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**Journal Title:** Kristallogragiya, Soviet Physics Crystallography

**Article Author:** Chamid, S.;Pobedimskaya, E.A.;Spiridonov, E.M.;Belov, N.V.

**Article Title:** Refinement of the structure of petzite, Au Ag3 Te2

**Volume:** 23

**Issue:**

**Month/Year:** 1978

**Pages:** 267-269 (scan notes and title/copyright pages for chapter requests)

**Imprint:**

**Trans. #: 1732664**

**Call #: QD901 .K7135 v.23 1978**

**Location: Science-Engineering Library**

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CODEN:SPHCA6 ISSN: 0038-5638

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23(3) May-June 1978

a translation of the journal КРИСТАЛЛОГРАФИЯ, Kristallografiya (Crystallography), Vol. 23, No. 3, pages 449-672, May-June 1978
published by the American Institute of Physics

7135

CODEN: SPHCA6

ISSN: 0038-5638

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# Refinement of the structure of petzite $AuAg_3Te_2$

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(Submitted August 8, 1977)

Kristallografiya **23**, 483–486 (May–June 1978)

The authors have refined the crystal structure of petzite $AuAg_3Te_2$ on a specimen from the Zhana-Tyube deposit in North Kazakhstan (Syntex $P\bar{1}$ autodiffractometer, λMo radiation, 140 reflections, $R_{hkl} = 8.9\%$). The unit-cell parameter $a = 10.385 \pm 0.0004$ Å was refined in the same autodiffractometer. The Fedorov group is $I\,4_132$. The structure is comparable with that of garnet. Taking account of the first coordination sphere, the Ag atoms have as neighbors four Te atoms distributed in a tetrahedron; the Au atoms have two Te atoms.

PACS numbers: 61.60.+m

The structure of the widely occurring telluride petzite was interpreted by Frueh[1] in 1959 with a discrepancy index R = 0.25. We have refined the structure on a rounded grain (diameter ~ 0.2 mm) of petzite from the Zhana-Tyube deposit (North Kazakhstan), which is rich in silver and gold tellurides.[2] Petzite was observed in intergrowths with tellurides – hessite, sylvanite, krennerite, antimony tellurobismuthite, altaite, frohbergite – and also with chalcopyrite, pyrite, and pyrrhotite, less frequently in isolated segregations in quartz and calcite reaching a size of 2 mm. The predominant part of the petzite grains contains the same amount of very fine hessite intergrowths, probably the decomposition products of a solid solution intermediate between petzite and hessite in composition. A smaller part of the petzite segregations is optically homogeneous, but they often consist of granular aggregates, and it is very difficult to find petzite single crystals.

The material for the investigations was collected from telluride concentrates obtained by dissolving specimens of the ores in HF. The chemical composition and physical properties were determined for optically homogeneous grains of petzite specimen Zh-7-72, from which petzite single crystals were extracted.

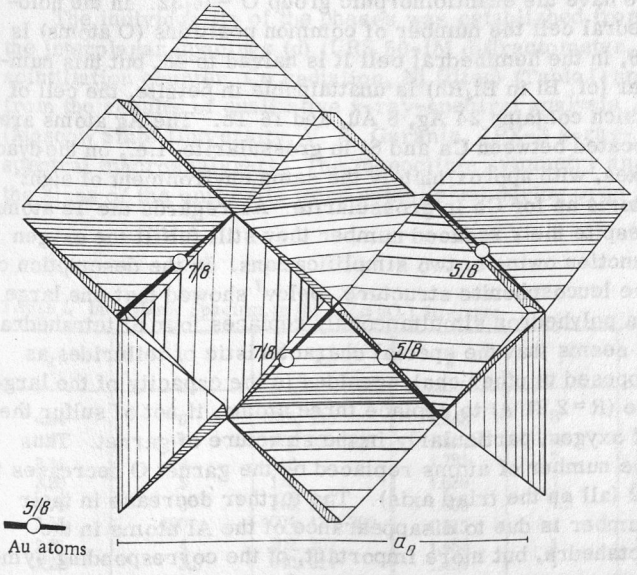


FIG. 1. Structure of petzite in polyhedra.

An electron microprobe revealed that silver, tellurium, gold, and copper are distributed uniformly within the grains. The composition of the petzite grains is stable, and for the test specimen (Table I) it is close to the theoretical one. The overall content of copper, iron, and mercury, present as impurities, is less than 1%. Recalculation of the composition to six atoms gave the formula $Au_{0.96}(Ag_{2.92}Cu_{0.08}Fe_{0.03})_{3.03}Te_{2.01}$.

