Journal of Alloys and Compounds 576 (2013) 134–139

Contents lists available at SciVerse ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jalcom

The crystal structure of novel silver sulphogermanate $Ag_{10}Ge_3S_{11}$

A.O. Fedorchuk [a], G. Lakshminarayana [b], Y.O. Tokaychuk [c], O.V. Parasyuk [d,*]

[a] Hetman Petro Sahaydachnyi Army Academy, Department of Chemistry, 32 Gvardiyska St., 79012 Lviv, Ukraine
[b] Materials Science and Technology Division (MST-7), Los Alamos National Laboratory, Los Alamos, NM 87545, USA
[c] Department of Inorganic Chemistry, Ivan Franko National University of Lviv, 6 Kyryla & Mefodiya St., 79005 Lviv, Ukraine
[d] Department of Inorganic and Physical Chemistry, Eastern European National University, 13 Voli Ave., 43025 Lutsk, Ukraine

ARTICLE INFO

Article history:
Received 7 February 2013
Received in revised form 12 April 2013
Accepted 16 April 2013
Available online 25 April 2013

Keywords:
Inorganic compounds
Crystal growth
Crystal structure
X-ray diffraction

ABSTRACT

The $Ag_{10}Ge_3S_{11}$ compound was synthesized by melting the calculated amounts of elements in evacuated quartz ampoules at 1170 K. The crystal structure of the compound was determined by the single crystal technique; it is a representative of its own structural type. The compound crystallizes in a non-centrosymmetric space group *Cc* with unit cell parameters $a = 2.6244(4)$, $b = 0.65020(5)$, $c = 2.5083(4)$ nm, $\beta = 109.910(1)^\circ$. The $Ag_{10}Ge_3S_{11}$ structure may be described as a packing of the fragments composed of two twin $[Ge_2S_7]^{6-}$ and two single tetrahedra $[GeS_4]^{4-}$. The Ag atoms are situated in the tunnels formed by these fragments. The relationship with the similar structures is discussed.

1. Introduction

The quasi-binary system Ag_2S–GeS_2 was repeatedly studied [1–13] but the results reported in these papers are contradictory and ambiguous about the number and the composition of the ternary compounds that form in the system. All authors note the formation of the Ag_8GeS_6 compound which is a synthetic analog of the argyrodite mineral and a progenitor of a rather large family of compounds named after it. However, the data on the part of the system enriched in the germanium disulphide differ significantly both in the number and the composition of the compounds. For instance, two new compounds, $Ag_6Ge_2S_7$ (40 mol.% GeS_2) and $Ag_8Ge_3S_{10}$ (~43 mol.% GeS_2), were discovered along with Ag_8GeS_6 (20 mol.% GeS_2) in [1] where the phase diagram of the Ag_2S–GeS_2 system in 0–50 mol.% GeS_2 range was studied. The argyrodite and $Ag_6Ge_2S_7$ melt congruently at 1223 K and 958 K, respectively. Later, Gorochov [2] confirmed the existence of the Ag_8GeS_6 compound with the congruent melting point of 1228 K and the phase transition temperature of 493 K. The high-temperature (HT) modification has a face-centered cubic structure ($a = 1.070$ nm) [2]. The low-temperature (LT) modification determined by Eulenberger [3] has an orthorhombic structure (space group *Pna2₁*, $a = 1.5149$, $b = 0.7476$, $c = 1.0589$ nm). Studying the ternary system Ag–Ge–S at 873 K, Moh and Jb [4] discovered only Ag_8GeS_6 though later he [5] reported data on $Ag_{10}Ge_3S_{11}$ (~43 mol.% GeS_2) that crystallizes in one of two monoclinic space groups *Cc* or *C2/c* with rather large unit cell ($a = 2.6206$, $b = 0.6481$, $c = 2.5043$ nm, $\beta = 109.57^\circ$) and Ag_2GeS_3 that crystallizes in the orthorhombic structure (possible space groups групи *Cmcm*, *Cmc2₁* or *Ama2*). In the same time frame Nagel and Range [6] who investigated the Ag_2S–GeS_2–AgI system have established that in the Ag_2S–GeS_2 system, in addition to Ag_8GeS_6, a Ag_2GeS_3 compound exists (50 mol.% GeS_2). They also determined the crystal structure of Ag_2GeS_3 (space group *Cmc2₁*, $a = 1.1791$, $b = 0.7079$, $c = 0.6344$ nm). The later reports [7,8] also confirm the formation of two compounds, Ag_8GeS_6 which melts congruently at 1213 K and has a polymorpous transition at 473 K; and Ag_2GeS_3 which is incongruent and forms in a peritectoid process $Ag_8GeS_6 + GeS_2 \Longleftrightarrow Ag_2GeS_3$ at 593 K. They were followed by a paper [9] on the construction of the phase diagram of the Ag_2S–GeS_2 system that asserts the existence of only one compound Ag_8GeS_6 ($T_m = 1223$ K, $T_{pt} = 488$ K) which was confirmed by the same authors in the investigation of the phase diagram of the quasi-ternary system Ag_2S–Ga_2S_3–GeS_2 [10]. The latest version of the phase diagram of the Ag_2S–GeS_2 system presented by Kokhan [11] contains three compounds, Ag_8GeS_6 (space group *Pna2₁*, $a = 1.5137$, $b = 0.7483$, $c = 1.0590$ nm), Ag_4GeS_4 (33.3 mol.% GeS_2) (triclinic, $a = 0.9072$, $b = 1.412$, $c = 0.3346$ nm, $\alpha = 95.90^\circ$, $\beta = 92.63^\circ$, $\gamma = 74.96^\circ$), and Ag_2GeS_3 (space group *Cmc2₁*, $a = 1.179$, $b = 0.7064$, $c = 0.6338$ nm). Ag_2GeS_3 and Ag_8GeS_6 melt congruently at 921 K and 1223 K, respectively, whereas Ag_4GeS_4 forms incongruently at 1013 K. Ag_2GeS_3 has a polymorpous transition at 579 K. Kokhan [11] defines also certain peculiarities of the Ag_2GeS_3 synthesis, in particular, that it forms only if the melt temperature exceeds the melting point by less than 50 K. It is due to such ambiguity of the literature data that we paid a great deal of

