

RARE SULFOSALTS FROM VULCANO, AEOLIAN ISLANDS, ITALY. II. MOZGOVAITE, $\text{PbBi}_4(\text{S,Se})_7$, A NEW MINERAL SPECIES

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ABSTRACT

Mozgovaite, a new mineral species, occurs as a high-temperature fumarole encrustation at La Fossa crater on Vulcano, Aeolian Islands, Italy. Associated minerals are bismuthinite, galenobismutite, cannizzarite and lillianite. The mineral occurs as tiny slender prismatic crystals, up to 0.2 mm long and 0.02 mm across. The color is silvery grey, with a metallic luster. Bireflectance is weak, and pleochroism is absent. Anisotropism is rather strong, but without color effects. The measured microhardness, VHN_{10} , is 116. Electron-microprobe investigations of type mozgovaite gave Pb 13.90, Cd 0.26, Fe 0.02, Cu 0.01, Bi 64.79, As 0.05, S 16.91, Se 1.63, sum 97.57 wt %. The empirical formula, based on 12 atoms, is $(\text{Pb}_{0.87}\text{Cd}_{0.03})_{\Sigma 0.90}(\text{Bi}_{4.01}\text{As}_{0.01})_{\Sigma 4.02}(\text{S}_{6.82}\text{Se}_{0.27})_{\Sigma 7.09}$; the idealized formula is $\text{PbBi}_4(\text{S,Se})_7$. The strongest six lines of the powder-diffraction pattern [d in Å(hkl)] are: 3.80(10)(280), 2.95(4B)(321), 2.34(4B)(0.16.0), 3.30(3)(400), 3.58(3)(141), and 3.40(2)(151). The unit-cell parameters of mozgovaite are: a 13.18(6), b 37.4(2), c 4.05(3) Å, $Z = 6$, space group $Bbmm$, $D_{\text{calc}} = 6.26(6)$ g/cm³. The mineral is named after Nadezhda Nikolaevna Mozgova, specialist of the mineralogy of ore assemblages (IGEM, Academy of Sciences, Moscow).

Keywords: mozgovaite, Pb–Bi sulfosalts, synthetic phase V, sublimates, fumaroles, Vulcano, Italy.

SOMMAIRE

La mozgovaïte, nouvelle espèce minérale, est le résultat d'activité fumerollienne à haute température dans le cratère de La Fossa, sur l'île de Vulcano, dans l'archipel des îles Eoliennes, en Italie. Lui sont associées bismuthinite, galénobismutite, cannizzarite et lillianite. Les cristaux sont très petits, prismatiques et très allongés, atteignant 0.2 mm en longueur et 0.02 mm en largeur. Ils ont une couleur gris argent, avec éclat métallique. La biréflectance est faible, et il n'y a aucun pléochroïsme. L'anisotropisme est plutôt forte, mais sans effets sur la couleur. La microdureté, VHN_{10} , est égale à 116. Les analyses à la microsonde électronique de la mozgovaïte-type ont donné Pb 13.90, Cd 0.26, Fe 0.02, Cu 0.01, Bi 64.79, As 0.05, S 16.91, Se 1.63, total 97.57% (poids). La formule empirique, fondée sur une base de 12 atomes, est $(\text{Pb}_{0.87}\text{Cd}_{0.03})_{\Sigma 0.90}(\text{Bi}_{4.01}\text{As}_{0.01})_{\Sigma 4.02}(\text{S}_{6.82}\text{Se}_{0.27})_{\Sigma 7.09}$; la formule idéale est $\text{PbBi}_4(\text{S,Se})_7$. Les six raies les plus intenses du spectre de diffraction X, méthode des poudres [d en Å(hkl)] sont: 3.80(10)(280), 2.95(4 floue)(321), 2.34(4 floue)(0.16.0), 3.30(3)(400), 3.58(3)(141), et 3.40(2)(151). Les paramètres réticulaires de la mozgovaïte sont: a 13.18(6), b 37.4(2), c 4.05(3) Å, $Z = 6$, groupe spatial $Bbmm$, $D_{\text{calc}} = 6.26(6)$ g/cm³. Le nom honore Nadezhda Nikolaevna Mozgova, spécialiste de la minéralogie des minerais affiliée à l'IGEM, Académie des Sciences, Moscou.