The powder pattern of petzite (Table II) is similar to the standard ASTM 12-424. The cubic lattice parameter of petzite Zh-7-72, calculated by the method of least squares from a set of all the reflections (taking account of reflections with large θ angles), is $a_0 = 10.39 \pm 0.01$ Å, i.e., close to the value 10.38 Å in Ref. 1. The x-ray density of the mineral is 9.09 g/cm$^3$.

In reflected light petzite is grayish white with a pale bluish tint, and isotropic. Its reflectance is similar to that in Ref. 3. The microhardness is 48 kg/mm$^2$ (eight measurements at a load of 10 g, the values determined on a PTM-3 microdurometer, calibrated against NaCl, ranging from 43 to 54 kg/mm$^2$).

To interpret the structure, 140 independent nonzero reflections were obtained on a Syntex $P\bar{1}$ automatic diffractometer (Mo radiation, graphite monochromator, $2\theta-\theta$ method, variable scanning rate 6-24 deg/min), $h \geq k \geq l$, $0 \leq h \leq 20$.

TABLE I. Chemical Composition of Petzite Zh-7-72

| Elements | Wt.% | Number of atoms | Formula units per six atoms |
|---|---|---|---|
| Au | 24.50 | 1244 | 0.96 |
| Ag | 40.85 | 3787 | 2.92 |
| Cu | 0.63 | 99 | 0.08 |
| Fe | 0.24 | 43 | 0.03 |
| Hg | 0.03 | 1 | – |
| Te | 33.26 | 2606 | 2.01 |
| Se | Traces | – | – |
| Total | 99.27 | – | 6 |

Remarks. We did not observe Pb, Bi, and Sb; the chemical composition was determined by means of an IKhA-5 electron probe; 25 kV; analytical lines Au μα; Ag Lα; Cu Kα; Fe Kα; Hg μα; Te Lα; Se Kα; standards: pure metals (Au, Ag, Cu, Fe), sylvanite $AuAgTe_4$, coloradoite HgTe, and clausthalite PbSe were analyzed chemically (standard method of calculation, analyst E. M. Spiridonov).

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TABLE II. Powder Pattern of Petzite Zh-7-72

| $I$ | $d_\alpha$ (mea) Å | $hkl$ | $d_\alpha$ (cal) Å | $I$ | $d_\alpha$ (mea) Å | $hkl$ | $d_\alpha$ (cal), Å |
|---|---|---|---|---|---|---|---|
| 6 | 7.32 | 110 | 7.35 | 2 | 1.278 | 811, 741, 554 | 1.279 |
| 3 | 3.67 | 220 | 3.67 | 4 | 1.208 | 831, 750 | 1.208 |
| 0.5 | 3.31 | 310 | 3.29 | 5 | 1.175 | 752 | 1.176 |
| 1.5 | 2.99 | 222 | 3.00 | 0.5 | 1.132 | 842 | 1.134 |
| 10 | 2.76 | 321 | 2.78 | 1 | 1.121 | 921, 761, 655 | 1.120 |
| 1 | 2.59 | 400 | 2.60 | 0.5 | 1.107 | 664 | 1.108 |
| 4 | 2.44 | 411, 330 | 2.45 | 1 | 1.096 | 930, 851, 754 | 1.095 |
| 5 | 2.31 | 420 | 2.32 | 4 | 1.074 | 932, 763 | 1.072 |
| 8 | 2.12 | 422 | 2.12 | 3 | 1.049 | 941, 853, 770 | 1.050 |
| 7 | 2.02 | 510, 431 | 2.04 | 1 | 1.009 | 950, 943 | 1.009 |
| 5 | 1.896 | 521 | 1.897 | 5 | 0.9903 | 1031, 952, 765 | 0.9905 |
| 3 | 1.835 | 440 | 1.837 | 0.5 | 0.9655 | 1040, 864 | 0.9647 |
| 0.5 | 1.780 | 530, 433 | 1.782 | 6 | 0.9262 | 1121, 1051, 963 | 0.9260 |
| 1.5 | 1.568 | 622 | 1.566 | 0.5 | 0.9192 | 880 | 0.9186 |
| 2 | 1.531 | 631 | 1.532 | 1 | 0.9110 | 970 | 0.9114 |
| 1.5 | 1.497 | 444 | 1.500 | 2 | 0.8972 | 1132, 1053, 972, 776 | 0.8972 |
| 2 | 1.468 | 710, 550, 543 | 1.469 | 3 | 0.8844 | 1141, 875 | 0.8843 |
| 1.5 | 1.444 | 640 | 1.441 | 0.5 | 0.8784 | 1062 | 0.8783 |
| 1.5 | 1.410 | 721, 633 | 1.414 | 3 | 0.8716 | 965<br>1211, 1150 | 0.8716 |
| 5 | 1.386 | 642 | 1.388 | 1.5 | 0.8602 | 1143, 981, 974 | 0.8601 |
| 8 | 1.318 | 732, 651 | 1.320 | 1 | 0.8368 | 1231, 983 | 0.8372 |
| 1.5 | 1.297 | 800 | 1.299 | 8 | 0.8266 | 1161, 1073 | 0.8266 |

Remarks. Conditions: RKD 57.3 mm, Cu anticathode, Ni filter, 35 kV, 16 mA; specimen—"rubber ball," diam. 0.2 mm. Indexing was performed by the analytical method by E. M. Spiridonov.

