

## Toward the crystal structure of nagyagite, $[\text{Pb}(\text{Pb},\text{Sb})\text{S}_2][(\text{Au},\text{Te})]$

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### ABSTRACT

Synthetic nagyagite was grown from a melt as part of a search for materials with high-temperature superconductivity. Electron microprobe analyses of synthetic nagyagite and of nagyagite from the type locality Nagyág, Transylvania (now Săcărîmb, Romania) agree with data from literature. The crystal chemical formula  $[\text{Pb}(\text{Pb},\text{Sb})\text{S}_2][(\text{Au},\text{Te})]$  was derived from crystal structure investigations. Nagyagite is monoclinic pseudotetragonal. The average crystal structure was determined from both synthetic and natural samples and was refined from the synthetic material to  $R = 0.045$  for 657 single-crystal X-ray data: space group  $P2_1/m$ ,  $a = 4.220(1) \text{ \AA}$ ,  $b = 4.176(1) \text{ \AA}$ ,  $c = 15.119(3) \text{ \AA}$ ,  $\beta = 95.42(3)^\circ$ , and  $Z = 2$ . Nagyagite features a pronounced layer structure: slices of a two slabs thick SnS-archetype with formula  $\text{Pb}(\text{Pb},\text{Sb})\text{S}_2$  parallel to (001) have a thickness of  $9.15 \text{ \AA}$ . Te and Au form a planar pseudo-square net that is sandwiched between the SnS-archetype layers; it is assumed that planar  $\text{Au}^{[4\text{Te}]\text{Te}_4}$  configurations are edge connected to chains and that Te atoms are in a zigzag arrangement. Ordering within the SnS-archetype and gold-tellurium layers, intense twinning and/or stacking variants are responsible for the often observed superstructure reflections. For buckhornite,  $[(\text{Pb}_2\text{Bi})_{\Sigma_3}\text{S}_3][(\text{AuTe}_2)_{\Sigma_3}]$ , a structure model is proposed considering a homologous series with nagyagite,  $[(\text{Pb}_3(\text{Pb},\text{Sb})_3)_{\Sigma_6}\text{S}_6][(\text{Au},\text{Te})_3]$ .

### INTRODUCTION

Werner (1789) [cited in Hintze (1904)] described a foliated gold ore from Nagyág, Transylvania (now Săcărîmb, Romania) and named it for the type locality “Nagiakererz.” Haidinger (1845) modified the name to nagyágite. Numerous synonyms like “Blättererz,” “Nagyager Erz,” “Blättertellur,” “Graugolderz,” “black tellurium,” “foliated tellurium,” “elasmose,” and “elasmosine” refer to the macroscopic behavior and the chemical composition; references to the historical descriptions are compiled by Hintze (1904). For a recent description of the ore deposit in Nagyág see Simon et al. (1995). Nagyagite exists at many other localities. Nagyagite occurs as foliated masses, crystalline plates, and massive granular particles. Despite the fact that crystals up to several millimeters in scale are known, the correct chemical formula and the crystal system remained uncertain to date; the crystal structure was unknown. There are three main reasons for this: (1) It was unclear which elements substitute for others in nagyagite. Occasionally Te and Sb or S and Te were grouped together. (2) The crystals are mechanically extremely unstable; plastic deformation does not allow to cut or break samples of extreme laminated to foliated habit without bending them. (3) Pervasive twinning was described even in early morphological investigations (Schrauf 1878; Palache et al. 1944). Associated stacking faults and structural defects prevented the detection of crystal symmetry and the determination of unit cell, Laue symmetry, extinction rules, and atomic arrangement.

The uncertainty in the symmetry of nagyagite was mentioned by practically all authors to date. Several crystal sym-

metries and cell parameters have been published. Schrauf (1878) mentioned a tetragonal pseudosymmetry, but could not work out the true symmetry and suggested orthorhombic symmetry as likely. Tetragonal and monoclinic symmetry was assumed by Dana and Dana (1877) and Palache et al. (1944), respectively, orthorhombic symmetry by Criddle and Stanley (1993). From X-ray film investigations Gossner (1935) found a pseudotetragonal or even tetragonal cell with  $a = 12.5 \text{ \AA}$  and  $c = 30.25 \text{ \AA}$ ; however, he mentioned that a tetragonal cell is not likely from the intensity distribution, one crystal had  $a = 1/3 \times 12.5 \text{ \AA} = 4.17 \text{ \AA}$ . Stanley et al. (1994) made the first attempt to determine the space-group. For an orthorhombic pseudotetragonal cell with  $a = 8.363(7) \text{ \AA}$ ,  $b = 30.20(1) \text{ \AA}$ ,  $c = 8.288(7) \text{ \AA}$ , they found the extinction symbol  $\text{Bb--}$ , but the authors mentioned some pseudoextinctions and classes of strong and weak reflections.

We encountered nagyagite during a search for high-temperature superconductive materials among sulfides rather than on the usually investigated oxides (Culetto 1996, 1997). Of the complex sulfides, selenides, and tellurides, nagyagite was thought to be a candidate for such a physical study due to symmetry reasons, the layered type structure expected from the marked cleavage, and the pronounced foliated habit. Appropriate chemical substitutions or high pressure should provide materials with anomalous normal-state properties, e.g., anomalous phonon frequency shift at low temperature. Successful materials synthesis encouraged us to solve the type structure of nagyagite.

