

$\text{Sb}_{10}\text{S}_{15}$, a Pb-free analogue of fülöppite, $\text{Pb}_3\text{Sb}_8\text{S}_{15}$

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Abstract

Bronze colored prisms found in a reaction product when coprecipitated Sb_2S_3 and Sb_2O_3 were heated at 250°C in a saturated Na_2CO_3 solution were isostructural with fülöppite, $\text{Pb}_3\text{Sb}_8\text{S}_{15}$, and have the stoichiometry $\text{Sb}_{10}\text{S}_{15}$, $a = 13.393(1)\text{\AA}$, $b = 11.7170(6)\text{\AA}$, $c = 16.737(1)\text{\AA}$, $\beta = 93.763(6)^\circ$, $Z = 4$. The structure was refined to $R = 0.062$, $\omega R = 0.056$ for 2893 observed reflections with anisotropic temperature factors and variable occupancy factors for three Sb atoms. Two of the Sb atoms correspond to the two crystallographically independent Pb atoms in fülöppite. The Sb–S distances are of the same lengths as those reported for fülöppite. The crystal structure of $\text{Pb}_3\text{Sb}_8\text{S}_{15}$ was re-refined using Nuffield's (1975) data permitting the occupancy factors for Pb(1), Pb(2) and Sb(3) to vary. The value of R decreased significantly to 0.057 from the reported value of 0.061. The Pb(1) site is fully occupied by Pb, but the occupancy factor for Pb(2) was 7.47(6) and for Sb(3) was 8.70(10) instead of 8 atoms per equivalent sites in the unit cell. Thus the Pb(2) site contains 0.825 Pb and 0.175 Sb and the Sb(3) site has 0.145 Pb and 0.865 Sb. The lead-free polymorph of stibnite is a metastable phase at room temperature.

Introduction

In an ongoing program to synthesize and investigate the physical properties of oxysulfide compounds we attempted the synthesis of kermesite, $\text{Sb}_2\text{S}_2\text{O}$, by the procedure described by Baumgardt and Kupcik (1977). Optical examination of the products of reaction showed the characteristic radial aggregates of needles of stibnite, Sb_2S_3 , which was confirmed by powder X-ray diffraction. In addition a major component consisted of black platelets. A few very small bronze-colored prisms were also found but we never observed crystals of $\text{Sb}_2\text{S}_2\text{O}$ in the reaction products. Single crystal diffraction patterns of the black plates showed that they were orthorhombic, $a = 53.72\text{\AA}$, $b = 11.09\text{\AA}$, $c = 3.851\text{\AA}$, $Pnam$. While this investigation was in progress a paper appeared by Koyama, et al. (1984) describing the crystal structure of $\text{Bi}_2\text{O}_2\text{S}$. On the basis of their unit cell parameters and results of X-ray energy dispersive analysis on our crystals we believe that the black plates are $\text{Sb}_2\text{O}_2\text{S}$ and that they crystallize with a superstructure of the $\text{Bi}_2\text{O}_2\text{S}$ structure in which $a \approx 14c$.¹ The details of this structure will be published elsewhere. The bronze-colored prisms were shown by X-ray energy dispersive analysis to consist only of Sb and S in about a 2:3 proportion. We could not identify this compound and therefore proceeded with a crystal structure analysis.

Experimental

A crystal having an irregular prismatic shape of volume $0.133 \times 10^{-5} \text{ cm}^3$ was selected from a product obtained by coprecipitating Sb_2S_3 and Sb_2O_3 at pH 9 from a solution of NaOH buffered with borax/HCl. The precipitate was sealed in a vycor tube with saturated Na_2CO_3 solution and heated at 250°C for 3 d. The crystal was mounted on a Krisel Automated Picker diffractometer equipped with a graphite monochromator, $\lambda(\text{MoK}\alpha) = 0.71069\text{\AA}$. The eight equivalent intensities of 20 independent reflections, $25.3 < 2\theta < 29.8^\circ$, were carefully centered and these 160 measured 2θ values were used in a least squares calculation to obtain the lattice parameters, $a = 13.393(1)\text{\AA}$, $b = 11.7170(6)\text{\AA}$, $c = 16.737(1)\text{\AA}$, $\beta = 93.763(6)^\circ$. The systematic absences were $hkl: h + k = 2n + 1, h0l: l = 2n + 1$, consistent with Cc and $C2/c$ with the latter shown to be correct by the subsequent crystal structure determination. Intensity data were collected by a ω -scan at 3.0 deg min^{-1} to $2\theta \leq 60^\circ$; 4 standard reflections were measured every 100 reflections and no significant change in intensities was observed. 3829 reflections were measured, $h = 0-18, k = 0-16, -23 \leq l \leq 23$.

