

selenium crystals has a decisive effect on the evolution 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.** Tatyana I. Mel'nikova<sup>a</sup>, Galina M. Kuz'micheva<sup>a</sup>, Victor B. Rybakov<sup>b</sup>, Nadezhda B. Bolotina<sup>c</sup>, A. Cousson<sup>d</sup>.  
<sup>a</sup>Lomonosov State Academy of Fine Chemical Technology, Moscow, Russia. <sup>b</sup>Lomonosov State University, Moscow, Russia. <sup>c</sup>Shubnikov Institute of Crystallography RAS, Moscow, Russia. <sup>d</sup>Laboratoire Leon Brillouin, Cea/Saclay, France.  
E-mail: [melti@list.ru](mailto:melti@list.ru)

The phases with general formula  $\text{Bi}_{24}\text{M}_2\text{O}_{40}$  or  $\text{Bi}_{24}(\text{M},\text{M}')_2\text{O}_{40}$  have sillenite structure ( $\gamma\text{-Bi}_2\text{O}_3$ , 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 ( $\text{Bi}_{24}[\text{M}_2]\text{O}_{40}$  (M=Si, Ge, Ti, Mn, Fe, V, (V+Sm)) and  $\text{Bi}_{24}[\text{Si}_{2-y}\text{M}_y]\text{O}_{40}$  (M=Mn, V) have been grown by hydrothermal method ( $t=400^\circ\text{C}\pm 10^\circ\text{C}$ ,  $p=150\text{MPa}$ ) 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 $\alpha$ , SHELXL-97 program and Xcalibur diffractometer–MoK $\alpha$ , JANA2000 program; graphite monochromator) and neutron (5C2, Orphee reactor,  $\lambda=0.828\text{\AA}$ ) studies. Besides, IR-spectroscopy results and crystallochemical analysis have been used.

The phases with  $\text{Bi}_{24}[\text{M}_2]\text{O}_{40}$  initial composition can describe by some models (sp.gr. *I23*) with different point defects:

1.  $\text{Bi}_{24}[\text{M}^{4+}_2]\text{O}_{40}$ :  $\text{M}^{4+} = \text{Si, Ge, Ti, Mn}$  ( $r(\text{M}) = 0.26\div 0.42\text{\AA}$ ,  $r(\text{M})$ -ionic radii; 000 - coordinates for M). These phases are known as "ideal" sillenites.

2.  $\text{Bi}_{24}[\text{M}^{3+}_{2-x}[\text{X}]](\text{Bi})\text{O}_{40-5}$  ( $\text{M}^{3+} = \text{B}$  [1],  $r(\text{B}) = 0.11\text{\AA}$ ; Fe and Ga [2],  $r(\text{M}) = 0.47\div 0.49\text{\AA}$ ;  $\sim 0.02\ 0.02\ 0.02$  -coordinates for Bi) or  $\text{Bi}_{24}[\text{M}^{3+}_{2-x}[\text{X}]]\text{O}_{40-5}$  ( $\text{M}^{3+} = \text{Fe, Bi}$  [2]).

3.  $\text{Bi}_{24}[\text{M}^{5+}_{2-x}[\text{X}]]\text{O}_{40}$  ( $\text{M}^{5+} = \text{P and As}$  [3];  $r(\text{M}) = 0.17\div 0.33\text{\AA}$ ) or  $\text{Bi}_{24}[(\text{V}^{5+}\text{O})_4(\text{BiO})_4]\text{O}_{32}$  (000 - coordinates for V and Bi; two sites for O atoms) [4],  $\text{Bi}_{24}[\text{Bi}_x\text{V}^{5+}_y][\text{O}_{40}(\text{O}_i)]$  ( $1/2\ 0\ 0$  - coordinates for O<sub>i</sub>) [2],  $(\text{Bi}_{2-2x}[\text{X}][\text{Bi}_{2-y}\text{V}^{5+}_y]\text{O}_{40})$ ,  $[\text{Bi}_{2-w}\text{Sm}_w][\text{Bi}_{2-y}\text{V}^{5+}_y]\text{O}_{40}$  ( $r(\text{V}) = 0.36\text{\AA}$ ,  $r(\text{Sm}) = 0.96\text{\AA}$ ).