Recalculation of the intensities to $F_{hkl}$, and the subsequent operations, were performed in the Computer Center of the Academy of Sciences of the USSR on a BESM-4M computer by the Kristall program,[3] without a correction for absorption. The systematic absences correspond to the group $O_9 = I4_132$, established in Ref. 1. The R-factor for the coordinates[1] was 0.20, permitting assumption of the reliability of the structural model. Further processing by the method of least squares reduced $R_{hkl}$ to 0.089 for all the reflections. The refined coordinates of all the atoms are given in Table III.

In the petzite structure, around each silver atom there are two Te atoms at a distance of 2.92 Å and another two at 2.96 Å. Two gold atoms and two silver atoms at a distance of 3.06 Å may be present in the coordination sphere; each Au atom has as neighbors two Te atoms at a distance of 2.61 Å ("dumbbell") and six Ag atoms at 3.06 Å. Thus we have similar eight-pointed coordination polyhedra for the Ag and Au atoms; as regards the Te atoms, they are bound to one Au atom at a distance of 2.61 Å, three Ag atoms at 2.92 Å, and another three Ag atoms at 2.96 Å, so that for tellurium we have a seven-pointed coordination polyhedron. Thus the structure mainly consists of eight-pointed polyhedra of similar volume, linked by common edges; but if we take account only of short distances less than 3.0 Å, specifically those between the Ag atoms and the two Te atoms, 2.92 Å, and the other two Te atoms, 2.96 Å, the Ag atoms are located in tetrahedra created by the tellurium atoms; the distance between the Au atoms and the two Te atoms in the dumbbell is 2.61 Å (Fig. 1). As far back as 1959, on the basis of the similarity of the space groups and lattice parameter, Frueh called the petzite structure "garnet-like." Tovbis et al.[4] noted the excellent mechanical qualities (ductility) of numerous readily synthesized garnets, and tried to acertain the reasons for them by comparison with nephrites, which have the same qualities. Belov[6] described the metallic garnet-like phase $Bi_4Rh$, in which the Bi atoms fulfill the "garnet" function of the O atoms, and the Rh atoms that of the Ca atoms in the Thomson cubes for the corresponding analogs of Al (in the octahedra) and Si (in the tetrahedra).

TABLE III. Coordinates of Basis Atoms in Petzite Structure

| Atoms | Number of occurrences | $x/a$ | $y/b$ | $z/c$ | $B_j$, Å² |
|---|---|---|---|---|---|
| Ag | 24 | 0.361 | 0 | 0.250 | 1.910 |
| Au | 8 | 0.125 | 0.125 | 0.125 | 1.802 |
| Te | 16 | 0.270 | 0.270 | 0.270 | 1.029 |

In the garnet-like telluride $AuAg_3Te_2$ the cubic symmetry is reduced: Instead of the higher group $O_h^{10} = Ia3d$ we have the enantiomorphic group $O^8 = I4_132$. In the holohedral cell the number of common positions (O atoms) is 96, in the hemihedral cell it is halved to 48, but this number (cf. Bi in $Bi_4Rh$) is unattainable in petzite, the cell of which contains 24 Ag, 8 Au, and 16 Te. The Ag atoms are located between Ca and Si in grossularite, i.e., on the dyad axes, with approximately the same environment of eight atoms as for Ca in grossularite. As regards the Te atoms, despite their reduced number they still fulfill the oxygen function owing to two simplifications. In the description of the leucosphenite structure, Belov[7] showed that one large Ba polyhedron simultaneously replaces four Si tetrahedra. It seems that the special characteristic of tellurides as opposed to other chalcogenides is the capacity of the large Te (R = 2.21 Å) to replace three atoms, if not of sulfur then of oxygen, particularly in the structure of garnet. Thus the number of atoms replaced by the garnet O decreases to 32 (all on the triad axis). The further decrease in their number is due to disappearance of the Al atoms in the octahedra, but more important, of the corresponding symmetry centers: The octahedra around Al are flattened into

a single triplet of Te atoms. In garnet[8] the trigonal prisms between the Al octahedra are empty; in petzite they are half populated with Au atoms, which owing to the tellurium atoms which have merged on the triad axis, now act as centers of the Te–Au–Te dumbbel, as they do in the structures of krennerite and sylvanite.[9, 10]