Intensities were corrected for Lorentz, polarization and absorption with $\mu_l = 111 \text{ cm}^{-1}$ based on a $\text{Sb}_{39}\text{S}_{60}$ unit cell content. The minimum and maximum transmission factors were 0.33 and 0.50. Standard deviations $\sigma(F^2)$ were calculated from [counting statistics + $(0.02I)^2$]^{1/2}. 2893 reflections were considered observed on the basis that $F > 4\sigma(F)$. The structure was solved by direct methods which showed all Sb and S positions. Full-matrix least squares refinement on F with $\omega = A/\sigma^2(F)$, $A = 2.98$, anisotropic temperature factors, variable occupancy factors for Sb(3) Sb(5) and Sb(6), scattering factor for neutral atoms corrected for real and imaginary parts of dispersion, (*International Tables for X-Ray Crystallography*, 1974), converged to $R = 0.0615$, $\omega R = 0.0564$ for the 2893 observed reflections; $(\Delta/\sigma)_{\text{max}} = 0.011$; maximum and

¹ Note added in proof: Preliminary structure analysis indicates $\text{Sb}_4\text{S}_5\text{O}$.

Table 1. Atomic and thermal parameters ($\times 10^4$) for $\text{Sb}_{10}\text{S}_{15}$

Atom	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃	U _{eq} , Å ²	Occupancy
Sb(1)	3754.9(.6)	1450.4(.8)	4952.2(.5)	257(4)	308(5)	267(4)	-36(4)	68(3)	-13(4)	275(3)	
Sb(2)	4090.8(.6)	1810.9(.7)	1535.9(.5)	211(4)	228(4)	200(4)	27(3)	11(3)	13(3)	213(2)	
Sb(3)	883.7(1.0)	522.6(1.1)	4149.7(.8)	492(8)	342(7)	451(8)	-53(5)	238(6)	-146(6)	419(4)	6.82(3)
Sb(4)	1414.6(.5)	2495.5(.7)	636.6(.5)	160(3)	279(4)	181(4)	14(3)	-2(3)	-25(3)	207(2)	
Sb(5)	3026.6(1.1)	4444.6(1.4)	3409.5(.9)	483(9)	600(11)	420(9)	-141(7)	194(6)	-211(7)	494(5)	6.18(3)
Sb(6)	0	3977.1(2.6)	$\frac{1}{2}$	497(18)	434(18)	796(25)	0	-144(15)	0	584(12)	2.33(2)
S(1)	3520(3)	442(3)	2510(2)	574(23)	256(18)	264(17)	-18(16)	28(15)	65(15)	365(11)	
S(2)	0	8109(4)	$\frac{1}{2}$	209(19)	283(23)	297(23)	0	-75(16)	0	267(13)	
S(3)	2640(2)	264(3)	364(2)	240(14)	199(15)	317(17)	18(12)	54(12)	55(13)	250(9)	
S(4)	1912(2)	2464(3)	3950(2)	243(14)	263(16)	329(17)	-6(13)	34(12)	-90(14)	278(9)	
S(5)	4656(2)	3640(3)	4619(2)	240(14)	227(15)	255(15)	36(12)	6(11)	-25(13)	241(9)	
S(6)	284(2)	4136(3)	878(2)	200(13)	226(15)	211(14)	-5(11)	-25(11)	-55(12)	214(8)	
S(7)	732(2)	1295(3)	1677(2)	243(14)	257(16)	217(14)	-31(12)	23(11)	22(12)	239(9)	
S(8)	2739(2)	3207(3)	1618(2)	196(13)	296(16)	262(15)	14(12)	-75(11)	-79(14)	255(9)	

The atom labeling follows that of Nuffield with our Sb(5)=Pb(2) and Sb(6)=Pb(1). The anisotropic thermal parameters are of the form: $\exp[-2\pi^2(U_{11}a^2h^2+U_{22}b^2k^2+U_{33}c^2l^2+2U_{12}a*b*hk+2U_{13}a*c*h+l+2U_{23}b*c*k+l)]$. U_{eq}=1/3 trace of orthogonalized U_{ij} tensor. Numbers in parentheses are standard deviations.

minimum values of $\Delta\rho$ are 5.1 and -4.5 eÅ⁻³. Table 1 contains the final parameters and Table 2 contains selected Sb-S bond distances. Table 3 contains a listing of $F(\text{obs})$ and $F(\text{calc})$.² Calculations were carried out with SHELX76 (Sheldrick, 1976), MULTAN78 (Main, et al., 1978) and BADTEA (Finger and Prince, 1975).

