PLUMBIAN BAKSANITE FROM THE TYRNYAUZ W–Mo DEPOSIT, BAKSAN RIVER VALLEY, NORTHERN CAUCASUS, RUSSIAN FEDERATION

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ABSTRACT

A sample of Pb-rich baksanite was recovered in a magnetite–andradite skarn from the Tyrnyauz W–Mo deposit, in the northern Caucasus, Baksan River valley, Kabardino–Balkaria Republic, Russian Federation. The rock sample forms part of the historical mineralogical collection of the Natural History Museum of the University of Florence. Associated minerals are bismuthinite, tetradymite, joséite-A and ingodite; gangue minerals are calcite and andradite. Electron-microprobe analyses gave the chemical formula $(Bi_{4.94}Pb_{0.96})_{\Sigma5.90}(Te_{2.03}S_{3.06})$. The mineral occurs as anhedral grains up to 0.5 mm across. Plumbian baksanite is dark steel-grey, shows a black streak, and has a perfect basal cleavage. Its calculated density (for $Z = 3$) is 7.44 g/cm^3 for the empirical formula and 7.51 g/cm^3 inferred for $(Bi_5Pb)(Te_2S_3)$. The mineral is greyish white in reflected light, weakly bireflectant, nonpleochroic, faintly anisotropic in yellowish gray tints. Reflectivity values (R_{min} and R_{max} in %) are 47.2, 50.3 (471.1 nm), 47.9, 50.7 (548.3 nm), 48.2, 51.3 (586.6 nm), and 48.5, 51.4 (652.3 nm), respectively. Indexing of the X-ray powder pattern indicates trigonal symmetry, space group $P\bar{3}m1$, with a 4.251(1), c 64.19(3) Å, V 1063.4(6) Å^3. The theoretical structural model proposed for the original baksanite is confirmed, and a comparison of intensities in the X-ray-diffraction patterns of the two samples strongly indicates that the Bi–Pb and Te–S atoms are disordered at the same positions. Therefore, even if a nearly perfect stoichiometry among the elements is observed, this material is not a new species but merely a plumbian variety of baksanite.

Keywords: baksanite, Bi–Pb sulfotellurides, chemical composition, physical properties, Tyrnyauz deposit, Russia.

SOMMAIRE

Un échantillon de baksanite plombifère a été prélevé d'un skarn à magnétite–andradite du gisement à W–Mo de Tyrnyauz, dans le nord du Caucase, dans la vallée de la rivière Baksan, République de Kabardino–Balkaria, Fédération Russe. L'échantillon de skarn fait partie de la collection minéralogique historique du Musée d'Histoire Naturelle de l'Université de Florence. Sont associés à la baksanite bismuthinite, tétradymite, joséite-A et ingodite; les minéraux de la gangue sont calcite et andradite. Les analyses à la microsonde électronique ont donné la formule chimique $(Bi_{4.94}Pb_{0.96})_{\Sigma5.90}(Te_{2.03}S_{3.06})$. Le minéral se présente en grains xénomorphes jusqu'à 0.5 mm de diamètre. La baksanite plombifère est gris-acier foncé, et possède une rayure noire et un clivage parfait. Sa densité calculée avec $Z = 3$ est 7.44 g/cm^3 pour la formule empirique et 7.51 g/cm^3 en supposant la composition $(Bi_5Pb)(Te_2S_3)$. Le minéral est blanc-grisâtre en lumière réfléchie, faiblement biréflectant, non pléochroïque, et légèrement anisotrope en teintes jaunâtres. Les valeurs de réflectivité (R_{min} et R_{max} en %) sont: 47.2, 50.3 (471.1 nm), 47.9, 50.7 (548.3 nm), 48.2, 51.3 (586.6 nm), et 48.5, 51.4 (652.3 nm), respectivement. L'indexation du spectre de diffraction X (méthode des poudres) indique une symétrie trigonale, groupe spatial $P\bar{3}m1$, avec a 4.251(1), c 64.19(3) Å, V 1063.4(6) Å^3. Le modèle structural théorique proposé pour la baksanite holotype est confirmé, et la comparaison entre les intensités des spectres de diffraction X des deux échantillons montre clairement que les atomes Bi–Pb et Te–S sont désordonnés aux mêmes positions. Malgré la stoechiométrie presque parfaite observée parmi les éléments, ce matériau ne serait pas une nouvelle espèce mais simplement une variété plombifère de la baksanite.

