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Synthesis and Lattice Constants of Luzonite-Famatinite Crystals

Yasuo KANAZAWA

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Abstract: Synthetic crystals of the luzonite (Cu_3AsS_4) - famatinite (Cu_3SbS_4) series were prepared by the silica tube method and the hydrothermal procedure. The hydrothermally grown luzonite tends to show an aggregate of tabular to short prismatic crystals. Twinning is quite common. On the other hand, famatinite occurs often as well-formed prismatic single crystals. The lattice constants increase almost linearly with Cu_3SbS_4 content: a=5.2905 (7) to 5.3862 (4) Å, c=10.438 (3) to 10.753 (1) Å and c/a=1.973 to 1.996. The chemical composition of a natural specimen can be conveniently determined from the lattice constants.

Introduction

The minerals of the system Cu_3AsS_4-Cu_3SbS_4, namely, enargite, luzonite and famatinite, most commonly occur in gold and/or copper deposits of epithermal type. They are usually associated with such minerals as pyrite, native gold, and quartz, often also with tetrahedrite-tennantite, barite and alunite.

Stability relation between these minerals was first studied by GAINES (1951). He synthesized two different forms of Cu_3AsS_4 crystal by hydrothermal procedure. One of them was found to be orthorhombic and stable above 300 °C, while the other to be tetragonal and stable below 300 °C, which corresponded to enargite and luzonite, respectively. On the basis of subsequent X-ray and chemical studies of some synthetic and natural specimens, GAINES (1957) suggested a complete solid solution series between luzonite (Cu_3AsS_4) and famatinite (Cu_3SbS_4). The suggestion was confirmed by a number of chemical analyses of the minerals by later workers such as SPRINGER (1969), HUANG (1974) and SUGAKI *et al.* (1976). According to SUGAKI *et al.* (1976) Japanese luzonite-famatinite and enargite have the compositions of 0–82 and 0–19 mole % Cu_3SbS_4, respectively.

Single crystal structural analysis of this group of minerals has so far been made only for two specific chemical compositions: $Cu_3As_{0.64}Sb_{0.36}S_4$ (MARUMO and NOWACKI, 1967) and Cu_3SbS_4 (GARIN and PARTHÉ, 1972). The structure is of sphalerite type. It is, however, unique because As and Sb atoms in the structure have a distorted tetrahedral coordination with respect to S atoms, whereas these atoms usually have a trigonal pyramidal coordination in sulfide minerals.

Although a number of chemical studies have been made on the luzonite-famatinite series of minerals, their crystallographic data are still limited. This paper is part of our studies of the crystal structure of the series. The synthesis of the crystals and the variation in the lattice constants are reported.

The mineral names, luzonite and famatinite, are here used for the range of Cu_3AsS_4-$Cu_3(As_{1/2}Sb_{1/2})S_4$ and $Cu_3(As_{1/2}Sb_{1/2})S_4$-$Cu_3SbS_4$, respectively.

Synthesis

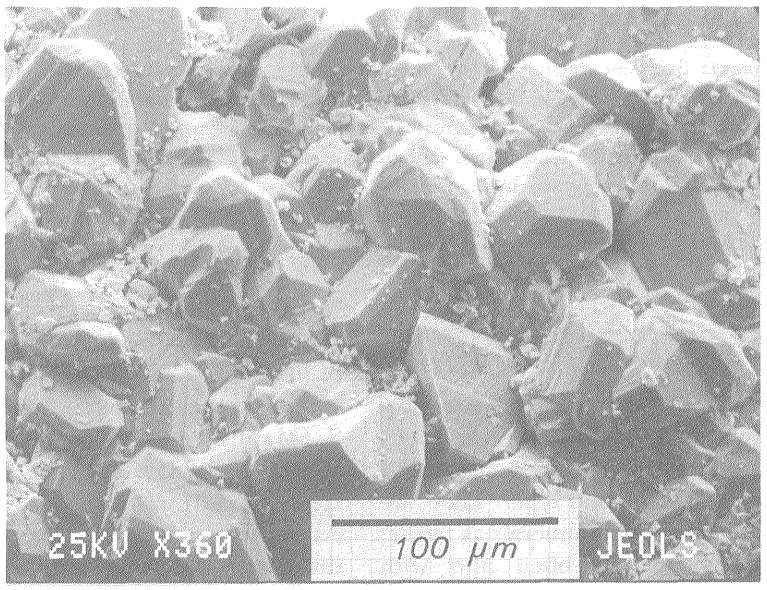
Synthesis of powder crystals

Crystals of the compositions 0, 20, 40, 60, 80 and 100 mole% Cu_3SbS_4 in Cu_3AsS_4-Cu_3SbS_4 series were synthesized in evacuated silica glass tubes. Starting materials were the mixtures of