Discussion

The unit cell content on the basis of the crystal structure analysis with full site occupancy for all atoms is $\text{Sb}_{44}\text{S}_{60}$ or $\text{Sb}_{11}\text{S}_{15}$, $Z = 4$; the refinement stopped at $R = 0.090$. Three of the Sb atoms, Sb(3) Sb(5) and Sb(6) had unusually large temperature factors and a refinement in which the occupancy factors for these atoms were permitted to vary provided reasonable values for the temperature parameters and converged to $R = 0.062$. The stoichiometry became $\text{Sb}_{9.8}\text{S}_{15}$, $Z = 4$. A careful analysis of the coordination polyhedra around Sb and their linkages led us to the conclusion that this structure might be similar to that of known Sb-Bi-Pb sulfides. An examination of a paper by Wuensch (1979) on superstructures in sulfide minerals revealed that the $\text{Sb}_{9.8}\text{S}_{15}$ was isostructural with fülöppite, $\text{Pb}_3\text{Sb}_8\text{S}_{15}$, the first member of the pligionite group of minerals. The phase which we synthesized corresponds to a lead-free fülöppite with the stoichiometry $\text{Sb}_{10}\text{S}_{15}$ and there are vacancies in the corresponding Pb and Sb sites in the mineral structure.

Detailed structures of fülöppite have been published by Edenharter and Nowacki (1975) and Nuffield (1975). A careful analysis of the temperature factors of the atoms of $\text{Pb}_3\text{Sb}_8\text{S}_{15}$ for both published structures shows that Pb(1), Pb(2), and Sb(3) (atom labeling corresponds to Nuffield) have the largest values. The Sb atoms in our phase corre-

sponding to those atoms, similarly, had very large temperature factors and for that reason led us to refine on the occupancy factors. If the high temperature coefficients in fülöppite are due to refinement with full occupancy factors, then it is conceivable that the stoichiometry of the mineral could be approximately $\text{Pb}_{2.1}\square_{0.9}\text{Sb}_{1.7}\square_{0.3}\text{Sb}_6\text{S}_{15}$. Edenharter and Nowacki (1975) provide a chemical analysis for their specimens obtained by means of an electron probe. On the basis of the reported value for S representing S_{15} the stoichiometry is $\text{Pb}_{2.6}\text{Sb}_{7.3}\text{S}_{15}$ and calculated $d = 4.77$ g cm⁻³ compared to $d_x = 5.18$ g cm⁻³. Unfortunately, no measured density is reported. Nuffield (1946) reports a measured $d = 5.22$ g cm⁻³. The crystals of $\text{Sb}_{9.8}\text{S}_{15}$ which we synthesized were so few and so small that no reliable density could be measured.

The occurrence of fülöppite was originally described by DeFinaly and Koch (1929). On the basis of an analysis on some "carefully selected crystals" they derive $\text{Pb}_2\text{Sb}_6\text{S}_{11}$ for fülöppite. We recalculated the formula on the basis of S_{15} and get $\text{Pb}_{2.73}\text{Sb}_{7.78}\text{S}_{15}$. The reported density obtained pyknometrically is 5.23 g cm⁻³. The agreement between the measured and X-ray densities for fülöppite strongly negates the vacancy model for its crystal structure.

The uncertainty in the composition caused us to reinvestigate the crystal structure of fülöppite using the F

Table 2. Interatomic distances (Å) for $\text{Sb}_{10}\text{S}_{15}$

Sb(1) -S(3)	2.622(3)	Sb(4) -S(6)	2.496(3)
-S(4)	2.451(3)	-S(7)	2.462(3)
-S(6)	2.579(3)	-S(8)	2.481(3)
Sb(2) -S(1)	2.445(4)	Sb(5) -S(1)	2.758(4)
S(2)	2.478(3)	-S(3)	2.485(4)
S(8)	2.450(3)	-S(7)	2.741(4)
Sb(3) -S(4)	2.692(4)	Sb(6) -2S(1)	2.623(4)
-S(5)	2.434(3)	-2S(6)	2.773(3)
-S(7)	2.651(3)		

² To obtain a copy of Table 3, order Document AM-84-274 from the Mineralogical Society of America, Business Office, 2000 Florida Ave., N.W., Washington, D.C. 20009. Please remit \$5.00 in advance for the microfiche.

