_{12}O_{28}$ CuO_6-octahedra and CuO_5- pyramids can be identified with Cu-O bonds smaller or equal to 2.7 Å, which are connected with each other in a different manner.
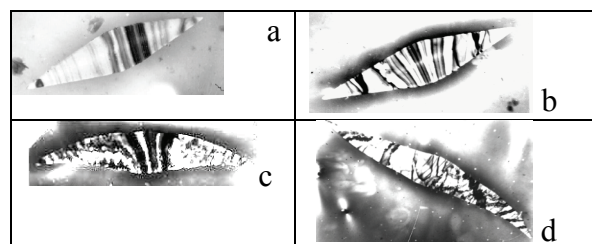
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