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Mots-clés: mozgovaïte, sulfosels Pb–Bi, phase synthétique V, sublimés, fumerolles, Vulcano, Italie.

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INTRODUCTION

The recurrence in 1990 of an episode of high-temperature fumarolic activity at the La Fossa crater of Vulcano, one of the Aeolian islands, in southern Italy, led to a systematic mineralogical investigation of the sublimates and fumarolic encrustations (Garavelli 1994, Garavelli & Vurro 1994, Garavelli *et al.* 1997). Of particular interest is the natural deposition of Pb–Bi sulfosalts, already documented in an earlier episode of high-temperature activity from some of the same vents about eighty years ago by Zambonini *et al.* (1924). We report here on a new mineral species, mozgovaite, ideally PbBi_4S_7 , and review previous findings in the synthetic system Pb–Bi–S.

Mozgovaite is considered an extremely rare species in the fumarolic encrustations. The holotype specimen consists of some slender acicular crystals, usually about 100 μm in length. Only two other such sprays of crystals have been found so far.

The new mineral is named after Dr. Nadezhda Nikolaevna Mozgova (b. 1931), mineralogist of IGEM, Academy of Sciences, Moscow, Russia, in recognition of her important contributions to the knowledge of ore mineralogy and, particularly, sulfosalt minerals. Both the mineral and the mineral name have been approved by the Commission on New Minerals and Mineral Names of the IMA (No. 98–060). The holotype is deposited in the mineralogical museum of the University of Bari (No. 5/nm).

MODE OF OCCURRENCE

Vulcano (Fig. 1) is the southernmost of the seven islands constituting the Aeolian archipelago in the southern Tyrrhenian sea, on the northern continental slope of Sicily. Together with Stromboli, it is the only active volcanic center of the Aeolian island arc. Presently, the volcanic activity is limited to fumarole emissions, mainly located around the northern rim of the

