

m36.p10

The crystal structure of the LEP compound PbBi_2S_4 (galenobismutite) at the hydrostatic pressures between 0 and 10 GPa

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Keywords: galenobismutite, high pressure, lone electron pairs

Galenobismutite, PbBi_2S_4 , is isostructural with CaFe_2O_4 and with the mantle-pressure polymorph of NaAlSiO_4 . In galenobismutite, however, all three distinct cation sites are occupied by cations, which exhibit lone electron pair activity. The M1 site has a slightly distorted octahedral coordination, the polyhedron of M2 is a lying monocapped trigonal coordination prism, and M3 is a standing, bicapped trigonal coordination prism. Pinto et al. (2005) found M1 to be a Bi position whereas M2 and M3 sites are mixed sites, with predominance of Bi and Pb, respectively.

High-pressure experiments were performed in an ETH-type diamond anvil cell with a mixture of methanol:ethanol=4:1 as medium, and quartz as a pressure indicator. A CCD-equipped Bruker AXS four-circle diffractometer with an appropriate structure solution program package was employed.

The 3rd order Birch-Murnaghan equation gives a zero-pressure volume of $700.6(2)\text{Å}^3$, bulk modulus K_0 43.9(7) and its derivative K' 6.9(3). The large M3 polyhedron is most compressible, the rigidity of M1 polyhedra slackens at 6GPa. Eccentricity of the M2 position remains preserved to the highest pressures, unlike the situation in bismuthinite Bi_2S_3 , and bond lengths separate into two tight groups. This behaviour is shared by M1. The longer bonds are reduced to 2.9Å as a lower limit; the short bonds are compressed much less, to $2.7\text{-}2.6\text{Å}$.

The coordination polyhedron of the M3 site appears to accommodate the configurational differences between different isotypes of CaFe_2O_4 . In PbBi_2S_4 the highly asymmetric character of this polyhedron remains preserved under compression and M1 approaches a 7-fold coordination at high pressures.

Our studies show that the behaviour of lone electron pairs under pressure depends on the structure type. In the framework-approaching structure of galenobismutite, the lone electron pairs of Bi remain stereochemically active up at least 10 GPa, whereas in the ribbon-like structure of Bi_2S_3 their activity decreases substantially.

m36.p11

Change of Real Structure During Growth of Spherulite Crystals in Amorphous Selenium Films

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Keywords: real structure, thin-films, selenium

The change of the real structure during growth of spherulite crystals in thin amorphous films of selenium was studied using the method of transmission electron microscopy. It was found that the change of the real structure during the formation of a spherulite from a monocrystalline nucleus of hexagonal selenium was accompanied by the following processes:

1. a nonuniform elastic or elastic-plastic rotational distortion of the crystal lattice in one, two or three mutually perpendicular directions;
2. appearance of interblock boundaries having variable crystallogometric parameters;
3. the change of the crystal lattice geometry from Euclidean to Riemannian.

The examination revealed block-free selenium crystals with a nonzero azimuthal misorientation of the lattice. They represented the initial formation of the texture of a spherulite crystal. A method was developed for measuring the Riemann curvature of the crystal lattice and values of the Riemann curvature of the crystal lattice were determined. It was shown that relaxation processes of a nonuniform elastic rotational distortion of the crystal lattice of hexagonal selenium about the C-axis played the decisive role in the formation of the spherulite structure [1]. The following types of relaxation processes were detected: 1) continuous nonuniform; 2) continuous linear; 3) continuous nonlinear; 4) continuous discrete. Separate types of relaxation processes were accompanied by their superposition in crystals with different stages of the formation of the spherulite structure. A regular feature of thin-film selenium crystals - an asymmetry of their real structure - was established. It was shown that physical properties were asymmetric in crystals having an asymmetric real structure (Fig. 1).



Fig. 3. Selenium crystal with the habit asymmetry and the asymmetry of the real structure. The crystal was grown in an amorphous film at 140°C . $\times 10000$

A variant of the classical scheme describing the formation of the structure of a spherulite from a monocrystalline nucleus was proposed [2]. This variant reduces to the introduction of a new state of crystals, which is referred to as an orientation unstable state. In the case of thin-film crystals of hexagonal selenium this state means a nonuniform elastic rotational distortion of the lattice about the C-axis.

[1] Malkov V.B., Malkov A.V., Malkov O.V., Shulgin B.V., Pushin V.G. Bending-torsion tensor and analysis of reasons for formation of the real structure of selenium crystals with the Riemann geometry of the lattice // Proc. Int. Conf. "Phase Transformations and Nonlinear Phenomena in Condensed Media". Makhachkala. September 21-25, 2004. pp. 348-351.

[2] Shubnikov A.V. On Nucleus Forms of Spherulites // Kristallografiya. 1957. v. 2. pp. 584-589.