Hexacopper(I) phosphorus(V) bromide penta(selenide/sulfide), $Cu_6P(Se_{0.7}S_{0.3})_5Br$

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This work illustrates possible diffusion paths for Cu^I ions in a highly disordered structure of a superionic conductor of the argyrodite family. The $Cu_6P(Se_{0.7}S_{0.3})_5Br$ cubic structure is built from a $[P(Se_{0.7}S_{0.3})_5Br]$ framework in which Cu^I ions are distributed in various tetrahedral, triangular and linear sites. There are two types of disorder in the structure. The first type results from the fact that there are fewer Cu^I ions than the number of positions available for them in the unit cell. The second type is due to the static distribution of Se and S atoms in the $[P(Se_{0.7}S_{0.3})_5Br]$ framework. The title compound is a solid solution of two efficient ionic conductors, namely Cu_6PSe_5Br and Cu_6PS_5Br, in which high ionic conductivity results from order–disorder phenomena in the copper substructure. To shed light on the distribution of Cu^I ions in disordered $Cu_6P(Se_{0.7}S_{0.3})_5Br$, we refined their positions using a combination of a nonharmonic approach and a split-atom model. At room temperature, Cu^I ions show strong anharmonic vibrations along the edge of the $(Br)_4$ tetrahedra. The probability density functions of the Cu^I ions overlap and reveal possible diffusion paths.

Comment

The crystal structures of copper and silver argyrodites have recently been studied extensively because of their promising properties for electrochemical devices. Copper- and silver-based argyrodites are efficient ionic conductors. However, the ionic conductivity shows a significant dependence on the composition (Beeken *et al.*, 2003, 2005; Gagor *et al.*, 2006).

As for previously described argyrodites (Nilges & Pfitzner, 2005; Gaudin *et al.*, 2000), the combination of a split-atom model and a nonharmonic development of displacement parameters in the structure determination reveals possible diffusion paths for the mobile ions. In the crystal structure of $Cu_6P(Se_{0.7}S_{0.3})_5Br$, 24 Cu atoms are distributed among 72 permissible positions in the unit cell. Cu ions are statistically
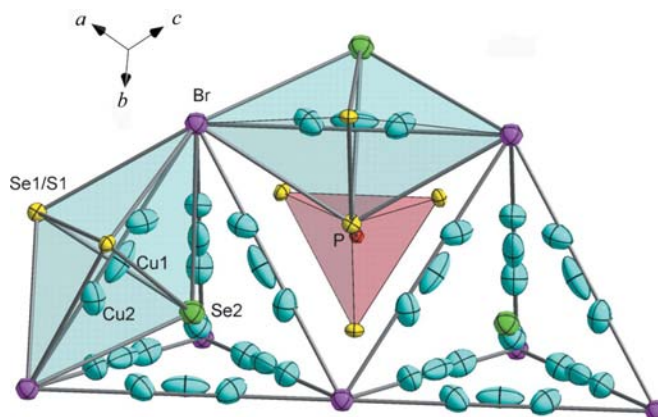

Figure 1
The coordination system in $Cu_6P(Se_{0.7}S_{0.3})_5Br$. Displacement ellipsoids are drawn at the 50% probability level.
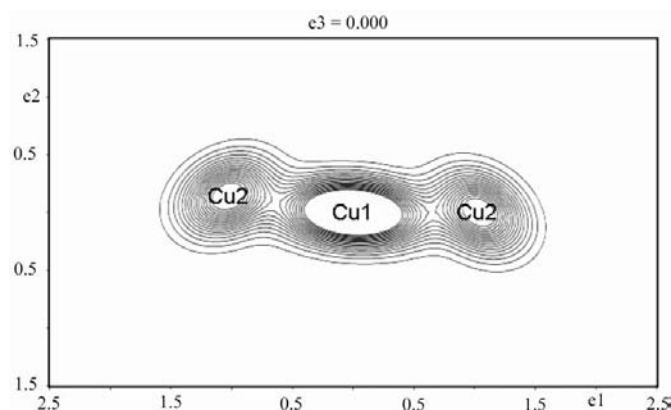

Figure 2
Joint probability density function map of atoms Cu1 and Cu2. Contour intervals are 0.1 atom $Å^{-3}$ and the positive cutoff is 1.6 atom $Å^{-3}$; plane (110).

located on the edge of the $(Br)_4$ tetrahedra and occupy two independent 24g and 48h Wyckoff positions. The 24g position is triangularly coordinated by Se/S, while the 48h position is tetrahedrally coordinated by Se/S and Br. Both triangular and tetrahedral environments are slightly deformed, because the Cu positions are shifted from the centre towards Se/S and the face of the tetrahedron, respectively. Fig. 1 shows the characteristic coordination and distribution of the Cu atoms in this phase.