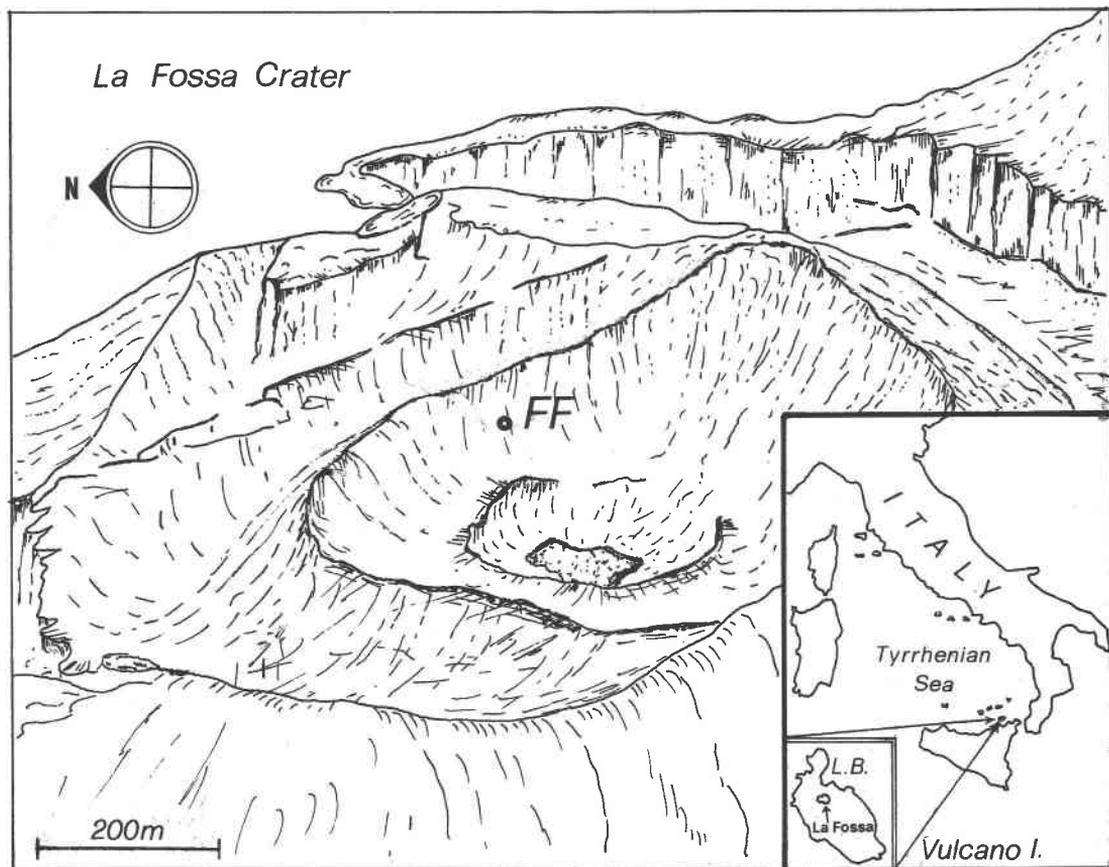


FIG. 1. Location of the La Fossa crater and sampling site at Vulcano (fumarole FF), Aeolian Islands, Italy.

crater (Fig. 1). The geological setting and description of fumaroles were given previously (Garavelli *et al.* 1997, Borodaev *et al.* 1998).

The fumarole activity at the crater has shown great and relatively rapid changes with time; for example, the temperature of emission rose from 200°C in 1913 to 615°C in 1923 (Sicardi 1956). After this peak value, the temperatures remained below 400°C. From 1987 onward, an increase in the flow rate of fumarolic vents and significant variations in the chemical and isotopic composition of discharged fluids were recorded. In particular, the maximum temperature of fumaroles, measured in the inner north slope of the La Fossa crater, increased from 334°C in 1987 to 689°C in 1992, and 695°C in 1993. Since then, the fumarole temperatures decreased, and now they are again below 400°C.

Since the beginning of the present thermal event, mineral assemblages evolved strongly with the increasing temperature of fumaroles and the chemical content of the discharging fluids. In 1987 (T_{\max} about 330°C), sulfur, sal ammoniac and sassolite were the only minerals deposited in the fumaroles of the La Fossa cone. In 1990 ($T_{\max} > 600^\circ\text{C}$), in the hottest fumaroles (situated along a fissure directed E–W on the inner north slope of the crater), a new assemblage of Pb–Bi sulfides and sulfosalts (galena, cannizzarite, wittite, galenobismutite, bismuthinite, lillianite, heyrovskyite and kirkiite) began to deposit massively again (Garavelli & Vurro 1994, Borodaev *et al.* 1998), and their deposition is still continuing.

The mozgovaite holotype consists of a sample collected in 1993 from fumarole FF ($T = 607^\circ\text{C}$) at the La Fossa cone. In addition, another sample of mozgovaite, collected from fumarole FF in 1990 ($T = 607^\circ\text{C}$), and a third sample from the MNHM (Paris), collected during the thermal culmination at the La Fossa crater from 1921 to 1925 (Zambonini *et al.* 1924), also are described.



FIG. 2. The homogeneous grains of mozgovaite in reflected light microscopy. Polished section; the main sheaf of crystals is 165 μm in length. The black matrix is epoxy. The black spots on the crystal are the trace of microhardness indenter.

MORPHOLOGY AND PHYSICAL PROPERTIES

The holotype of mozgovaite consists of four very tiny acicular crystals associated with bismuthinite (dominant), galenobismutite, cannizzarite and lillianite. The crystals are silvery grey with a metallic luster. In polished section, mozgovaite occurs as tiny prismatic crystals, up to 0.2 mm long and only 0.02 mm across; in some cases, rectangular sections are observed (Fig. 2). Physical properties were measured on the largest crystal of the holotype material (Fig. 2).