---

[*] Corresponding author.
E-mail address: oleg@univer.lutsk.ua (O.V. Parasyuk).

0925-8388/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jallcom.2013.04.110

attention to the Ag_2S–GeS_2 system in the course of the investigation of quasi-ternary systems Ag_2S–HgS–GeS_2 [12] and Ag_2S–CdS–GeS_2 [13] as it is a bounding system for both of these systems. The formation of three compounds, Ag_8GeS_6, $Ag_{10}Ge_3S_{11}$ and Ag_2GeS_3, was confirmed which agrees well with the character of the phase equilibria in the quasi-ternary systems. In this paper we present the results of the determination of the crystal structure of the $Ag_{10}Ge_3S_{11}$ compound by the single crystal X-ray diffraction technique.

2. Experimental

The $Ag_{10}Ge_3S_{11}$ alloy was prepared from high-purity elements (Ag, 99.9 wt.%; Ge, 99.9999 wt.%; S, 99.997 wt.%) in an evacuated quartz ampoule. The synthesis was performed in two stages. At the first stage the ampoule was heated in the oxygen-gas burner flame to complete bonding of the elementary sulphur. The second stage included rapid heating ($50\ K\ h^{-1}$) of the ampoule in a shaft-type furnace to 1170 K and a 6-h homogenization of the melt with periodic vibrational mixing. This was followed by the cooling (10 K/h) to 670 K, then annealing for 250 h and cooling the alloy with the furnace turned off. The obtained alloy was a compact black ingot from which a single crystal was picked out. The crystal structure was studied by the single crystal technique using STOE IPDS diffractometer (Mo Kα-radiation). The extinction analysis of the obtained diffraction pattern evidences the possibility of two space groups: *C2/c* and *Cc*. For both cases, Patterson synthesis established the position of the heaviest atom, in this case Ag, that was localized in 12 crystallographic positions for space group *Cc* and six positions for *C2/c* case. Further, the Fourier analysis localized the position of the remaining Ag atoms that occupy, together with the above-mentioned ones, 27 crystallographic positions of which 12 are occupied fully and 15 others partially, and of Ge and S atoms for space group *Cc*. The count of the partially occupied positions were limited to those with the occupation factor ~1/3. In the course of the structure determination, we have tested a version of the structure with a larger number of positions with lower occupation by splitting the defective positions, but this had practically no effect on the R-factor value, therefore we assumed the above limitation. After the refinement of the obtained model, the best separation of the positions and the best values of the goodness factor were achieved for space group *Cc*. All computations of the determination and the refinement of the structure were performed using WinCSD program package [14]. The conditions of the recording of the X-ray data set and the crystallographic parameters of $Ag_{10}Ge_3S_{11}$ are listed in Table 1.

