

**s11.m1.p3** The crystal structure of arsentsumebite,  $\text{Pb}_2\text{Cu}[(\text{As,S})\text{O}_4]_2(\text{OH})$  N.V. Zubkova<sup>1</sup>, D. Yu. Pushcharovsky<sup>1</sup>, G. Giester<sup>2</sup>, E. Tillmanns<sup>2</sup>; <sup>1</sup> *Geology Department, Moscow State University, 119899 Moscow, Russia*; <sup>2</sup> *Inst. für Mineralogie und Kristallographie, Universität Wien, A-1090 Wien, Austria*  
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Arsentsumebite,  $\text{Pb}_2\text{Cu}[(\text{As,S})\text{O}_4]_2(\text{OH})$ , a rare hipergenious sulphato-arsenate of lead and copper belongs to a brackebuschite - group of lead minerals with the general formula  $\text{Pb}_2\text{Me}(\text{XO}_4)(\text{YO}_4)(\text{Z})$  where  $\text{Me} = \text{Cu}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ;  $\text{X} = \text{S}$ ,  $\text{Cr}$ ,  $\text{V}$ ,  $\text{As}$ ;  $\text{Y} = \text{P}$ ,  $\text{As}$ ,  $\text{V}$ ,  $\text{S}$ ;  $\text{Z} = \text{OH}$ ,  $\text{H}_2\text{O}$ . All the members of this series have similar compositions, they are characterized by pronounced structural distinctions: different dimensions of Pb polyhedra, different coordination numbers of Pb atoms, sizes of tetrahedral complexes, etc.

The investigated sample of arsentsumebite was found in oxydation zone of Berezovskoye gold deposit, Middle Ural, Russia. A single crystal of arsentsumebite was selected for X-ray study on a Nonius Kappa CCD diffractometer,  $\text{MoK}\alpha$  radiation,  $\lambda = 0.71073 \text{ \AA}$ . Monoclinic unit cell parameters were:  $a = 7.804(8)$ ,  $b = 5.890(6)$ ,  $c = 8.964(8) \text{ \AA}$ ,  $\beta = 112.29(6)^\circ$ ,  $V = 381.2 \text{ \AA}^3$ . The structure was refined on the basis of atomic coordinates of tsumebite,  $\text{Pb}_2\text{Cu}(\text{SO}_4)(\text{PO}_4)(\text{OH})$ , with space group  $P2_1/m$ . The program JANA98 was utilised in the structure refinement. A difference Fourier with residual peaks around Pb and As,S atoms showed that their positions should be refined using the anharmonic thermal displacement factors (Gram-Charlier expansion of tensors  $F(\text{ijklmn})$ ). The final residual  $R_{\text{hkl}}$  is 0.0540 and the largest difference peak and hole are 3.52 and  $-2.11 \text{ e/\AA}^3$ , respectively.

Arsentsumebite can be considered as a member of the group of copper oxysalt minerals which structures are based on infinite chains. The basic unit of the mixed chains in arsentsumebite is the column  $[\text{Cu}_2\phi_8]$  formed by edge-sharing Cu octahedra, which contacts are reinforced by (As,S) tetrahedra. The heteropolyhedral  $[\text{Cu}(\text{As,S})_2\text{OH}]$  chains are parallel to  $[010]$  and thus b-edge of the unit cell depends on the size of cations located in the centres of octahedra and tetrahedra.  $\text{Cu}^{2+}$  cations are localised in the inversion centres. Cu has a  $[2+4]$  coordination forming distorted tetragonal bipyramide (i.e. an axially compressed octahedron) Both independent (As,S) tetrahedra are characterised by different As/S ratio. The chains are linked by irregular 7-fold and 6-fold Pb polyhedra. The number of ligands included in Pb polyhedra was confirmed by the sum of the bond strengths on anions and is within the range 6 - 11 reported for other minerals of brackebuschite group. The irregular shape of Pb polyhedra is attributed with  $6s^2$  lone pair of lead.

**s11.m1.p4** New Phases in RE-Borosilicate Systems (RE=La, Nd, Gd, Ho). E.P. Shvanskii<sup>1</sup>, N.I. Leonyuk<sup>1</sup>, G. Bocelli<sup>2</sup> and L. Righi<sup>2</sup>. <sup>1</sup>*Department of Crystallography and Crystallochemistry, Geological Faculty, Lomonosov Moscow State University, Moscow 119899, Russia*; <sup>2</sup>*Centro di Studio per la Strutturistica Diffraattometrica CNR, Viale delle Scienze, Parma 43100, Italy*  
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A number of borate and silicate crystals has found widespread use in science and modern applications. In this paper, we summarize our recent results on the flux growth and structural characteristics of new lanthanum and neodymium borosilicate crystals. First of all, the main attention was paid to the stillwellite like compounds because these ferroelectrics possess non-linear optical and piezoelectric properties. Moreover, neodymium doped stillwellite crystals can be considered as a new laser material.

Crystals of stillwellite-like La- and La,Nd-borosilicates were grown from high temperature solutions. The choice of fluxes was based on the lithium and potassium di- and trimolybdates with an excess of lithium and potassium fluorides (up to 20 wt. %). Best results on the growth of stillwellite crystals were obtained in the cases of fluxes 80 wt.%  $\text{K}_2\text{Mo}_3\text{O}_{10}$  - 20 wt.% KF and 30-35 wt.%-concentrated solutions. Also, new borosilicates,  $\text{RE}_3\text{BSi}_2\text{O}_{10}$  (RE=La, Nd, Gd and Dy) were synthesized in the run of these experiments. The composition of grown crystals was studied by electron microprobe analysis, and structural characteristics were determined by X-ray powder and single crystal diffraction methods.

$\text{La}_3\text{BSi}_2\text{O}_{10}$  belongs to the orthorhombic system: *Pbca* space group with  $a$ ,  $b$  and  $c$  cell constants equal to 9.977(2), 7.269(2) and 23.410(2)  $\text{Å}$  respectively. The lanthanum atoms show a seven-membered coordination, which result in mono-capped trigonal prisms, while the silicon atoms show the usual tetrahedral coordination. The Si-O bond distances are similar ranging from 1.627(3) to 1.650(1)  $\text{Å}$ , while, on the contrary, those La-O are significantly different ranging from 2.395(1) to 2.685(2)  $\text{Å}$ . The La trigonal prisms and the Si tetrahedra are distributed in layers perpendicular to the  $c$  axis. The planar  $\text{BO}_3$  triangles are intercalated to the preceding layers at around the 0 and  $1/2 c$  level.

In summary, some aspects of the synthesis of new La and La,Nd borosilicates with controlled and desirable composition, structure and properties for NLO applications will be discussed.

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