### MATERIALS SYNTHESIS

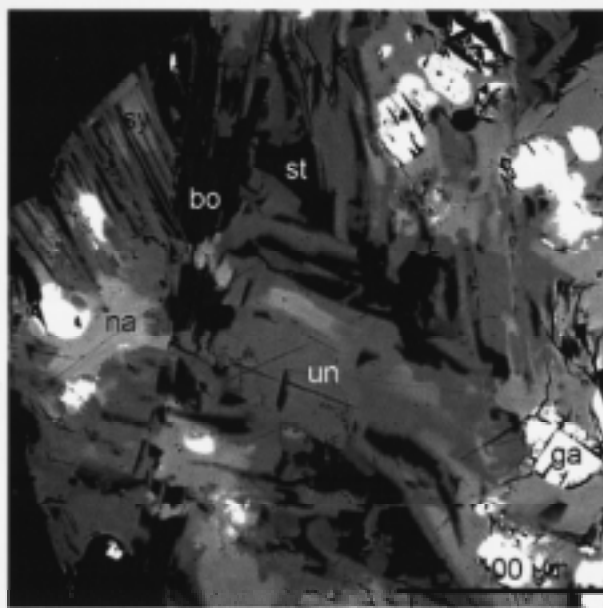
Multi-phase samples in the Ag-Au-Pb-Sb-S-Te system were prepared by a two-step procedure. For the preparation of AuTe<sub>2</sub> precursor material, stoichiometric portions of 4N fine gold grains (ÖGUSSA) and 5N tellurium pieces (STREM) have been sealed in a Duran glass ampulla at 0.2 bar N<sub>2</sub> atmosphere. The ampulla was then heated from 350 to 500 °C at a rate of 4 K/min in a Naber Labotherm furnace and kept at 500 °C for 3.5 h. The reaction was completed by a subsequent five hours annealing process at 465 °C. The sample was then slowly cooled down to room temperature.

In a second step, pieces of the brittle AuTe<sub>2</sub> precursor material and the analytical or higher grade reagents Ag<sub>2</sub>S (FLUKA), Sb (MERCK), Pb (BMG), S (FLUKA), and Te (STREM) weighed out according to the initial composition AgAuSb<sub>3</sub>Pb<sub>13</sub>S<sub>16</sub>Te<sub>6</sub> were sealed as above. Later synthesis runs were performed with variable ratios of elements. The total sample mass for the second reaction step was chosen as ~1 g. The vertically positioned ampulla was heated to 480 °C at a rate of 4 K/min and kept there for 30 min. Reactions already started below 400 °C and partial melting was visible, general surface melting was observed above 620 °C. Temperature rise maintaining the rate of 4 K/min produced a silvery melt with metallic luster containing numerous bubbles. Finally the melt was kept at 780 °C for 5 min and then cooled down at a rate of 2 K/min in a vertical temperature gradient of approximately 0.5 K/cm.

The regulus showed a pitted surface and contained numerous vesicles ranging from less than one to several mm in size. Extremely thin-tabular crystals of chemically homogeneous synthetic nagyagite, intergrown in fan-shaped aggregates were grown. Some of the larger crystals showed a rectangular outline with the corners being truncated by small faces. Crystal fragments detached from the cavities served for single-crystal X-ray investigations. Thin slices of different orientation were cut from the regulus, embedded in resin, ground, and polished for electron microprobe investigations. The major reaction product is nagyagite, minor phases include hessite, stuetzite, boulangerite, tellurantimony, galena, three chemically different phases related to sylvanite, poorly crystallized phases in the system Ag-Sb-Te (some of them are unknown), as well as small quantities of valentinite (Fig. 1). Electron microprobe analyses and/or single-crystal X-ray diffractions were performed on the products. The presence of metallic lead exceeding 0.5 vol% in samples of comparable composition and reaction conditions can be excluded by low temperature ac- and dc-susceptibility results from Michor and Hilscher (1997, personal communication).

### CHEMICAL COMPOSITION

Previous analyses of nagyagite from the type locality as well as from the other localities showed it to be a lead dominated sulfide-telluride. Sb and Au were always found as essential constituents. Recently the substitution of Sb by As in nagyagite was described by Simon et al. (1994), that of Sb by Bi by Johan et al (1994). Stumpfl (1970) mentioned the lack of a wide compositional variation in this complex mineral from different localities. Uncertainties in the recalculation of the results of chemical analyses existed due to the lack of a structural for-



**FIGURE 1.** Complex assemblage of synthetic nagyagite (na) rimmed by the unknown phase "X" (un) and intergrown with sylvanite (sy), stuetzite (st), boulangerite (bo), and galena (ga).

mula. The commonly proposed solid solution between S and Te, or grouping together of Sb and Te, did not yield integer stoichiometry. The element substitutions proposed from structural investigation in parts are unexpected. Nagyagite has to be considered as a composite structure formed by an alternate stacking of sulfide and telluride layers. Solid solution between Pb-Sb(-As-Bi) has to be considered for the cation positions within the SnS-type layers; these layers are separated by planar gold-tellurium sheets of anionic character. Table 1 compiles the previous chemical analyses after recalculation based on the present results. Within the analytical error, they agree with our structural formula.

Quantitative chemical analyses of nagyagite and of synthetic material were performed using an electron microprobe. Two polished sections were investigated, one containing natural nagyagite from the type locality (no. 5588, collection of the Institut für Mineralogie und Kristallographie, Universität Wien), the other contained fragments from the syntheses' products. A JEOL Superprobe 8600, controlled by a LINK-EXL system operated at 25 kV with a beam current of 30 nA was used. The raw data were processed by the ZAF-4 on-line program. Pure metals (AuL $\alpha$ , AgL $\alpha$ , SbL $\alpha$ ), synthetic CdTe (TeL $\alpha$ ), and natural PbS (PbL $\alpha$ , SK $\alpha$ ) were used as standards. The results are compiled in Table 2. A different set of standards (Bi<sub>2</sub>Te<sub>3</sub>: TeL $\alpha$ ; Sb<sub>2</sub>S<sub>3</sub>: SbL $\alpha$ ; Au-Ag alloy (60:40): AuL $\alpha$ ) yielded slightly increased Te and decreased Sb and Au values (+0.2, -0.1, and -0.2 wt%, respectively).