(Traduit par la Rédaction)

Mots-clés: baksanite, sulfotellurures de Bi–Pb, composition chimique, propriétés physiques, gisement de Tyrnyauz, Russie.

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INTRODUCTION

Baksanite, ideally $Bi_6(Te_2S_3)$, is a complex sulfotelluride of bismuth that was recently described by Pekov *et al.* (1996) in a magnetite–andradite skarn from the Tyrnyauz W–Mo deposit, Baksan River valley (northern Caucasus), Kabardino–Balkaria Republic, Russian Federation. The mineral occurs in voids in aggregates of andradite, calcite, chlorite, and stilpnomelane, and contains inclusions of native gold and, rarely, intergrowths of ingodite and joséite-A. On the basis of electron-microprobe data, Pekov *et al.* (1996) obtained the chemical formula $(Bi_{5.78}Pb_{0.16}Sb_{0.02})_{\Sigma5.96}$ $(Te_{1.77}S_{3.27})$ and classed the mineral as a new member of the tetradymite group (II/D. 10–70, Strunz & Nickel 2001). They described the mineral as trigonal, space group $P\bar{3}m1$, with a 4.249(2), c 62.82(5) Å, V 982(1) Å³.

In the course of a research project dealing with the characterization of telluride minerals in the historical mineralogical collection of the Natural History Museum of the University of Florence, we discovered a sample of Pb-rich baksanite in a magnetite–andradite skarn from the type locality (catalogue number 2383/I, labeled tetradymite). Associated minerals are bismuthinite, tetradymite, joséite-A and ingodite; gangue minerals are calcite and andradite. The mineral occurs as anhedral grains up to 0.5 mm across, closely associated with bismuthinite (Fig. 1).

The major purpose of our investigation is to provide optical and physical properties, reflectivity, chemical and X-ray data for the plumbian variety of baksanite and to test the theoretical structural model proposed for the original baksanite.

OCCURRENCE

The tungsten and molybdenum mining and beneficiation complex in the Northern Caucasus was the former Soviet Union's largest producer of tungsten from tungsten skarns (0.14% WO_3), with an original annual capacity of 42,000 t of tungsten concentrate. At the Tyrnyauz deposit, mining began in 1940, and surface mining was stopped in 1995. Only underground mining of the deepest and richest deposits (with an average WO_3 content of 0.19%) remained profitable in the second half of the 1990s. The main ore minerals, molybdian scheelite, scheelite and molybdenite, crystallized during the acid-leaching and deposition stages of the hydrothermal–metasomatic process. The physicochemical conditions of deposition of molybdian scheelite, scheelite and molybdenite and the relevant assemblages were studied as a function of the concentration of metal and alkali chlorides, activity of sulfur and oxygen, acidity–alkalinity and temperature of ore-bearing solutions by Rekharskii *et al.* (1997).

PHYSICAL PROPERTIES

Plumbian baksanite is dark steel-grey in color and shows a black streak. The mineral is opaque with a metallic luster. It has a perfect {0001} cleavage, whereas the fracture is uneven. As in other members of the tetradymite group (Bayliss 1991, Clarke 1997, Spiridonov *et al.* 1989), some fragments of baksanite exhibit a platy to flaky morphology (Fig. 2). The dominant form is {0001}, and twinning is not observed. The calculated density of this mineral (for $Z = 3$) is 7.44 g/cm³ for $(Bi_{4.94}Pb_{0.96})_{\Sigma5.90}(Te_{2.03}S_{3.06})$ and 7.51 g/cm³ for
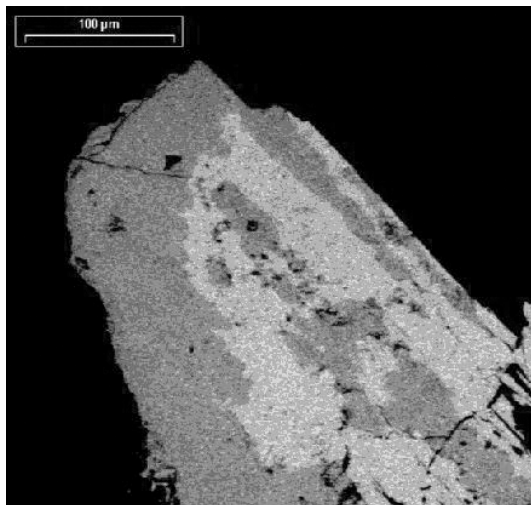

FIG. 1. Back-scattered electron microphotograph showing the relations between plumbian baksanite (white grey) and bismuthinite (dark grey). Scale bar is indicated.