At room temperature, Cu atoms show strong anharmonic vibrations along the edge of the $(Br)_4$ tetrahedra. Taking into account both the close proximity of the Cu1 and Cu2 positions and their partial occupation, it is probable that a jump of a Cu ion between them is readily thermally activated and Cu ions are able to overcome the potential barrier to the neighbouring lattice site. The probability density functions (PDFs) of the Cu atoms overlap. The joint function reveals a possible pathway for copper migration [for more details concerning joint PDF analysis, see Bachmann & Schulz (1984)]. Fig. 2 shows the joint PDF of atoms Cu1 and Cu2 along the edge of the $(Br)_4$ tetrahedra. From the shape of the joint PDF, we can categorize $Cu_6P(Se_{0.7}S_{0.3})_5Br$ as a type 1 copper argyrodite, according to

the classification introduced by Nilges & Pfitzner (2005). A similar copper substructure is demonstrated in the crystal structures of Cu_6PS_5I, Cu_6PS_5Br and Cu_6AsS_5I. For type 1 argyrodites, the most probable path of copper migration leads through a double tetrahedron face and a new 16e position.

Experimental

Single crystals of $Cu_6P(Se_{0.7}S_{0.3})_5Br$ were obtained by the conventional vapour-transport method at Uzhhorod State University. For details of the crystal preparation, see Studenyak *et al.* (2003).

Crystal data

$Cu_6P(Se_{0.7}S_{0.3})_5Br$	$Z = 4$
$M_r = 816.8$	Mo $K\alpha$ radiation
Cubic, $F\bar{4}3m$	$\mu = 29.58$ mm^{-1}
$a = 9.9821$ (11) Å	$T = 298$ (2) K
$V = 994.64$ (19) Å^3	$0.31 \times 0.12 \times 0.08$ mm

Data collection

Kuma KM-4 diffractometer with a CCD area-detector	4723 measured reflections
Absorption correction: numerical (X-RED; Stoe & Cie, 1999)	275 independent reflections
	259 reflections with $I > 3\sigma(I)$
$T_{min} = 0.028$, $T_{max} = 0.227$	$R_{int} = 0.059$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.027$	$\Delta\rho_{max} = 0.82$ e Å^{-3}
$wR(F^2) = 0.043$	$\Delta\rho_{min} = -0.73$ e Å^{-3}
$S = 1.48$	Absolute structure: Flack (1983), with 121 Friedel pairs
275 reflections	
23 parameters	Flack parameter: -0.02 (6)

The displacement parameters of atoms Cu2 were refined in the third-order anharmonic approximation using the Gram–Chalier model [for more details, see Kuhs (1983)]. The calculated tensor C_{ijk} parameters (multiplied by 10^5) are as follows: $C_{112} = C_{113} = -0.36$ (4), $C_{122} = C_{133} = 0.22$ (3), $C_{222} = C_{333} = -0.38$ (5), $C_{223} = C_{233} = 0.14$ (4), $C_{123} = -0.10$ (6). The nonharmonic refinement of the Cu2 displacement parameters improved the residual factor R_1 and reduced the electron residuals in the difference Fourier map in the vicinity of the Cu2 position. Anharmonic displacement parameters were refined

separately. The occupancy, coordinates and anisotropic displacement parameters of the Cu2 position were constrained. For atom Cu1, anisotropic refinement was applied.

A separate refinement of the occupancy factors of the Se2 and Br1 positions was performed. The refined occupancies of Se2 and Br1 were 1.01 (1) and 0.99 (1), respectively. As a result, the occupancies of these two positions were set at 1 and were not refined. The sum of the occupancies of atoms Se1 and S1 was constrained to 1.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2007); cell refinement: *CrysAlis CCD*; data reduction: *CrysAlis RED* (Oxford Diffraction, 2007); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *JANA2000* (Petříček *et al.*, 2000); molecular graphics: *DIAMOND* (Brandenburg & Putz, 2006); software used to prepare material for publication: *JANA2000*.

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