The chemical composition of the investigated natural samples compares well with published data on Au-rich nagyagite (Paar and Chen 1982). Synthetic samples (isolated crystals and the central portion of crystal aggregates) are equivalent to natural nagyagite. The unknown compound "X" covering the nagyagite nucleus of larger crystals is deficient in Pb

TABLE 1. Electron microprobe analyses

Pb	Sb	Pb+Sb	Au	Ag	S	Te	Au+Te	total
<b>Weight percents</b>								
55.98(19)	7.60(20)		11.15(8)	0.00	11.14(15)	14.61(19)		100.48*
57.30	7.70		11.10	0.00	10.50	14.90		101.60†
56.50	7.20		10.90	0.00	10.70	15.10		100.50‡
56.84	7.66		7.66	0.07	11.07	17.10		100.40‡
56.78	7.68		7.47	0.12	10.83	16.97		99.85‡
55.79(30)	8.70(10)		6.28(9)	0.00(4)	11.02(8)	18.36(14)		100.16§
45.99(50)	11.42(8)		7.83(16)	0.18(8)	10.27(8)	24.35(30)		100.05
<b>Atomic proportions</b>								
3.18	0.73	3.91	0.66		4.08	1.34	2.00*	
3.27	0.75	4.02	0.67		3.91	1.39	2.06†	
3.23	0.71	3.94	0.66		3.99	1.42	2.08†	
3.20	0.74	3.94	0.46		4.03	1.57	2.03‡	
3.23	0.75	3.98	0.46		3.99	1.57	2.03‡	
3.13	0.83	3.96	0.37		4.00	1.67	2.04§	

Notes: Results are given in weight percent and recalculated for a total of 10 atoms corresponding to the number of atoms within the average unit cell.

Source of materials and analytical data are as follows:

\* This work; sample from Nagyág, Transylvania (now Săcărîmb, Romania), collection of the Institut für Mineralogie und Kristallographie, Universität Wien (no. 5588), standard deviation in parentheses from 5 analyses.

† Paar and Chen (1982); samples from Schellgaden, Austria.

‡ Stanley et al. (1994); samples from Nagyág, Transylvania (now Săcărîmb, Romania).

§ Synthetic nagyagite, standard deviation in parentheses from 18 analyses.

|| Unknown synthetic phase "X", standard deviation in parentheses from 14 analyses.

and enriched in Sb and Te as compared to the nagyagite core. Further investigation of this compound was abandoned because no pure fragments could be isolated.

## STRUCTURE INVESTIGATION

For structure investigation, dozens of crystal fragments from several synthesis runs and natural material from Nagyag and Cripple Creek (from in the Mineralogical Collection of the Institut für Mineralogie und Kristallographie, Universität Wien) were investigated by Weissenberg and precession film techniques and with a Nonius four-circle diffractometer equipped with a CCD-detector. The major part of crystals gave extremely broad X-ray reflection profiles even if their optical behavior suggested sufficient quality. After many trials, a small crystal chip of synthetic material with monoclinic symmetry was found to be suitable for structure investigation, the only extinction rule ( $0k0$ ):  $k = 2n + 1$  is characteristic for the space groups  $P2_1$  or  $P2_1/m$ . The structure was solved by direct methods and sub-

TABLE 2. Recalculated chemical formulae of natural nagyagites based on the total of 10 atoms for the average unit cell

Recalculated formula	Reference
$[(Pb_{3.20}Sb_{0.71}Fe_{0.09})_{\Sigma 4.00}S_{3.93}][Au_{0.44}Te_{1.63}]_{\Sigma 2.07}^*$	Sipöcz (1886)
$[(Pb_{3.46}Sb_{0.74})_{\Sigma 4.22}S_{3.76}][Au_{0.46}Te_{1.56}]_{\Sigma 2.02}^{\dagger}$	Stumpfl (1970)
$[(Pb_{3.46}Sb_{0.77})_{\Sigma 4.26}S_{3.79}][Au_{0.54}Te_{1.41}]_{\Sigma 1.95}^{\ddagger}$	Stumpfl (1970)
$[(Pb_{3.26}Sb_{0.70})_{\Sigma 3.96}S_{3.98}][Au_{0.65}Te_{1.41}]_{\Sigma 2.06}^{\S}$	Paar and Chen (1982)
$[(Pb_{3.30}Sb_{0.75})_{\Sigma 4.05}S_{3.90}][Au_{0.66}Te_{1.39}]_{\Sigma 2.05}^{\S}$	Paar and Chen (1982)
$[(Pb_{3.30}Sb_{0.77}Cu_{0.02}Ag_{0.01}Fe_{0.02})_{\Sigma 4.12}S_{3.90}][Au_{0.46}Te_{1.53}]_{\Sigma 1.98}^{\dagger}$	Criddle and Stanley (1993)
$[(Pb_{3.14}Sb_{0.74}Ag_{0.03})_{\Sigma 3.91}S_{4.24}][Au_{0.32}Te_{1.53}]_{\Sigma 1.85}^{\dagger}$	Cioffica et al. (1993)
$[(Pb_{3.00}Sb_{0.88})_{\Sigma 3.88}S_{4.36}][Au_{0.20}Te_{1.56}]_{\Sigma 1.76}^{\dagger}$	Cioffica et al. (1993)
$[(Pb_{3.34}Sb_{0.57}Bi_{0.17})_{\Sigma 4.08}S_{3.91}][Au_{0.64}Te_{1.37}]_{\Sigma 2.01}^{\dagger}$	Johan et al. (1994)
$[(Pb_{2.95}Sb_{0.04}As_{0.82})_{\Sigma 3.79}S_{4.02}][Au_{0.66}Te_{1.53}]_{\Sigma 2.19}^{\dagger}$	Simon et al. (1994)
$[(Pb_{3.06}Sb_{0.55}As_{0.34})_{\Sigma 3.97}S_{3.97}][Au_{0.60}Te_{1.46}]_{\Sigma 2.06}^{\dagger}$	Simon et al. (1994)
$[(Pb_{2.92}Sb_{0.30}As_{0.61})_{\Sigma 3.83}S_{3.98}][Au_{0.58}Te_{1.61}]_{\Sigma 2.19}^{\dagger}$	Simon et al. (1994)
$[(Pb_{3.20}Sb_{0.73}As_{0.03})_{\Sigma 3.96}S_{4.02}][Au_{0.63}Te_{1.39}]_{\Sigma 2.02}^{\dagger}$	Simon et al. (1994)
$[(Pb_{3.25}Sb_{0.75})_{\Sigma 4.00}S_{4.00}][Au_{0.50}Te_{1.50}]_{\Sigma 2.00}^{\dagger}$	Stanley et al. (1994)