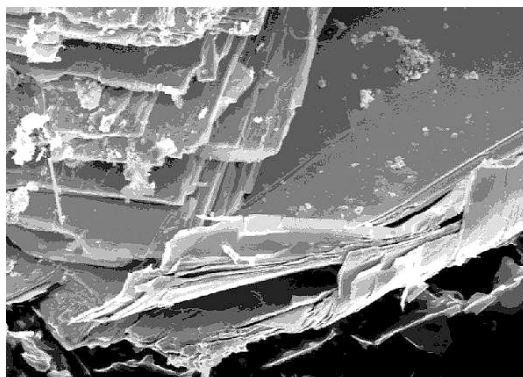FIG. 2. Secondary electron photograph showing the platy morphology of plumbian baksanite. Width of field of view: 375μm.

the expected $(Bi_5Pb)(Te_2S_3)$. Unfortunately, density could not be measured because of the small grain-size. The micro-indentation measurements carried out with a VHN load of 15 g gave a mean value of 65 kg/mm^2 (range: 63–66), corresponding to a Mohs hardness of about 1½ to 2.

OPTICAL PROPERTIES

In reflected light, plumbian baksanite is greyish white, weakly bireflectant, nonpleochroic, faintly anisotropic in yellowish grey tints. Internal reflections are absent. No evidence of growth zonation is observed.

Reflectance measurements were performed in air by means of a MPM–200 Zeiss microphotometer equipped with a MSP–20 system processor on a Zeiss Axioplan ore microscope. Filament temperature was approximately 3350 K. An interference filter was adjusted, in turn, to select four wavelengths for measurement (471.1, 548.3, 586.6, and 652.3 nm). Readings were taken for specimen and standard (SiC) maintained under the same focus conditions. The diameter of the circular measuring area was 0.1 mm. Measurements of reflectivity (in %) for R_{min} and R_{max} are 47.2, 50.3 (471.1 nm), 47.9, 50.7 (548.3 nm), 48.2, 51.3 (586.6 nm), and 48.5, 51.4 (652.3 nm), respectively. These data are consistent with the visual impression of very low bireflectance.

As evident from Figure 3, the reflectance percentages obtained for plumbian baksanite are consistent with the values measured by Pekov *et al.* (1996) for type baksanite. The Pb enrichment in the sample studied here accounts for the slightly lower values of reflectivity observed.
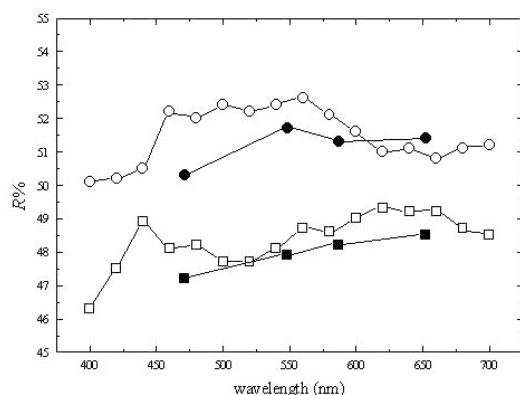

FIG. 3. Reflectivity curves for baksanite samples in air. Open symbols refer to holotype baksanite (Pekov *et al.* 1996), filled symbols refer to plumbian baksanite (this study). Circles and squares refer to R_{max} and R_{min} values, respectively.