The structures of solid solutions with  $\text{Bi}_{24}[\text{Si}_{2-y}\text{M}_y]\text{O}_{40}$  (M=Mn, V) initial composition are related to the first model. Their real compositions may be exhibited following ways:

1.  $\text{Bi}_{24}[\text{Bi}^{3+}_{2-y}\text{M}_y]\text{O}_{40}$  (M=Mn<sup>4+</sup>) (sp. gr. *P23*)  
2.  $\text{Bi}_{24}[\text{Si}^{4+}_{2-y}\text{M}_y]\text{O}_{40}$  (M=Mn<sup>4+</sup>, Mn<sup>4+</sup>+Mn<sup>5+</sup>) (sp. gr. *P23*)  
3.  $\text{Bi}_{24}[\text{Si}^{4+}_{2-x-y}\text{Bi}^{3+}_x\text{M}_y]\text{O}_{40}$  (M=Mn<sup>4+</sup>, V<sup>4+</sup>+V<sup>5+</sup>, V<sup>5+</sup>) (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

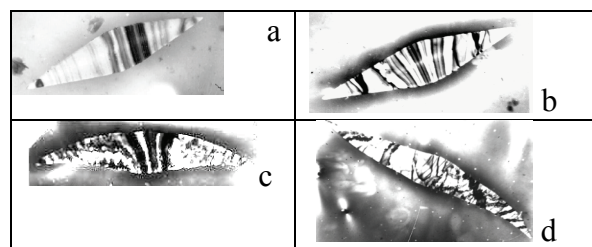
**New phases in the Li-Cu-B-O system:  $\text{Li}_3\text{CuB}_3\text{O}_7$ ,  $\text{Li}_2\text{Cu}_9\text{B}_{12}\text{O}_{28}$  and monoclinic  $\text{Cu}_3\text{B}_2\text{O}_6$ .** Daria Mikhailova<sup>a,b</sup>, Natalia Kuratieva<sup>a,c</sup>, Helmut Ehrenberg<sup>a</sup>.

<sup>a</sup>Institute for Complex Materials, IFW Dresden, Germany. <sup>b</sup>Institute for Materials Science, Technische Universität Darmstadt, Germany. <sup>c</sup>Institute of Inorganic Chemistry SB Russian Academy of Science, Russia.  
E-mail: [d.mikhailova@ifw-dresden.de](mailto:d.mikhailova@ifw-dresden.de)

