

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

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Structural Peculiarities of Sillenites. Tatyana I. Mel'nikova^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 $\text{Bi}_{24}\text{M}_2\text{O}_{40}$ 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 α , SHELXL-97 program and Xcalibur diffractometer–MoK α , 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 $\text{Bi}_{24}[\text{M}^{3+}_{2-x}\text{[x]O}_{40-5}$ ($\text{M}^{3+} = \text{Fe, Bi}$ [2]).

3. $\text{Bi}_{24}[\text{M}^{5+}_{2-x}\text{[x]O}_{40}$ ($\text{M}^{5+} = \text{P and As}$ [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_i) [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=Mn⁴⁺) (sp. gr. *P23*)
2. $\text{Bi}_{24}[\text{Si}^{4+}_{2-y}\text{M}_y]\text{O}_{40}$ (M=Mn⁴⁺, Mn⁴⁺+Mn⁵⁺) (sp. gr. *P23*)
3. $\text{Bi}_{24}[\text{Si}^{4+}_{2-x-y}\text{Bi}^{3+}_x\text{M}_y]\text{O}_{40}$ (M=Mn⁴⁺, V⁴⁺+V⁵⁺, V⁵⁺) (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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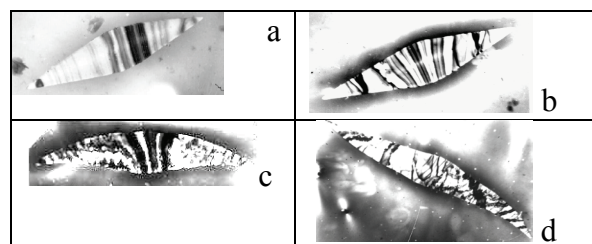
New phases in the Li-Cu-B-O system: $\text{Li}_3\text{CuB}_3\text{O}_7$, $\text{Li}_2\text{Cu}_9\text{B}_{12}\text{O}_{28}$ and monoclinic $\text{Cu}_3\text{B}_2\text{O}_6$. Daria Mikhailova^{a,b}, Natalia Kuratieva^{a,c}, Helmut Ehrenberg^a.

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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 $\text{Li}_4\text{CuB}_2\text{O}_6$, $\text{Li}_2\text{Cu}_2\text{B}_2\text{O}_6$ 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 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 $\text{Cu}_3\text{B}_2\text{O}_6$ [4], layers are linked with each other by 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 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 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 $\text{Li}_2\text{Cu}_9\text{B}_{12}\text{O}_{28}$ 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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