CHEMICAL COMPOSITION

Two fragments of plumbian baksanite were analyzed with a JEOL JXA–8600 electron microprobe. Concentrations of the major and minor elements were determined at an accelerating voltage of 20 kV and a beam current of 40 nA, with variable counting times: 30 s were used for Pb, Bi, Te and S, and 60 s for the minor elements Fe, Sb, As, Cu, Au, and Ag. For the wavelength-dispersion analyses, the following lines were used: Pb$M\alpha$, Sb$L\alpha$, Au$M\alpha$, Te$L\alpha$, S$K\alpha$, Fe$K\alpha$, As$L\alpha$, Cu$K\alpha$, Bi$M\beta$, Ag$L\alpha$. We employed the following standards: galena (Pb, S), pure gold (Au), pure silver (Ag), synthetic GaAs (As), pure copper (Cu), marcasite (Fe), synthetic Sb_2Te_3 (Sb, Te), and pure bismuth (Bi). The fragments were found to be homogeneous within the analytical error. The average chemical composition (15 analyses on different spots on each fragment), together with ranges of wt. % of elements, is reported in Table 1. On the basis of 11 atoms, the formula of plumbian baksanite is $(Bi_{4.94}Pb_{0.96})_{\Sigma5.90}(Te_{2.03}S_{3.06})$, close to $(Bi_5Pb)(Te_2S_3)$.

X-RAY CRYSTALLOGRAPHY

For our single-crystal investigation of the structure, we checked several fragments by Weissenberg and precession film techniques and with a Nonius CAD4 four-circle diffractometer. All the crystals gave extremely broad X-ray-diffraction profiles, even if their optical behavior suggested an adequate quality; a powder-diffraction study thus was the only possible method of X-ray investigation.

Selected grains were characterized by powder XRD methods using a Philips diffractometer with Cu$K\alpha$ radiation. In Table 2, we report the X-ray-diffraction pattern for plumbian baksanite, together with that reported by Pekov *et al.* (1996) for the type specimen. All reflections were indexed and unit-cell parameters were refined by means of least-squares methods: a 4.251(1), c 64.19(3) Å, V 1063.4(6) Å^3, space group $P\bar{3}m1$. Apart

TABLE 1. COMPOSITION* (MEANS, RANGES AND STANDARD DEVIATIONS) OF PLUMBIAN BAKSANITE, TYRNYAUZ W–Mo DEPOSIT

Pb wt.%	12.47	12.22 – 12.85	0.30
Au	0.02	0.01 – 0.03	0.01
Ag	0.03	0.02 – 0.03	0.02
As	0.02	0.02 – 0.04	0.02
Cu	0.00	0.00 – 0.01	0.01
Fe	0.01	0.01 – 0.02	0.01
Sb	0.00	0.00 – 0.01	0.01
Bi	64.71	64.44 – 64.88	0.30
Te	16.24	16.12 – 16.39	0.20
S	6.15	6.12 – 6.18	0.10
total	99.65		

* Electron-microprobe data.

from some slight differences in the intensities of the reflections, the patterns are quite similar. The a parameter is close to that observed for baksanite, 4.249(2) Å (Pekov *et al.* 1996), and it is in the range observed in the tetradymite-group minerals (4.13–4.45 Å, Strunz & Nickel 2001). The c parameter is larger than that observed for baksanite [62.82(5) Å, Pekov *et al.* 1996] owing to the greater size of Pb with respect to Bi.

By means of a calculation of the theoretical X-ray pattern and subsequent comparison with the experimental one, Pekov *et al.* (1996) found a structural model for baksanite consisting of 33 alternating closest-packed layers of disordered (Bi,Pb,Sb) and (Te,S,Se), respectively. This model can easily be described as an alternation of modules (Fig. 4) of an ingodite-type structure [$Bi_2(S,Te)$, a 4.25, c 23.22 Å, $P\bar{3}m1$, structural model consisting of 12 layers (two slabs in Fig. 4); Zav'yalov & Begizov (1981)] and of a joséite-A-type structure [Bi_4TeS_2, a 4.25, c 39.77 Å, $R\bar{3}m$, structural model consisting of 21 layers (three slabs in Fig. 4); Zav'yalov & Begizov (1983)]. By considering the unit-cell parameters, indeed, the following polysomatic relationship can be easily drawn: $c_{bak} = c_{ing} + c_{jos} = 62.99$ Å. This value is in excellent agreement with both the c parameter determined by Pekov *et al.* (1996) and that refined in this study. In addition, the chemical formula of baksanite can be easily obtained by the scheme: ingodite $Bi_2(S,Te)$ + joséite-A Bi_4TeS_2 = baksanite $Bi_6(Te_2S_3)$. Chemical analyses of the ingodite and joséite-A that are associated with the plumbian baksanite yielded the following formulae (means of five analyses): $(Bi_{1.78}Pb_{0.32})(S_{1.01}Te_{0.95})$ (ingodite), $(Bi_{3.64}Pb_{0.40})(Te_{0.91}S_{1.94})$ (joséite-A), thus indicating a Pb-rich environment of formation for the baksanite studied here.