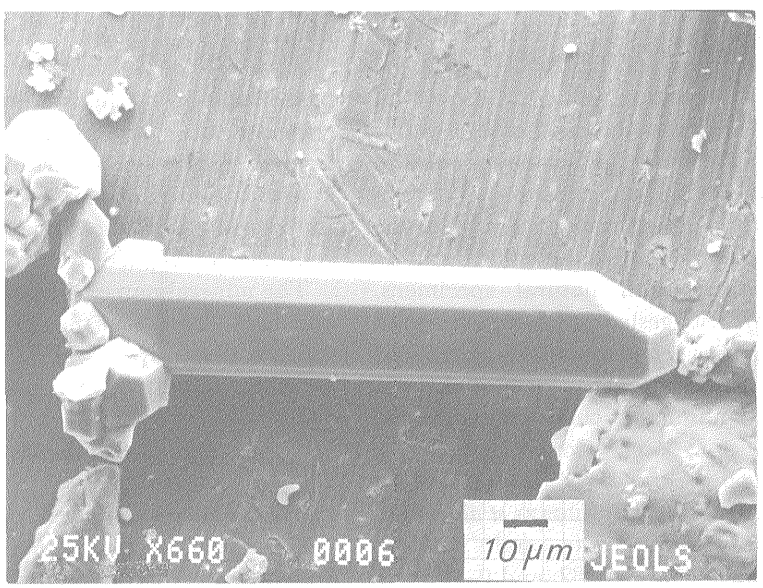
* Mineral Deposits Department

elemental components: copper, arsenic, antimony and sulfur. Copper and sulfur of 99.999% purity were obtained from the Kanto Chemical Co. To remove possible surface oxidation products, the copper sample was reduced under the hydrogen gas flow at 600°C. The arsenic of vacuum packed spectrographic grade, 99.9999% purity and the antimony of 99.999% purity were obtained from the Wako Pure Chemical Industries, LTD.

The mixtures were kept for two days at 550°C and were then slowly cooled down to the room temperature in one day. The products were ground under acetone. The procedure was repeated twice. The products of Cu_3AsS_4 composition were further kept for a week at 270°C,



(a)



(b)

Fig. 1 Scanning electron microphotographs of (a) luzonite, Cu_3AsS_4 and (b) famatinite, Cu_3SbS_4 crystals.

Table 1 Products synthesized by silica tube method and their lattice constants.

run	starting composition	product	lattice constants
1.	Cu_3AsS_4	enargite	a=6.426(2) b=7.401(3) Å c=6.146(2) Å
2.	$Cu_3(As_{0.8}Sb_{0.2})S_4$	enargite+luzonite	
3.	$Cu_3(As_{0.6}Sb_{0.4})S_4$	luzonite	a=5.330(1) c=10.574(4) Å c/a=1.984
4.	$Cu_3(As_{0.4}Sb_{0.6})S_4$	famatinite	a=5.345(1) c=10.626(2) Å c/a=1.988
5.	$Cu_3(As_{0.2}Sb_{0.8})S_4$	famatinite	a=5.366(1) c=10.690(3) Å c/a=1.992
6.	Cu_3SbS_4	famatinite	a=5.382(1) c=10.759(6) Å c/a=1.999

below the phase transition point of luzonite to enargite (300 °C).

Hydrothermal synthesis

Larger size single crystals of Cu_3AsS_4 and Cu_3SbS_4 were prepared with hydrothermal techniques for morphological and X-ray single crystal studies. A gold tube of 5 mm inside diameter and about 50 mm in length was employed as the reaction vessel. Nutrients are the powder crystals of synthetic Cu_3AsS_4 and Cu_3SbS_4 described above. About 30 mg of the nutrient sulfide was sealed in a gold tube with 5 m NH_4Cl solution. The tube was then placed in a test-tube type autoclave and was heated in a horizontal furnace applying a thermal gradient by means of two heaters controlled independently. Two reaction runs were carried out each for 10 days, applying a pressure of 300 kg/cm² and temperatures 250–300 °C and 300–350 °C, respectively, over the length of the tube.

Products

The synthetic products were identified by X-ray powder method. Among the products of silica tube method, the Cu_3AsS_4 end is found to be enargite, while the product containing 20 mole% Cu_3SbS_4 in Cu_3AsS_4-Cu_3SbS_4 series is a mixture of two phases, enargite and luzonite. All the products of 40–100 mole% Cu_3SbS_4 are monophase, that is either luzonite or famatinite.