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Translated by S. E. Hall

# The crystal structures of $LiZn[BO_3]$ and $LiMn[BO_3]$


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(Submitted November 2, 1977)

Kristallografiya **23**, 487–490 (May–June 1978)



The authors have made an x-ray structural investigation of $LiZn[BO_3]$ (I) and $LiMn[BO_3]$ (II) crystals obtained by hydrothermal synthesis (automatic diffractomer, λMo, $2\theta$–$\theta$ method, max $\sin\theta/\lambda = 1.08$ Å, 1239 and 1726 independent reflections ($I \geq 2\sigma I$), method of least squares in the isotropic approximation to $R_{hkl} = 0.067$ and 0.067 for I and II respectively. The structures are "two-layer" hexagonal close packing of O atoms, the tetrahedral cavities of the four layers of which (along the $c$-axis) are filled with Li, Zn(Mn) cations, displaced (statistically) from the centers of the tetrahedra in such a way that the Li and Zn(Mn) atoms are located in the centers of five-pointed polyhedra, and the B atoms in the centers of triangles.



PACS numbers: 61.60.+m


Working in conjunction with A. N. Ivashchenko and O. K. Mel'nikov, we obtained crystals of these two phases in the Hydrothermal Synthesis Laboratory of the Institute of Crystallography, Academy of Sciences of the USSR, in an investigation of crystallization in the system $ZnO-B_2O_3-Li_2O-H_2O$ with small additions of MnO as activator in copper capsules at T = 250 and 450°C respectively and P ~ 1000 atm.

The individuality of the phases was established from the interplanar spacings (d) (URS 50-IM diffractometer, scintillation counter, Cu radiation, Ni filter) (Table I) and from the results of qualitative x-ray-spectral analysis (Moscow State University, V. K. Garanin, JPX-3 x-ray-spectral macroanalyzer). The monoclinic symmetry and the sizes of the unit cells were established during preliminary x-ray investigations by the Laue and oscillation (RKOP camera, Mo radiation) methods and then refined on a $P\bar{1}$ automatic diffractometer:

| $LiZn[BO_3]$ | $LiMn[BO_3]$ |
|---|---|
| $a$=5.094(1) Å | $a$=5.188(2) Å |
| $b$=8.806(3) Å | $b$=8.952(2) Å |
| $c$=10.374(4) Å | $c$=10.367(3) Å |
| β=91.09(3)° | β=91.75(3)° |
| $V$=463.2(3) Å$^3$ | $V$=481.3(3) Å$^3$ |

$Z$=8, Fed. gr. $C_{2h}^6 = C2/c$.

The pseudohexagonality of both phases,[1)] confirmed by the ratio of the axes $b/a \approx \sqrt{3}$, and the similarity of the parameters to the corresponding values for $LiZn[BO_3]$ (Ref. 1) (hexagonal system, $a$ = 5.10, c = 8.08 Å, d = 3.60 g/cm$^3$), suggested that the synthesized phases are the monoclinic varieties of $LiZn[BO_3]$ and $LiMn[BO_3]$ (Ref. 1). This supposition was confirmed during subsequent investi-

TABLE I. Interplanar Spacings in the $LiZn[BO_3]$ Structure

| d | I | hkl | d | I | hkl |
|---|---|---|---|---|---|
| 4.34 | 6 | 020, 110 | 1.848 | 6 | 115, 223 |
| 4.01 | 10 | 111, 02$\bar{1}$, 021 | 1.811 | 1.5 | 134, 13$\bar{4}$ |
| 3.34 | 6 | 11$\bar{2}$ | 1.791 | 2 | 204 |
| 3.29 | 5 | 112 | 1.639 | 1 | 24$\bar{1}$, 31$\bar{1}$ |
| 2.71 | 3 | 11$\bar{3}$, 023 | 1.606 | 1.5 | 11$\bar{6}$ |
| 2.56 | 100 | 00$\bar{4}$, 130, 200 | 1.513 | 1 | 22$\bar{5}$, 04$\bar{5}$, 045 |
| 2.28 | 4 | 20$\bar{2}$, 202 | 1.485 | 1 | 243 |
| 2.21 | 3,5 | 040, 024 | 1.459 | 1 | 33$\bar{0}$, 06$\bar{0}$ |
| 2.14 | 2 | 22$\bar{1}$, 041 | 1.426 | 1 | 13$\bar{6}$, 20$\bar{6}$ |



0038-5638/78/2303-0269 $02.40


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