A good way to differentiate between a centrosymmetric and an acentric structure is the presence of non-linear optical properties. The piezoelectric tensor d_{33} was measured by a method described in [15]. We have found that the piezoelectric coefficient was equal to about 0.13–0.15 pm/V. This confirms unambiguously that for the studied sample there exists a presence of non-centrosymmetry, though its value is relatively small.

Table 1
Results of the crystal structure determination of $Ag_{10}Ge_3S_{11}$.

Compound	$Ag_{10}Ge_3S_{11}$
Number of formula units per unit cell	8
Space group	*Cc*
a (nm)	2.6244(4)
b (nm)	0.65020(5)
c (nm)	2.5083(4)
β (°)	109.91(1)
Cell volume (nm^3)	4.024(2)
Number of atoms in the cell	191.8
Calculated density (g/cm^3)	5.434(2)
Absorption coefficient (1/cm)	149.31
Radiation and wavelength	Mo 0.071073 nm
Diffractometer	STOE IPDS
Mode of refinement	$F(hkl)$
Restrictions	$F(hkl) > 4.00sig\ (F)$
Extinction formalism	Sheldrick-2 0.000056
Number of atomic sites	55
Number of free parameters	512
2Θ and $\sin\Theta/\lambda$ (max)	66.86 0.775
Number of measured reflections	16613
Independ reflections	2532
R_F, R_w	0.0429 0.0436
Goodness of fit	1.080
Scale factor	1.4302(7)

Table 2
Atomic coordinates and isotropic temperature factors for the $Ag_{10}Ge_3S_{11}$ structure.