values and parameters reported by Nuffield (1975). Our calculation using unit weights results in $R = 0.06094$, agreeing with Nuffield's value of 0.0607; $RG = 0.06956$ where $RG = [\sum \omega |F_0 - F_c|^2 / \sum \omega F_0^2]^{1/2}$. We refined these parameters by least squares on F yielding $R = 0.06107$, $RG = 0.06929$. We now permitted the occupancy factors for Pb(1), Pb(2) and Sb(3) to vary in a least squares refinement. The values of R and RG converged to 0.05731 and 0.06619 and the occupancy factors were 3.97(5), 7.46(7) and 8.69(10) respectively. The Pb(1) site, thus, is fully occupied and we now calculated a least squares refinement permitting the occupancy factors for Pb(2) and Sb(3) to vary. The refinement converged to $R = 0.05727$, $RG = 0.06619$ and occupancy values Pb(2) = 7.47(6) and Sb(3) = 8.70(10). A Hamilton ratio test (*International Tables*, 1974) using RG values for Nuffield's structure refined with full occupancy, 0.06929, and with the Pb(2) and Sb(3) variable occupancies, 0.06619, yields $R_{2,1444,0.005} = 1.0468$ as compared with the theoretical value 1.0036 at the 0.005 significance level.

Ideally the Pb(2) and Sb(3) occupancy factors should be 8. The measured density confirms that the stoichiometry for fülöppite is correct so the explanation for the apparent vacancy in the Pb(2) site and excess occupancy in the Sb(3) site must be sought in terms of electron density. A "vacancy" implies X-ray scattering power less than Pb, i.e. some of the Pb is replaced by Sb, and "excess" implies scattering power greater than Sb, i.e. some of the Sb is replaced by Pb. Conserving the overall stoichiometry $Pb_3Sb_8S_{15}$ the Pb(2) site contains 0.825 Pb and 0.175 Sb and the Sb(3) site has 0.145 Pb and 0.865 Sb. The sums $Pb = 0.970$ and $Sb = 1.04$ are unity within experimental error, charge balance is maintained on the basis of divalent Pb and trivalent Sb and the measured and X-ray densities are reconciled.

The stoichiometry $Sb_{9.8}S_{15}$ based on the crystal structure analysis is $Sb_{10}S_{15}$ within experimental error and only trivalent Sb exists in the structure. The presence of vacancies in the three Sb sites preserves charge neutrality.

Numerous experiments to grow larger crystals were fruitless. When the power to the furnace was shut off and cooling took place by heat transfer to the environment the products consisted of stibnite Sb_2S_3 , Sb_2O_2S and a very few $Sb_{10}S_{15}$ crystals. An experiment in which the furnace was programmed to cool slowly over a period of 12 h from 250–125°C yielded a product consisting only of Sb_2O_2S

crystals. We believe that the lead free fülöppite, $Sb_{10}S_{15}$, is metastable at the temperature of the experiment and that a small amount of this polymorph of stibnite is retained during rapid cooling.

Acknowledgments

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References

- Baumgardt, E. M. and Kupcik, V. (1977) Synthesis of kermesite Sb_2S_2O . *Journal of Crystal Growth*, 37, 346–348.
- DeFinaly, I. and Koch, S. (1929) Fülöppite, a new Hungarian mineral of the plagiomite-semseyite group. *Mineralogical Magazine*, 22, 179–184.
- Edenharter, A. and Nowacki, W. (1975) Die Kristallstruktur von Fülöppit ($Sb_8S_{15}|Pb^{VIII}Pb_2^{VII}$). *Zeitschrift für Kristallographie*, 142, 196–215.
- Finger, L. W. and Prince, E. (1975) A system of Fortran IV Computer Programs for Crystal Structure Computations. National Bureau of Standards Technical Note 854. U.S. Government Printing Office, Washington, D.C. 20402.
- International Tables for X-Ray Crystallography* (1974) Vol. IV, Birmingham: Kynoch Press.
- Koyama, E., Nakai, I. and Nagashima, K. (1984) Crystal chemistry of oxide-chalcogenides. II. Synthesis and crystal structure of the first bismuth oxide-sulfide, Bi_2O_2S . *Acta Crystallographica*, B40, 105–109.
- Main, P., Hull, S. E., Lessinger, L., Germain, G., Declercq, J. P. and Woolfson, N. M. (1978) MULTAN 78. A System of Computer Programs for the Automated Solution of Crystal Structures from X-ray Diffraction Data, Univs. of York, England and Louvain, Belgium.
- Nuffield, E. W. (1975) The crystal structure of fülöppite, $Pb_3Sb_8S_{15}$. *Acta Crystallographica*, B31, 151–157.
- Nuffield, E. W. (1946) University of Toronto Geological Series 50, 49–62.
- Sheldrick, G. M. (1976) SHELX76, Program for crystal structure determination. University of Cambridge, England.
- Wuensch, B. J. (1979) Superstructures in sulfide minerals. In J. M. Cowley et al., Eds., AIP Conference Proceedings No. 53, *Modulated Structures-1979*. American Institute of Physics, New York.

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