The hydrothermally treated Cu_3AsS_4 consists mainly of enargite with minor amounts of luzonite, whereas the Cu_3SbS_4 gives only famatinite. The two runs with different temperatures return essentially the same results.

Table 2 Products synthesized by hydrothermal method and their lattice constants.

starting material	product	lattice constants*)
Cu_3AsS_4 (enargite)	enargite+luzonite	a=5.2905(7) Å c=10.438(3) Å c/a=1.973
Cu_3SbS_4 (famatinite)	famatinite	a=5.3862(4) Å c=10.753(1) Å c/a=1.996

*) Constants of luzonite and famatinite are shown.

The hydrothermal products were also examined under a scanning electron microscope. The luzonite crystals occur as a massive aggregate as shown in Fig. 1 (a). They have tabular to short prismatic forms and most of them show twinning. The grain size is less than 100 μm. On the other hand, the famatinite crystals are largely prismatic as seen in Fig. 1 (b). The length of the prism often exceeds 100 μm. The morphological difference observed seems to be consistent with the report that some famatinite occurs in larger single grains attaining 5 mm in the largest dimension while luzonite-famatinite are usually massive and fine-grained (Gaines, 1957).

Lattice Constants

Determination of lattice constants

Lattice constants of the crystals were determined on the products of silica tube method. Powder diffraction peaks were recorded using a Rigaku RAD-rA automated powder diffrac-

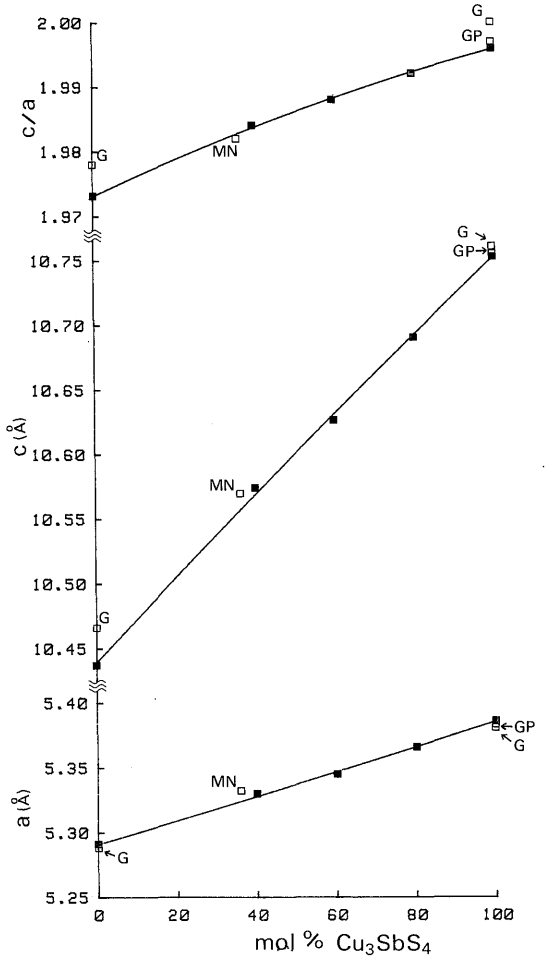


Fig. 2 Lattice constants of luzonite-famatinite series as a function of chemical composition. Black squares are the present data and white squares are previous workers' data; G (GAINES, 1957), MN (MARUMO & NOWACKI, 1967) and GP (GARIN & PARTHÉ, 1972). Fitting curves with data points are drawn by the least-squares method assuming a quadratic equation.

tometer with graphite-monochromated Cu $K\alpha$ radiation. Appropriate 8 to 12 reflections were selected in the range of $2\theta < 110°$. The 2θ values were corrected by the standard silicon powder crystals whose diffraction peaks were taken before and after the specimen measurements.

The lattice constants of single crystals prepared by the hydrothermal method were also determined using a Rigaku AFC-5 automated

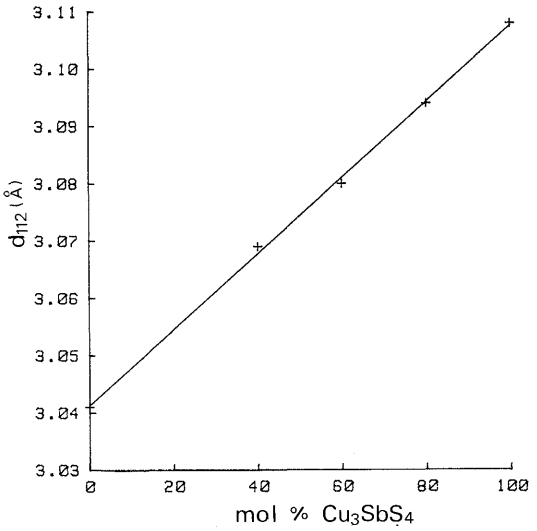


Fig. 3 Relation between d_{112} value and chemical composition of luzonite-famatinite series.

four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation. Twenty-five 2θ values were measured in the range of higher diffraction angles, where the diffractions by $K\alpha_1$ and $K\alpha_2$ were separated.