\* Ag, Cu, and Fe are arbitrarily grouped with Pb and Sb.

† Samples from the type locality Nagyág.

‡ Samples from Cripple Creek, Colorado.

§ Samples from Schellgaden, Austria.

sequent difference Fourier summations and it was refined in space group  $P2_1/m$ .

One specimen of natural nagyagite from the type locality (sample no. 5588) was found to be suitable for structure investigation. Although the reflection profile was broader than that of the synthetic sample, there is no doubt about the identity of the two phases. The structural parameters for both data sets are equal within three standard deviations. The powder pattern of natural nagyagite (Stanley et al. 1994) compares well with that recalculated from the atomic parameters obtained from structure refinement. Cell metrics and details on data collection and structure refinements are summarized in Table 3. Due to the higher accuracy, structural data obtained from the refinement

TABLE 3. Single-crystal X-ray data collection and structure refinements for synthetic nagyagite

<i>a</i>	4.220(1) Å	Crystal dimensions	60 × 45 × 5 μm <sup>3</sup>
<i>b</i>	4.176(1) Å	Range of data collection	3° < 2θ < 56.4°
<i>c</i>	15.119(3) Å	Integration diameter	0.55 mm
β	95.42(3)°	per reflection	
<i>V</i>	265.3 Å <sup>3</sup>	μ(MoKα)	61 mm <sup>-1</sup>
Space group	$P2_1/m$	Absorption correction	crystal shape
<i>Z</i>	2	Total measured reflections	3847
<i>P</i> <sub>calc</sub>	7.29 g/cm <sup>3</sup>	Observed unique reflections	(n)689
<i>R</i> <sub>int</sub>	$[\sum(F_o^2 - F(\text{mean})^2)/\sum F_o^2]$	Reflections with $F_o > 4\sigma(F_o)$	657
<i>R</i>	$[\sum( F_o -  F_c  )/\sum F_o]$ (657/689 data)		0.056
<i>wR2</i>	$[\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$		0.045/0.048
Variable parameters ( <i>p</i> )			0.106
Goof = $(\sum[w(F_o^2 - F_c^2)^2]/(n-p))^{0.5}$			34
Max Δ/σ			1.161
Extinction parameter			≤ 0.001
Final difference Fourier map			0.0098(11)
			-1.99 to +3.79 eÅ <sup>-3</sup>

Note: Nonius four-circle diffractometer equipped with a CCD detector (Mo tube, graphite monochromator), unit-cell parameters were obtained by least-squares refinements of accurate 2θ values. Data collection in the φ-scan mode (rotation 360°), scan speed: 0.1°/min; Δφ = 2°/frame; frame size: 621 × 576 pixels, binned mode; detector-to-sample distance: 28 mm. Corrections for Lorentz and polarization effects; neutral-atomic complex scattering functions (Wilson 1992), programs SHELX-76, SHELXS-97, and SHELXL-97 (Sheldrick 1976, 1997a, 1997b).  $w = 1/(\sigma^2(F_o^2) + [0.037*P]^2 + 10.50*P)$ ;  $P = ([\max(0, F_o^2)] + 2*F_c^2)/3$ . Formula from electron-microprobe analysis is  $[(Pb_{1.56}Sb_{0.42})_{\Sigma 1.98}S_{2.00}][Au_{0.18}Te_{0.84}]_{\Sigma 1.02}$ .

**TABLE 4.** Structural parameters (e.s.d.'s in parentheses) for synthetic nagyagite

atom	x	y	z	$U_{11}$	$U_{22}$	$U_{33}$	$U_{13}$	$U_{eq}$
Me1	0.16212(19)	1/4	0.80260(5)	0.0351(5)	0.0325(5)	0.0371(5)	0.0026(3)	0.0350(4)
Me2	0.3578(3)	1/4	0.40183(7)	0.0443(7)	0.0274(6)	0.0326(7)	0.0087(4)	0.0344(5)
X	0.7364(4)	1/4	-0.00056(8)	0.0518(10)	0.0357(9)	0.0286(8)	0.0050(5)	0.0386(6)
S1	0.3484(11)	1/4	0.2323(3)	0.025(2)	0.021(2)	0.037(3)	0.0080(17)	0.0277(10)
S2	0.0744(13)	1/4	0.6111(3)	0.035(3)	0.060(4)	0.026(2)	0.0077(19)	0.0398(13)

Notes: The anisotropic displacement parameters are defined as:  $\exp[-2\pi^2 \sum_{i,j,k} U_{ij} a_i^* a_j^* h_i h_j]$ ,  $B_{eq}$  according to Fischer and Tillmanns (1988). The occupation factors were refined from scattering power by least-squares methods: Me1 is occupied by Pb atoms; the ratio Sb:Pb is 0.524(13):0.476(13) for the position Me2, the ratio Te:Au is 0.867(16):0.133(16) for the position X.  $U_{12} = U_{23} = 0$  for all atoms.

of the synthetic crystal are given in Table 4, the interatomic bond distances and bond angles are given in Table 5; the discussion is based on these results. The list of structure factors is given in Table 6<sup>1</sup>.