CONCLUDING REMARKS

The XRD study carried out on the plumbian baksanite confirms the structural model and the modular approach proposed by Pekov *et al.* (1996) for type baksanite. Furthermore, the close similarity in the intensities of the X-ray-diffraction pattern between the two samples strongly suggests that the Bi–Pb and Te–S atoms are disordered at the same positions. Therefore, even though a nearly perfect stoichiometry among the metal atoms is observed, it does not appear possible to consider this material as a new species but only as a plumbian variety of baksanite.

Discussion on charge balance, degree of metallic bonding in the mineral and degree of order in the structure must await the availability of suitable crystals, although the soft platy nature of the mineral makes it unlikely that they will easily be found.

TABLE 2. CALCULATED AND OBSERVED X-RAY POWDER-DIFFRACTION DATA FOR BAKSANITE

h k l	1			2		
	I	d_{meas}	d_{calc}	I	d_{meas}	d_{calc}
0 0 5	6	12.8	12.84	4	12.3	12.56
0 0 11	18	5.83	5.835	14	5.65	5.71
0 0 14	35	4.59	4.585	46	4.50	4.49
1 0 0	5	3.68	3.681	3	3.68	3.681
1 0 3	8	3.63	3.628	10	3.63	3.625
1 0 4	25	3.59	3.588	22	3.58	3.584
1 0 5	19	3.54	3.538	15	3.53	3.532
0 0 19	27	3.38	3.378	20	3.30	3.305
0 1 11	100	3.115	3.113	100	3.09	3.094
1 0 22	30	2.287	2.287	38	2.255	2.256
1 1 0	20	2.124	2.125	25	2.126	2.125
0 1 25	4	2.107	2.106	2	2.083	2.075
0 1 27	4	1.998	1.997	2	1.965	1.966
1 1 14	-	-	-	5	1.921	1.920
0 0 33	4	1.946	1.945	4	1.903	1.903
1 1 15	3	1.905	1.903	4	1.893	1.895
0 2 5	1	1.821	1.822	1	1.822	1.821
1 1 19	3	1.798	1.799	1	1.789	1.788
2 0 11	9	1.756	1.755	12	1.755	1.752
1 1 24	8	1.664	1.664	6	1.649	1.650
0 2 22	14	1.556	1.557	12	1.547	1.547
2 0 25	1	1.497	1.496	2	1.485	1.485
1 1 33	5	1.434	1.435	6	1.416	1.418
1 2 11	10	1.352	1.353	12	1.351	1.352
1 2 17	2	1.306	1.306	1	1.301	1.301
2 1 22	7	1.255	1.256	5	1.250	1.251
3 0 0	12	1.228	1.227	10	1.225	1.226

Note: 1: observed and calculated powder pattern and indexing for plumbian baksanite (this study). 2: observed and calculated powder pattern and indexing reported by Pekov *et al.* (1996).
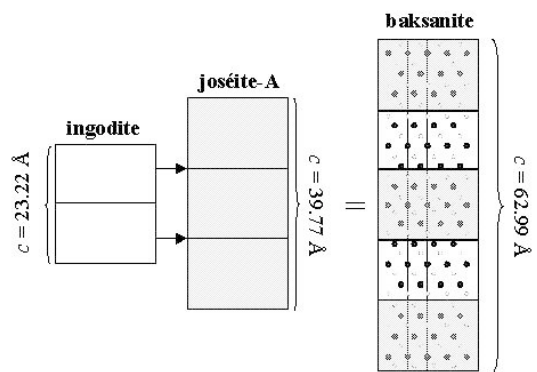

FIG. 4. Theoretical structure of baksanite projected on (11$\bar{2}$0) plane (after Pekov *et al.* 1996). White and black circles refer to (Bi,Pb) and (Te,S) atoms, respectively. The polysomatic relationships with ingodite and joséite-A are outlined by the intercalation of light and shaded blocks.

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