Atom	Position	*x/a*	*y/b*	*z/c*	Occupation	$B_{eq.} \times 10^2$, nm^2
Ag1	*4a*	0.29379(8)	0.7866(4)	0.49592(1)	1.000	4.29(7)
Ag2	*4a*	0.47163(1)	0.8644(4)	0.95896(1)	1.000	5.77(10)
Ag3	*4a*	0.1493(2)	0.0256(3)	0.8872(2)	1.000	4.16(6)
Ag4	*4a*	0.32655(1)	0.3759(4)	0.81433(1)	1.000	6.71(13)
Ag5	*4a*	0.22640(1)	0.6429(4)	0.98300(1)	1.000	5.42(9)
Ag6	*4a*	0.00394(8)	0.2037(4)	0.77632(9)	1.000	4.29(7)
Ag7	*4a*	0.06541(1)	0.6429(4)	0.78446(1)	1.000	4.83(8)
Ag8	*4a*	0.40085(1)	0.7331(6)	0.8110(2)	1.000	8.37(15)
Ag9	*4a*	0.08717(1)	0.3883(5)	0.93295(1)	1.000	6.68(11)
Ag10	*4a*	0.39501(9)	0.2409(5)	0.96069(1)	1.000	7.02(12)
Ag11	*4a*	0.20879(1)	0.6765(7)	0.7244(2)	1.000	10.1(2)
Ag12	*4a*	0.70264(1)	0.1535(6)	0.13430(1)	1.000	7.27(13)
Ag13	*4a*	0.2759(2)	0.0471(6)	0.7198(2)	0.681(11)	7.0(2)
Ag14	*4a*	0.09450(1)	0.6286(5)	0.63483(1)	0.658(8)	2.95(9)
Ag15	*4a*	0.8055(3)	0.0164(10)	0.1053(2)	0.372(10)	5.1(3)
Ag16	*4a*	0.9680(2)	0.0491(10)	0.6406(2)	0.489(10)	5.7(2)
Ag17	*4a*	0.58795(1)	0.1561(6)	0.0374(2)	0.539(10)	6.4(2)
Ag18	*4a*	0.70944(1)	0.1252(4)	0.34274(1)	0.759(9)	3.76(10)
Ag19	*4a*	0.0270(2)	0.0279(6)	0.0616(2)	0.723(11)	6.5(2)
Ag20	*4a*	0.4819(2)	0.0249(8)	0.1607(2)	0.693(10)	7.3(2)
Ag21	*4a*	0.2035(6)	0.445(2)	0.8193(5)	0.283(13)	9.9(7)
Ag22	*4a*	0.3282(3)	0.5645(15)	0.6208(3)	0.519(12)	10.8(4)
Ag23	*4a*	0.5307(8)	0.855(3)	0.1576(6)	0.31(2)	15.2(9)
Ag24	*4a*	0.9962(4)	0.963(2)	0.6199(7)	0.367(15)	15.7(9)
Ag25	*4a*	0.3222(2)	0.0375(13)	0.1330(2)	0.763(14)	16.0(4)
Ag26	*4a*	0.5789(3)	0.302(2)	0.0566(2)	0.454(12)	16.7(7)
Ag27	*4a*	0.4618(4)	0.201(5)	0.1463(4)	0.342(14)	22(2)
Ge1	*4a*	0.17583(8)	0.1451(3)	0.04818(9)	1.000	1.68(6)
Ge2	*4a*	0.00298(8)	0.8498(3)	0.89427(8)	1.000	1.37(5)
Ge3	*4a*	0.37928(8)	0.7060(3)	0.02900(9)	1.000	1.83(6)
Ge4	*4a*	0.29247(8)	0.8536(3)	0.87694(8)	1.000	1.56(6)
Ge5	*4a*	0.91585(8)	0.7023(3)	0.74182(8)	1.000	1.45(5)
Ge6	*4a*	0.11824(7)	0.1469(3)	0.72155(8)	1.000	1.31(5)
S1	*4a*	0.1925(2)	0.2673(7)	0.9712(2)	1.000	1.69(13)
S2	*4a*	0.2405(2)	0.2499(8)	0.1288(2)	1.000	2.05(15)
S3	*4a*	0.2161(2)	0.7358(7)	0.8815(2)	1.000	1.64(14)
S4	*4a*	0.3005(2)	0.7579(8)	0.7955(2)	1.000	1.62(13)
S5	*4a*	0.9846(2)	0.8539(9)	0.7293(2)	1.000	2.27(15)
S6	*4a*	0.3707(2)	0.6943(9)	0.9356(2)	1.000	2.07(15)
S7	*4a*	0.4982(2)	0.6875(8)	0.8794(2)	1.000	1.85(14)
S8	*4a*	0.8361(2)	0.8446(8)	0.7085(2)	1.000	2.20(15)
S9	*4a*	0.1243(2)	0.8085(7)	0.7287(3)	1.000	2.6(2)
S10	*4a*	0.0795(2)	0.7362(10)	0.8891(2)	1.000	2.9(2)
S11	*4a*	0.3848(2)	0.3823(7)	0.0582(2)	1.000	2.3(2)
S12	*4a*	0.1761(2)	0.8083(9)	0.0446(2)	1.000	2.6(2)
S13	*4a*	0.9306(2)	0.6860(8)	0.8370(2)	1.000	1.99(14)
S14	*4a*	0.4609(2)	0.1459(10)	0.5613(2)	1.000	2.5(2)
S15	*4a*	0.0941(2)	0.2681(8)	0.0428(2)	1.000	2.07(15)
S16	*4a*	0.4899(2)	0.2711(8)	0.9749(2)	1.000	1.73(13)
S17	*4a*	0.0559(2)	0.2650(8)	0.6438(2)	1.000	1.97(14)
S18	*4a*	0.3022(2)	0.1868(8)	0.8914(2)	1.000	2.6(2)
S19	*4a*	0.9127(2)	0.3800(9)	0.7117(2)	1.000	2.08(14)
S20	*4a*	0.1980(2)	0.2737(11)	0.7309(2)	1.000	3.0(2)
S21	*4a*	0.1047(2)	0.2705(9)	0.7970(2)	1.000	2.09(14)
S22	*4a*	0.3121(3)	0.8540(9)	0.0480(3)	1.000	3.3(2)

$^*B(\mathrm{eq}) = 1/3\cdot[B_{11}\cdot a^{*2}\cdot a^2 + \cdots 2B_{23}\cdot b^*\cdot c^*\cdot b\cdot c\cdot\cos\alpha]$.

3. Results and discussion

The $Ag_{10}Ge_3S_{11}$ compound crystallizes in the monoclinic structure (Table 1) and is a representative of a new structural type. This non-centrosymmetric phase (space group *Cc*) has eight formula units per unit cell with a rather large volume of $4.024\ nm^3$. The coordinates of the atoms in the $Ag_{10}Ge_3S_{11}$ structure are listed in Table 2, their anisotropic temperature parameters are given in Table 3. The coordination surrounding of Ag atoms formed by the sulphur atoms is tetrahedral or, less often, triangular. The interatomic distances Ag–S range from 0.2343(6) to 0.2980(15) nm which agrees well with such distances in the structures of well-known compounds Ag_8GeS_6 (0.2492–0.2944 nm) [3] and $Ag_{10}Si_3S_{11}$