In search of a crystal suitable for structure refinements, doubled and tripled cell parameters  $a$  and  $b$  as well, as a doubled cell parameter  $c$  going along with a variable intensity distribution were commonly observed for distinct natural and synthetic crystals. Occasionally, different multiples of the lattice parameters were found for samples obtained from the same nagyagite crystal. The intensities of reflections responsible for the multiple cell parameters  $a$  and  $b$  are lower than those responsible for double length  $c$ . For some cells and in cases of  $c' = 2c$  the angle  $\beta$  was found to be close to  $90^\circ$  and the intensity distribution suggests orthorhombic symmetry; the extremely broad reflections just allowed crude estimation. These results correspond to the

multiple problems and different observations described by the former authors. Attempts to refine atomic arrangements from data sets with any "larger" unit cell failed to date. It is likely that pervasive twinning and stacking variants as well as partial ordering at the Me2 = (Pb,Sb) and X = (Au,Te) positions of the average structure are responsible for the different behavior of the X-ray diffraction patterns. From crystal chemical considerations, mutual substitutions are expected between the elements Pb and Sb; for Te and Au distinct ordering is assumed. Additional reflections expected for a multiplication of the unit cell volume were absent in the single-crystal X-ray patterns of the two crystals used for structure investigation.

## RESULTS AND DISCUSSION

The monoclinic crystal structure of nagyagite, a pronounced layer structure composed of two types of layers with tetrago-

**Table 5.** Interatomic bond distances (Å) and bond angles ( $^\circ$ ) for synthetic nagyagite

Me1-S2	2.884(5)	S2-Me1-S1 <sup>a</sup>	78.60(12) 2×
Me1-S1 <sup>a</sup>	3.011(3) 2×	S2-Me1-S1 <sup>b</sup>	81.37(13) 2×
Me1-S1 <sup>b</sup>	3.018(3) 2×	S1 <sup>a</sup> -Me1-S1 <sup>a</sup>	87.82(13)
Me1-X	3.619(2)	S1 <sup>a</sup> -Me1-S1 <sup>b</sup>	88.85(4) 2×
Me1-X	3.641(1) 2×	S1 <sup>b</sup> -Me1-S1 <sup>b</sup>	87.55(12)
Me1-X	3.656(1)		
Me2-S1	2.561(5)	S1-Me2-S2 <sup>a</sup>	88.94(13) 2×
Me2-S2 <sup>a</sup>	2.767(4) 2×	S1-Me2-S2 <sup>b</sup>	83.08(12) 2×
Me2-S2 <sup>b</sup>	3.198(4) 2×	S1-Me2-S2 <sup>c</sup>	159.15(14)
Me2-S2 <sup>c</sup>	3.487(5)	S2 <sup>a</sup> -Me2-S2 <sup>a</sup>	97.98(18)
		S2 <sup>a</sup> -Me2-S2 <sup>b</sup>	89.75(3) 2×
		S2 <sup>a</sup> -Me2-S2 <sup>c</sup>	77.51(13) 2×
		S2 <sup>b</sup> -Me2-S2 <sup>b</sup>	81.51(13)
		S2 <sup>b</sup> -Me2-S2 <sup>c</sup>	112.25(10) 2×
X-X <sup>a</sup>	2.889(2) 2×	X <sup>a</sup> -X-X <sup>a</sup>	92.56(9) 2×
X-X <sup>b</sup>	3.050(2) 2×	X <sup>a</sup> -X-X <sup>b</sup>	90.52(2) 2×
X-Me1	3.619(2)	X <sup>b</sup> -X-X <sup>b</sup>	86.40(8)
X-Me1	3.641(1) 2×		
X-Me1	3.656(2)		
X-S1	4.020(5)		
X-S1	4.065(4) 2×		
X-S1	4.164(5)		
S1-Me2	2.561(5)	Me2-S1-Me1 <sup>a</sup>	96.80(12) 2×
S1-Me1 <sup>a</sup>	3.011(3) 2×	Me2-S1-Me1 <sup>b</sup>	103.22(13) 2×
S1-Me1 <sup>b</sup>	3.018(3) 2×	Me1 <sup>a</sup> -S1-Me1 <sup>a</sup>	87.82(13)
		Me1 <sup>a</sup> -S1-Me1 <sup>b</sup>	88.85(4) 2×
		Me1 <sup>b</sup> -S1-Me1 <sup>b</sup>	87.55(12)
S2-Me2 <sup>a</sup>	2.767(4) 2×	Me2 <sup>a</sup> -S2-Me2 <sup>a</sup>	97.98(18)
S2-Me1	2.884(5) 2×	Me2 <sup>a</sup> -S2-Me1	95.29(13) 2×
S2-Me2 <sup>b</sup>	3.198(4) 2×	Me2 <sup>a</sup> -S2-Me2 <sup>b</sup>	89.75(3) 2×
S2-Me2 <sup>c</sup>	3.487(5)	Me2 <sup>a</sup> -S2-Me2 <sup>c</sup>	102.49(13) 2×
		Me1-S2-Me2 <sup>b</sup>	92.03(13) 2×
		Me1-S2-Me2 <sup>c</sup>	152.68(2)
		Me2 <sup>b</sup> -S2-Me2 <sup>b</sup>	81.51(13)
		Me2 <sup>b</sup> -S2-Me2 <sup>c</sup>	67.75(10) 2×

