Crystal structure of nonasilver hexathioaluminate, Ag9AlS6, *the γ phase*
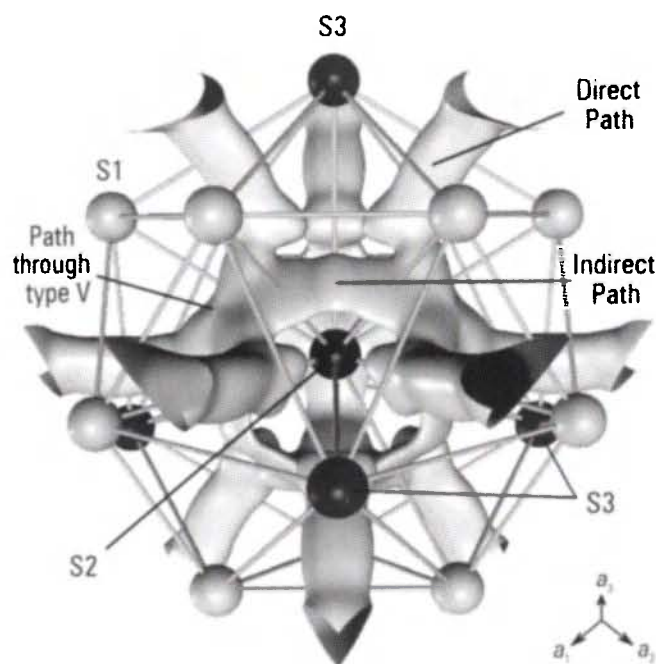
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Abstract

Ag9AlS6, cubic, $F\bar{4}3m$ (no. 216), $a = 10.739(1)$ Å,
$V = 1238.5$ Å^3, $Z = 4$, $R_{gt}(F) = 0.034$, $wR_{ref}(F^2) = 0.049$,
$T = 293$ K.

Source of material

For the preparation of Ag9AlS6 stoichiometric mixtures of silver, sulfur and Al2S3 are reacted in dry evacuated quartz glass ampules, which were protected with a thin carbon layer by pyrolysis of acetone vapor. Melting the raw product at 1270 K, quenching in ice water, homogenizing under argon atmosphere and annealing for two weeks at 1060 K yielded the title compound as air sensitive, black crystalline product. Neither by standard X-ray diffraction nor by EDXS and WDXS measurements a significant contamination was observed.

Experimental details

A refinement strategy similar to the one for γ-Ag9AlSe6 [1] was used. The Ag occupancies were refined under using of a restraint, $s.o.f.(Ag1) = 0.375 - s.o.f.(Ag2) - s.o.f.(Ag3) - s.o.f.(Ag4)$. (The free refinement of these parameters starting from the final values led to the same results within the experimental error.) Fractional atomic coordinates of mode positions with the associated probability densities are available in the CIF.

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Discussion

The title compound belongs to the structure family of argyrodites [2] where the anions are arranged in a tetrahedrally close-packed structure. The packing of the sulfur atoms corresponds to the framework of Mg and Cu atoms in the cubic Laves phase MgCu2. The three dimensional network of face-sharing tetrahedra of S atoms is partially occupied by Al atoms in an ordered way. In an earlier work [3] the title compound was preliminary characterized based on powder samples. However, the crystal structure has not been investigated yet. γ-Ag9AlS6 is the high temperature form of Ag9AlS6 and is characterized in particular by a high ionic conductivity. This property is based on a dynamical disorder of the Ag$^+$ over a great variety of interstitial positions. Due to the high mobility of the silver ions the consideration of the joint probability density function (jpdf) is helpful for the discussion of the de localization. In γ-Ag9AlS6, silver shows a high flexibility regarding the sulfur environment. Accordingly, tetrahedral, trigonal planar and approximately linear coordinations are observed. Combining a Gram-Charlier expansion of the atomic displacement factor for two silver positions with a split model for one sulfur atom the silver diffusion paths can be pursued within the [AlS6]$^{9-}$ matrix.

In the title crystal structure silver is distributed statistically over a large number of tetrahedral interstices. However, the single crystal structure analysis exhibits that the tetrahedral vacancies are not occupied by silver evenly. At ambient temperature the silver diffusion takes place along three of the four possible silver pathways. Several pseudo clusters are formed, which are interconnected and form a three-dimensional silver network. This network interpenetrates the one of S^{2-}. By systematic analysis of the two or three-dimensional jpdf a link of these preferred paths with structural arguments becomes feasible. Electrostatic repulsion between silver and Al atoms causes a structure-directing influence. The silver ions always favor distances to Al, which are as large as possible. The comparison of the structural characteristics of γ-Ag9AlS6 with those of γ-Ag7PSe6 [4] leads to new comprehensive insights. On the one hand the most pronounced positions along the direct path are roughly the same in both solids. On the other hand the preference of the diffusion path through the type-*V* tetrahedra in γ-Ag9AlS6 and the exactly linear coordinated position between Se2 and Se3 in γ-Ag7PSe6 differ considerably. Further details are discussed in [5].

Table 1. Data collection and handling.

Crystal:	metallic luster, well shaped isometric, size 0.375 × 0.455 × 0.628 mm
Wavelength:	Ag K_α radiation (0.56087 Å)
μ:	78.51 cm^{-1}
Diffractometer, scan mode:	Enraf-Nonius CAD4, $\omega/2\theta$
$2\theta_{max}$:	59.76°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	3771, 298
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 3\,\sigma(I_{obs})$, 268
$N(param)_{refined}$:	42
Programs:	JANA98 [6], WinGX [7], SCIAN [8]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	Occ.	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Al	4b		½	½	½	0.0173(2)	U_{11}	U_{11}	0	0	0
S(1)	16e		0.61940(3)	x	x	0.0266(1)	U_{11}	U_{11}	-0.0030(1)	U_{12}	U_{12}
S(2)	16e	0.25	-0.0165(1)	x	x	0.0378(8)	U_{11}	U_{11}	-0.0115(3)	U_{12}	U_{12}
S(3)	4c		¼	¼	¼	0.0431(3)	U_{11}	U_{11}	0	0	0
Ag(1)	48h	0.188(3)	-0.1750(2)	x	0.0279(4)	0.0906(6)	U_{11}	0.071(1)	$0^{i)}$	0.0193(9)	U_{13}
Ag(2)	24g	0.641(3)	-¼	-¼	0.0235(2)	0.190(2)	U_{11}	0.0435(2)	0.137(2)	0	0
Ag(3)	48h	0.139(2)	-0.1816(3)	-0.0532(4)	y	0.077(1)	0.279(4)	U_{22}	-0.097(2)	U_{12}	0.067(3)
Ag(4)	48h	0.102(2)	-0.1519(3)	-0.0442(6)	x	0.088(1)	0.095(3)	U_{11}	-0.030(1)	-0.023(2)	U_{12}

i) fixed at 0 (to avoid diverging of correlated C_{ijk} values)

Table 3. Anharmonic displacement parameters (in 10^{-3} Å^3).

Atom	C_{111}	C_{222}	C_{333}	C_{112}	C_{113}	C_{122}	C_{123}	C_{133}	C_{223}	C_{233}
Ag(1)	0.0130(4)	0.0130	-0.0069(6)	-0.0054(3)	0.0025(3)	-0.0054	-0.0051(5)	-0.0040(4)	0.0025	-0.0040
Ag(2)	0	0	$0^{ii)}$	0	-0.0072(7)	0	-0.0097(7)	0	-0.0072	0

ii) fixed at 0 (element smaller than 3σ)

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