Lattice constants calculations were carried out on a HP-9845 computer with a BASIC program written by the author, that is a modification of RSLC-3 program (SAKURAI, 1967).

Results

Lattice constants of all the products are summarized in Table 1 and 2 and are plotted as a function of chemical composition in Fig. 2 together with the previously reported data. As shown in the figure, both a and c increase almost linearly with Cu_3SbS_4 content. The result is reasonable because antimony has a larger atomic radius than that of arsenic. The axial ratio, c/a also increases with antimony content and goes up to nearly 2 ($c/a=1.996$) at the Cu_3SbS_4 end. This indicates that the sphalerite type subcell is almost a cube at the Cu_3SbS_4 end while for the As-rich members it is shrunk along c-axis as compared to a axis. The near cube subcell of Cu_3SbS_4 might explain the less-twinned, large and distinct crystal shape mentioned above, though further study is needed before any conclusion.

Fig. 2 also indicates that the chemical composition of any specimen of the luzonite-famatinite series can be determined on the basis of lattice constants. The composition may be more conveniently determined from d_{112} value which is the strongest line on the powder diffraction pattern (Fig. 3). However, it should be noted that because of frequent occurrence of zoning (ROSENZWEIG, 1975 and SUGAKI *et al.*, 1976) chemical composition of this group of minerals can be quite variable even in a single grain of crystal. The maximum variation was reported to be ± 15 mole% in the Cu_3AsS_4-Cu_3SbS_4 series over a length of 4 mm (ROSENZWEIG, 1975). Therefore, the lattice constants of any given natural specimen determined by ordinary X-ray powder diffraction method may only give us an average chemical composition of the specimen.

Acknowledgements

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References

GAINES, R. V. (1951) The mineralogy, synthesis, and genetic significance of luzonite, famatinite and some related minerals. Ph. D. thesis, Havard Univ.

———— (1957) Luzonite, famatinite and some related minerals. *Amer. Mineral.*, vol. 42, p. 766–779.

GARIN, J. and PARTHÉ, E (1972) The crystal structure of Cu_3PSe_4 and other ternary normal tetrahedral structure compounds with composition 1_356_4. *Acta Cryst.*, vol. B28, p. 3672–3674.

HUANG, C. K. (1974) Antimony contents of enargite and luzonite-famatinite from the Chinkuashih mine, Taiwan. *Acta Geologica Taiwanica*, no. 17, p. 1–5.

MARUMO, F. and NOWACKI, W. (1967) A refinement of the crystal structure of luzonite, Cu_3AsS_4. *Z. Kristallogr.*, vol. 124, p. 1–8.

ROSENZWIG, A. (1975) Zonal composition of luzonite-famatinite and enargite from the Chinkuashih mine, Taiwan. *Proc. Geol. Soc. China*, p. 128–130.

SAKURAI, T. (1967) Universal crystallographic Computation Program System (II), *Cryst. Soc. Japan*, p. 99–108.

SPRINGER, G. (1969) Compositional variation in enargite and luzonite. *Mineralium Deposita*, vol. 4, p. 72–74.

SUGAKI, A., SHIMA, H. and KITAKAZE, A. (1976) Study on the chemical composition of enargite and minerals of luzonite-famatinite series from the Kasuga and Akeshi mines, Kagoshima prefecture. *Journ. Miner. Soc. Japan*, vol. 12, Spec. Issue, p. 206–213 (in Japanese).

ルゾナイト—ファマチナイト結晶の合成とその格子定数変化

金 沢 康 夫

要 旨

乾式法及び熱水法によりルゾナイト（Cu_3AsS_4）-ファマチナイト（Cu_3SbS_4）結晶を合成した．両結晶は正方晶系に属し，完全な固溶体を作っているが，熱水合成では，その成長形態に次のような差異が認められる．ルゾナイトは板状から短柱状結晶の集合体として成長し，双晶が普通に見られる．一方，ファマチナイトは比較的大きな柱状単結晶として成長する．また，格子定数は Cu_3SbS_4 のモル% とともにほぼ直線的に増加する．その変化は a=5.2905(7)—5.3862(4)Å, c=10.438(3)—10.753(1)Å c/a=1.973–1.996である．この化学組成と格子定数の関係を使えば，天然産結晶の格子定数を測定することにより，結晶の平均的な化学組成を求めることが可能である．

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