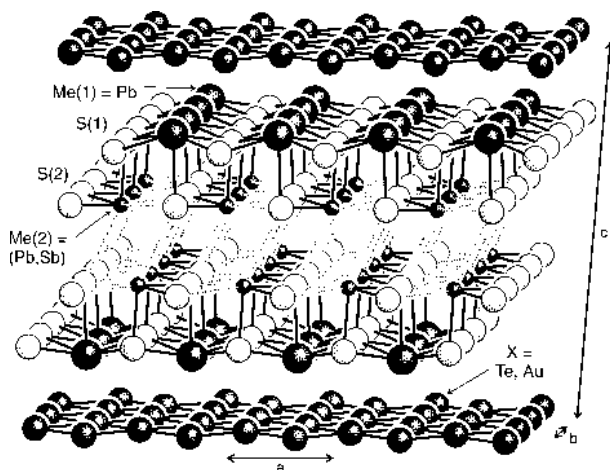


FIGURE 2. The average crystal-structure of nagyagite formed by  $\text{SnS}$ -archetype layers  $\text{Pb}(\text{Pb,Sb})\text{S}_2$  separated by a planar pseudosquare net of gold and tellurium atoms (program ATOMS, Dowty 1997).

nal pseudosymmetry, agrees with the macroscopic behavior of this mineral. Double layers with formula  $[\text{Pb}(\text{Pb,Sb})\text{S}_2]_2$  form a two slabs thick  $\text{SnS}$ -archetype (Makovicky 1993) parallel to (001). The square net of Au and Te atoms is sandwiched between these double layers. During the present investigation, the average structure of nagyagite was solved and some ordering schemes were derived; details on ordering, intergrowths, twinning or stacking variants have to be subject of further work. Within the average cell all atoms have site symmetry  $m$ . The type structure is shown in Figure 2.

Within the  $[\text{Pb}(\text{Pb,Sb})\text{S}_2]_2$  double-layer package, two stereochemically different cation positions occur. Me1 has five S atoms within the first coordination sphere: four S1 atoms are in an approximate plane, the fifth S2 atom is slightly nearer, the Me1 cation is shifted out of the plane defined by the S1 atoms towards the gold-tellurium layer. Thus, a one-sided coordination figure is formed. From scattering power and from stereochemistry an occupation solely by Pb atoms has to be assumed. The other cation position Me2 is pyramidally surrounded by three S atoms in an [1+2] coordination. Three additional S atoms complete the coordination figure to a strongly distorted octahedron. This pronounced threefold coordination and refinements of the scattering power suggest that Sb is concentrated at the Me2 position; also an analogous accumulation of As within the arsenic nagyagites (Simon et al. 1994) or of Bi in nagyagite associated with buckhornite (Johan et al. 1994) is probable. In accord with the chemical analyses of natural and synthetic nagyagite that gave an excess of Pb as compared to  $\text{Sb}+\text{As}+\text{Bi}$ , local disorder might adopt the Me2 position for both the stereochemical requirements of the Pb and Sb atoms: the larger anisotropy of the displacement parameters observed for the Me2 position (amplitudes 0.046, 0.030, and 0.027  $\text{\AA}^2$ )

as compared to that of Me1 (amplitudes 0.038, 0.035, and 0.033  $\text{\AA}^2$ ) corresponds with that assumption. The maximum amplitudes of the anisotropic displacement parameters of the S2 position (0.060, 0.037, and 0.023  $\text{\AA}^2$ ) are in [010], those of S1 (0.039, 0.023, and 0.021  $\text{\AA}^2$ ) in [001] i.e., both in the direction of the shortest Me2-S bonds.

The first coordination spheres of both the cation positions Me1 and Me2 are one-sided, which is characteristic for elements with lone-pair electrons, and they compare well with those of other sulfides. Further interactions are evident from the Me1 positions to two or three Te atoms as well as from the Me2 position to three S2 atoms. In complex lead sulfides, a coordination number of 5 for Pb atoms is often found; those coordinations agree with the  $\langle \text{Pb-S} \rangle$  bond distance of 2.969  $\text{\AA}$  in nagyagite. Also mixed (Pb,Sb) positions were found, e.g., in robinsonite,  $\text{Pb}_4\text{Sb}_6\text{S}_{13}$ , boulangerite,  $\text{Pb}_5\text{Sb}_4\text{S}_{11}$  or  $\text{Pb}_2\text{Sb}_2\text{S}_5$  (Skowron and Brown 1990a, 1990b, 1990c). In galena (PbS) an octahedral coordination with six Pb-S bond distances of 2.966  $\text{\AA}$  (Noda et al. 1987) occurs. Pb-Te is shorter in PbTe (3.219  $\text{\AA}$ , Noda et al. 1987) than in nagyagite ( $\geq 3.619$   $\text{\AA}$ ). In stibnite ( $\text{Sb}_2\text{S}_3$ ), [3+3] and [3+4] coordinated Sb atoms (Bayliss and Nowacki 1972) feature close relations to the Me2 position in nagyagite.