Li-containing borates with 3d elements attract a large interest in the last years as potential intercalation electrode materials for Li batteries. For example,  $\text{LiFeBO}_3$  with chains of distorted edge-shared  $\text{FeO}_5$ -units with  $\text{Fe}^{2+}$ , 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  $\text{BO}_3$ -triangles and  $\text{BO}_4$ -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  $\text{Cu}^{2+}$  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  $\text{Li}_4\text{CuB}_2\text{O}_6$ ,  $\text{Li}_2\text{Cu}_2\text{B}_2\text{O}_6$  and  $\text{Li}_2\text{CuB}_4\text{O}_8$  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  $\text{Li}_3\text{CuB}_3\text{O}_7$ ,  $\text{Li}_2\text{Cu}_9\text{B}_{12}\text{O}_{28}$  and a new polymorphic modification of  $\text{Cu}_3\text{B}_2\text{O}_6$  [3]. This new  $\text{Cu}_3\text{B}_2\text{O}_6$ -polymorph with a pseudo-layered monoclinic structure has both  $\text{BO}_3$ -triangles and  $\text{B}_2\text{O}_6$ -units consisting of corner-sharing  $\text{BO}_3$ -triangles and  $\text{BO}_4$ -tetrahedra. In contrast to the well-known triclinic form of  $\text{Cu}_3\text{B}_2\text{O}_6$  [4], layers are linked with each other by  $\text{BO}_4$ -tetrahedra. Crystal structures of  $\text{Li}_3\text{CuB}_3\text{O}_7$  and  $\text{Li}_2\text{Cu}_9\text{B}_{12}\text{O}_{28}$  exhibit only  $\text{BO}_3$ -triangles, which are connected with each other via corners.  $\text{Li}_3\text{CuB}_3\text{O}_7$  demonstrates infinite Cu-O-chains from  $\text{Cu}_2\text{O}_8$ -units consisting of edge-sharing  $\text{CuO}_5$ -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  $\text{Li}_2\text{Cu}_9\text{B}_{12}\text{O}_{28}$   $\text{CuO}_6$ -octahedra and  $\text{CuO}_5$ -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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investigation of the  $B_2O_3$ -CuO- $Li_2O$  ternary system". [3] N. A. Kuratieva, D. Mikhailova, H. Ehrenberg, "A new polymorph of  $Cu_3B_2O_6$ ", *Acta Cryst. C* 65 (2009) 185-186. [4] Behm, H. (1982). *Acta Crystallogr. B* 38, 2781, "Pentadecacopper (II) Bisborate Hexaorthoborate Dioxide".

**Keywords:** Jahn-Teller distortion of Cu(II), layered structure, anisotropic thermal expansion

#### FA2-MS16-P42

**Crystallographic Orientation Relationship between Bastnaesite, Fluocerite and Cerianite in a Single Crystal from the Pikes Peak Pegmatites.** Mathis M. Müller, Hans-Joachim Kleebe. *GeoScience, Technical University Darmstadt, Germany.*

E-mail: [mueller@geo.tu-darmstadt.de](mailto:mueller@geo.tu-darmstadt.de)

A fluocerite (Ce,Lu)F<sub>3</sub> single crystal intergrown with bastnaesite (Ce,Lu)[CO<sub>3</sub>]F from the Pikes Peak area in Colorado, USA was prepared for the investigation of the crystallographic orientation relationship between the two mineral phases via transmission electron microscopy. The epitaxial overgrowth of bastnaesite on fluocerite was confirmed by evaluating the electron diffraction patterns of the relevant mineral phases. During the examination, a third mineral phase, which was unexpected in this phase assemblage, was detected and identified as cerianite CeO<sub>2</sub> by EDS in conjunction with electron diffraction. Its orientation relationship to the main mineral phases can be described as a syntactical growth. The La-concentration of the bastnaesite changed with the distance from the cerianite interface, as confirmed by EDS. The reduction of La-content near the interface together with the respective crystallographic relationship yielded a model explaining the formation of the encountered mineral assemblage of bastnaesite, fluocerite and cerianite. The orientation matrix and the direction-plane relation for the three mineral phases was established.

**Keywords:** bastnaesite, orientation relationship, orientation matrix

#### FA2-MS16-P43

**Ordering in intercalated Co atoms and electron density distributions of layered compounds Co<sub>x</sub>TiS<sub>2</sub>**

Ken-ichi Ohshima, Takuro Kawasaki, Miwako Takahashi *Institute of Materials Science, University of Tsukuba, Tsukuba305-8573, Japan.*  
E-mail: [ohshima@bk.tsukuba.ac.jp](mailto:ohshima@bk.tsukuba.ac.jp)

A structural study of layered compounds Co<sub>x</sub>TiS<sub>2</sub> (x=0.26,0.43, and 0.57) by X-ray diffraction analysis was performed to investigate both the ordered atomic arrangement and disordering behavior of intercalated Co atoms, and the nature of the chemical bond from the electron density distribution (EDD) obtained by the maximum entropy method. The 2ax2ax2c superstructure of the Co atoms is observed for x=0.26 and 0.57, and disappears at 510 and 550K, respectively. On the other hand,  $\sqrt{3}ax\sqrt{3}ax2c$  superstructure of the Co atoms is observed for x=0.43, and disappears at 610 K. It is understood that the type of the transition is second-order-like. The overlapping of the EDD between Co and S atoms & Ti and S atoms are clearly seen, which are corresponding to the covalent bonding in the van der Waals gap layer and in the TiS<sub>2</sub> one. It is expected that nature of covalent bonding

between Co and S atoms causes decreasing of the interlayer distance.