The  $\text{Me}2\text{S}_3$  pyramids are corner-connected among each other to form rows in [010], and are linked in (001) by the longer Me2-S bonds to a formally two-dimensional arrangement with formula  $\text{Me}2\text{S}$ . The frequently observed doubled cell parameter  $b$  (or  $a$ ) indicates an ordering at the Me2 position: a total molar ratio  $\text{Pb:Sb} = 3:1$  would enable an alternate occupation by Sb and Pb atoms. The  $\text{Me}1\text{S}_5$  polyhedra are linked via the four S1-S1 edges of the equatorial plane to an approximate tetragonal arrangement. They share the four edges between the S1 atoms within the equatorial plane and the vertex S2 with the

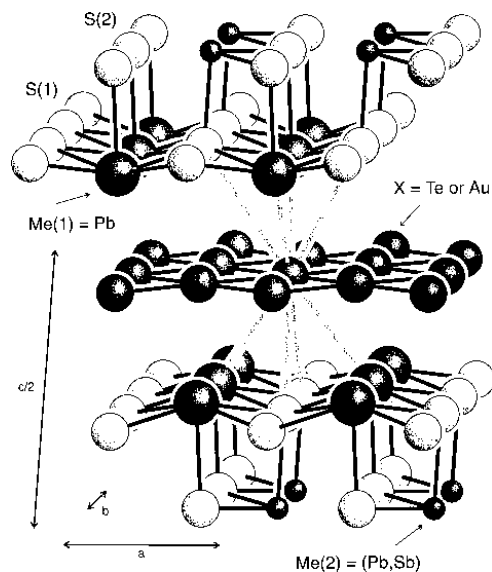


FIGURE 3. The connection between the  $\text{SnS}$ -archetype layers and the gold-tellurium layers in the average crystal-structure of nagyagite: the eight weak bonds are shown for one  $X = (\text{Au,Te})$  atom only (program ATOMS, Dowty 1997).

<sup>1</sup>For a copy of Table 6, document item AM-99-007, contact the Business Office of the Mineralogical Society of America (see inside front cover of recent issue) for price information. Deposit items may also be available on the American Mineralogist web site at <http://www.minsocam.org>.

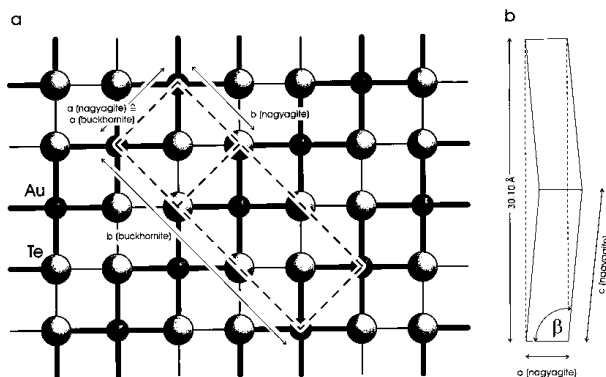
coordination polyhedron of a Me2 atom. This connection type gives a  $\sim 9.15$  Å thick layer package of two SnS-archetype slabs, the layer sequence is Me1S-Me2S-Me2S-Me1S. Analogous layers were found in some chalcogenides with composite incommensurate structures (so-called “misfits”). Among them are the minerals franckeite and lengenbachite, recently investigations on the synthetic compounds  $\sim[(\text{Pb Sb})_2\text{S}_2][\text{NbS}_2]$  and  $[(\text{Pb}_{1.82}\text{Sb}_{0.46})_{2.28}\text{S}_{2.28}][\text{NbS}_2]$  were performed by Lafond et al. (1996, 1997); surveys are given by Makovicky and Hyde (1992) and by Wieggers and Meerschaut (1992). Slices or rods of the PbS or SnS-archetype are marked structural features of many complex sulfosalts. Often they are recombined to adapt different coordination polyhedra according to the stereochemical behavior of the individual cations. For compilations the reader is referred to Makovicky (1989, 1993), Mumme (1990), Makovicky et al. (1991, 1992), and to references therein.

Although solid solution between gold and tellurium is not likely, these two atoms paradoxically have to be assigned to one atomic position in the average structure of nagyagite. They form a square-planar net; weak interactions towards the Me1 and S1 atoms are evident (Fig. 3). Structural data on gold tellurides are rare. Approximately one dozen of naturally occurring tellurides with an essential content of gold have been described, for some of them and for a few synthetic compounds structural data are available. Extensive structural investigations were performed on sylvanite, calaverite, and krennerite by Van Tendeloo et al. (1983, 1984), Pertlik (1984a, 1984b), and Reithmayer et al. (1993), and Mössbauer measurements by Wagner et al. (1994, 1995) and Stanek (1995). The atomic arrangement in petzite is discussed by Shapur Chamid et al. (1978), that of kostovite by Van Tendeloo and Amelinckx (1986), for montbrayite a structural proposal was given by Bachechi (1971). From these investigations, an octahedral (dis-

torted toward an elongated tetragonal bipyramidal) or square planar configuration of tellurium around  $\text{Au}^{3+}$  atoms is most likely. The  $3^+$  valence state was assigned to planar fourfold-coordinated Au atoms in  $\text{AuTe}_2\text{Cl}$  and  $\text{AuTe}_2\text{I}$  (Haendler et al. 1974),  $\text{AuTeI}$  (Fenner and Mootz 1978); Au-Te bond lengths are 2.64 to 2.69 Å. Within these compounds and also within tellurides of other cations,  $[\text{Te}_2]$  dumbbells have often been found, in krennerite a triple group  $[\text{Te}_3]$  with a bond angle Te-Te-Te of  $96.3^\circ$  occurs. Native tellurium (Adenis et al. 1989) consists of infinite helices with Te-Te = 2.835 Å ( $2\times$ ) and Te-Te-Te =  $103.14^\circ$ , additional bonds are 3.491 Å ( $4\times$ ).

In the average structure of nagyagite, the Au and Te atoms are located at one crystallographic position. An order based on square planar Au (coordinated by four Te atoms) is assumed; for tellurium a contact to two Te atoms (in a cis-arrangement) and bonds to two Au atoms are most likely. The average Au-Te bond distance of  $\sim 2.7$  Å found for the nearest neighbor environment in gold tellurides and the  $\sim 2.8$  Å bond distance associated with a covalent Te-Te bond are much shorter, unbonded Te-Te contacts are longer than the average atom-atom distance of 2.97 Å within the gold-tellurium net in nagyagite. A local shift of the atoms caused by adaption of suitable coordinations seems to be responsible for the anisotropy of the displacement parameters. The largest values are in (001), the amplitudes of the displacement parameters for the X-position are 0.052, 0.036, and  $0.028 \text{ \AA}^2$ . The large displacement seems to be responsible for the obviously too small Au:Te ratio determined by the least-squares refinement of the scattering functions (Tables 1 and 4). The Te and Au atoms are centered above the “squares” formed by the Me1 and S1 atoms of the neighboring PbS-archetype layer (Fig. 3). A shift of the Au and Te atoms within (001) should favor shorter distances for Au-Te and for Te-Te in case of covalently dominated bonds; for Au-Au distances and unbonded Te-Te contacts an increase of the interatomic distances is expected. Considering the often observed tripled cell parameter  $a$  (or  $b$ ) and an ideal Au:Te ratio of 1:2, a theoretical model for an ordered arrangement can be derived (Fig. 4a). The postulated chains of Au (in square planar coordination with 4 Te) connected by trans-arranged edges are a new structural unit. This model might be verified for tessellated blocks within the nagyagite crystals. The ratio of covalent Te-Te bonds and unbonded Te-Te contacts might serve for formal charge balance. The fact that the Au:Te ratio is variable and that it can be diminished down to  $\sim 1:3$  (Table 2) gives evidence for intense faults. These results are in accordance with the Mössbauer investigations of nagyagite (Udubaşa et al. 1993; Johan et al. 1994), indicating a trivalent valence state for both Sb and Au atoms and one atomic site for the Au atoms. On the other hand it cannot safely be excluded from structural data that in parts formally monovalent Au atoms with the typical linear coordination might be accommodated by the local displacement within the planar gold-tellurium layers.

Nagyagite crystals with a doubled cell parameter  $c$  are common. In these cases broad reflection profiles did not allow the determination of the cell metrics with certainty but the angle  $\beta$  scatters around  $90^\circ$ . This behavior might be explained by multiple twinning on the plane (001) resulting in a zigzag arrangement of the average nagyagite cell in [001]; consequently orthor-



**FIGURE 4.** (a) A theoretical ordering scheme within the gold-tellurium layer for nagyagite based on the ratio Au:Te = 1:2 and considering the often observed tripled cell parameter  $a$ . The average cell of the structure model with Te and Au at one position used during the present work ( $a_{\text{nagyagite}}$  and  $b_{\text{nagyagite}}$ ) is indicated. Assuming structural analogies between nagyagite and buckhornite, the cell parameters given by Francis et al. (1992) for buckhornite ( $a_{\text{buckhornite}}$  and  $b_{\text{buckhornite}}$ ) correspond to those of a theoretical and ordered gold-tellurium layer in nagyagite. (b) Multiple twinning on (001) results in an orthorhombic symmetry for nagyagite with doubled cell parameter  $c$ .

hombic symmetry is obtained (Fig. 4b). The extremely weak bonds between the SnS-archetype and the tellurium-gold layers and the fact that  $a \sim b$  in the average cell, might enable succeeding layers in [001] to be twisted for  $90^\circ$  against each other, resulting in a local tetragonal symmetry (and a multiplied cell parameter  $c$ ). These assumptions are in accordance with the macroscopic symmetry observations of the former authors.

A remark on the crystal structure of buckhornite and on its probable structural relationship to nagyagite is relevant. Many similarities of morphology and physical properties exist. Francis et al. (1992) determined orthorhombic symmetry and cell parameters of  $a_{\text{buckhornite}} = 4.092(2) \text{ \AA} \sim a_{\text{nagyagite}}$ ,  $b_{\text{buckhornite}} = 12.245 \text{ \AA} \sim 3 \times b_{\text{nagyagite}}$ ,  $c_{\text{buckhornite}} = 9.322 \text{ \AA} = c_{\text{nagyagite}} - 5.797 \text{ \AA}$ ; the difference in  $c$  corresponds to twice the Pb-S bond distance. The chemical composition of buckhornite was given as  $\text{Au Pb}_2\text{BiTe}_2\text{S}_3$ , which can be rewritten as  $[(\text{Pb}_2\text{Bi})_{\Sigma 3}\text{S}_3] [(\text{AuTe})_{\Sigma 3}]$ ,  $Z = 2$ ; the analogous nagyagite formula for the tripled average cell is  $[(\text{Pb}_3(\text{Pb,Sb}))_{\Sigma 6}\text{S}_6][(\text{Au,Te})_3]$ ,  $Z = 2$ . This suggests that buckhornite and nagyagite can be considered as part of a homologous series (see Francis et al. 1992) and that they form stacking variants: It is assumed that in buckhornite two (Pb,Bi)S sheets form one slice of the SnS-archetype, which is intercalated between gold-tellurium layers whereas in nagyagite four (Pb,Sb)S layers form the corresponding slice with a thickness of two SnS-archetype slabs. Within the cylindrite-franckeite homologous series similarly one and two slabs of the SnS-archetype are sandwiched between pseudo-hexagonal layers (Makovicky and Hyde 1992; Lafond et al. 1996, 1997). In nagyagite, primarily the shift between the two slabs of the SnS-like structure motif is responsible for the deviation of the average unit cell from orthogonal metrics. Due to the fact that Au:Te in buckhornite is 1:2, an ordering as shown in Figure 4a might be verifiable. Furthermore, the Pb:Bi ratio of 2:1 suggests an ordered arrangement of the latter two cations. These ordering schemes agree with the cell metrics of buckhornite.

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