**Keywords:** layered compounds, ordering of the Co atoms, EDD

#### FA2-MS16-P44

**Structural trends in the (emim)<sub>m</sub>[A<sub>n</sub>(Mo<sub>8</sub>O<sub>26</sub>)] (emim = 1-ethyl-3-methylimidazolium; m=2,3; n=1,2; A=K, Rb, Cs) group of compound.** Anna Pakhomova, Sergey Krivovichev. *Saint-Petersburg State University, Russian Federation.*

E-mail: [a.s.pakhomova@mail.ru](mailto:a.s.pakhomova@mail.ru)

Polyoxometalates (POMs) have many properties that make them attractive for applications in medicine, biology, magnetism, materials science and catalysis. POMs are a kind of competent structure-tunable building block because they exhibit a wide variety of structural motifs of different sizes and topologies. As far as we know, all known octamolybdates has been synthesized by hydro- and solvothermal methods. To the best of our knowledge, ionothermal methods were not used, although they recently have shown high promise in the preparation of novel metal-organic frameworks.<sup>1</sup> We have used ionic liquid (emim)Br (emim=1-ethyl-3-methylimidazolium) as both solvent and template for the purpose of construction of novel organic-inorganic polymolybdates of alkali metals. The three novel octamolybdates (emim)<sub>3</sub>K(Mo<sub>8</sub>O<sub>26</sub>) (1), (emim)<sub>3</sub>Rb(Mo<sub>8</sub>O<sub>26</sub>) (2) and (emim)<sub>2</sub>Cs<sub>2</sub>(Mo<sub>8</sub>O<sub>26</sub>) (3) (emim = 1-ethyl-3-methylimidazolium) have been obtained in the ionothermal reactions. The structures of these compounds are described on the basis of octamolybdate anions [ $\beta$ -Mo<sub>8</sub>O<sub>26</sub>]<sup>4-</sup>. In compounds 1 and 2, [ $\beta$ -Mo<sub>8</sub>O<sub>26</sub>]<sup>4-</sup> units are linked by metal cations to form chain structures, while Cs cations in the compound 3 link to polyoxoanions to form layer structure.

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[1] Ranham E.R.; Morris R.E. *Acc. Chem. Res.* 2007, 40, 1005.

**Keywords:** ionothermal synthesis, alkali polyoxomolybdates, X-Ray crystal structure determination

#### FA2-MS16-P45

**Comparison of HP data for X-ray diffraction in Beand diamond-backed DACs.** Benedetta Periotto<sup>a</sup>,

Fabrizio Nestola<sup>b</sup>, Lars Olsen<sup>a</sup>, Tonci Balic-Zunic<sup>c</sup>, Ronald Miletich<sup>d</sup>, Ross J. Angel<sup>e</sup>. <sup>a</sup>*Department of Geography and Geology, Univ. of Copenhagen.*

<sup>b</sup>*Dipartimento di Geoscienze, Univ. di Padova.* <sup>c</sup>*Natural History Museum, Univ. of Copenhagen.* <sup>d</sup>*Institut für Geowissenschaften, Universität Heidelberg.*

<sup>e</sup>*Crystallography Laboratory, Virginia Tech.*

High-pressure cells reduce significantly the accessible reciprocal space in single-crystal studies and, moreover, the parts of cells traversed by radiation produce as a rule strong background features. In order to increase the quality of measured data and accuracy of calculated structural parameters it is of primary importance to reduce these deleterious effects. In Diamond Anvil Cells (DAC) diamond anvils must be supported by a strong and X-ray transparent