In the MNHN sample, one polished section showed three platy, striated whiskers of mozgovaite; the largest of those measures $600 \times 25 \mu\text{m}$. These three crystals are associated with 15 fibers of bismuthinite and six of galenobismutite, and one lamella of cannizzarite.

Under reflected light, mozgovaite is white. Bireflectance is very weak, and pleochroism is absent. Anisotropism is rather strong, but without color effects. No internal reflections are present.

Reflectance was measured in air from 420 to 700 nm on randomly oriented grains using an automatic polarization microspectrophotometer unit MSFU-312L (LOMO, Saint Petersburg), with Si as standard and a 20×0.40 objective. The results for the two extreme R_1 and R_2 curves encountered are given in Table 1, with the spectral curves in Figure 3. These curves, slightly decreasing, are very close to those obtained for R_a and R_b of bismuthinite by Vendrell-Saz & Nogues-Carulla (1978, in "Quantitative Data File" of Criddle & Stanley 1993), whereas galenobismutite, the closest Pb–Bi sulfosalt, presents higher values of reflectance, but with a lower bireflectance (Criddle & Stanley 1993).

The microhardness VHN_{10} of mozgovaite, measured on the holotype with an indentation-hardness tester PMT-3M, is 116.

CHEMICAL DATA

Four electron-microprobe analyses were obtained of the holotype material (Table 2). This is the only sample of mozgovaite for which chemical, X-ray data and

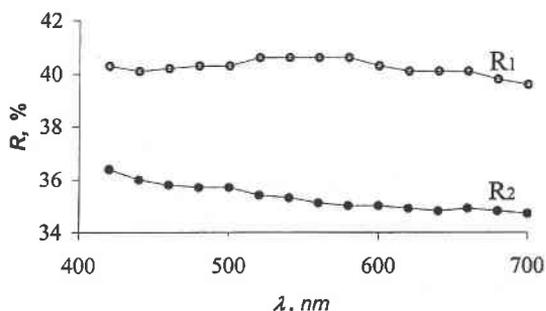


FIG. 3. Reflectance spectra of mozgovaite in air.

TABLE 1. REFLECTANCE DATA FOR MOZGOVAITE FROM VULCANO, ITALY*

nm	R ₁	R ₂	nm	R ₁	R ₂
420	40.3	36.4	580	40.6	35.0
440	40.1	36.0	600	40.3	35.0
460	40.2	35.8	620	40.1	34.9
480	40.3	35.7	640	40.1	34.8
500	40.3	35.7	660	40.1	34.9
520	40.6	35.4	680	39.8	34.8
540	40.6	35.3	700	39.6	34.7
560	40.6	35.1			

* Standard: Si. The reflectance data are expressed in %.

physical properties are available. In the same table, the chemical composition of additional samples of mozgovaite collected at Vulcano in 1923 and 1990 also is given (anal. 6 and 7, respectively); for these samples no X-ray data are available.

Three analyses of type material (anal. 1–3) were obtained with a CAMEBAX SX-50 electron microprobe (Moscow State University) under the following conditions: voltage 20 kV, beam current 30 nA, standards (element, emission line): PbS (PbM α , SK α), Bi and Cd metals (BiM α and CdL α), GaAs (AsL α), and ZnSe (SeL α). The fourth analysis on the holotype (anal. 4) as well as the analysis on the 1990 sample (anal. 7) were obtained with a ARL-SEM-Q95 electron microprobe (Centro Studi Geominerari e Mineralurgici, CNR, Cagliari): voltage 20 kV, beam current 20 nA, standards: PbS (PbM α , SK α), Bi₂S₃ (BiM α , SK α), CdS (CdL α), FeAs₂ (AsL α), ZnS (ZnK α), Cu₂S (CuK α), and metallic selenium (SeL α). The analytical data in row 5 of Table 2 represent the average composition of holotype mozgovaite. Composition 6 is an average of the results obtained on the three crystals of the NMHN sample with a CAMECA microprobe, CAMEBAX type (BRGM – CNRS – University Common Laboratory, Orléans): voltage 15 kV, beam current 20 nA, standards: pyrite (FeK α and SK α), PbSe (PbM α and SeL α), Bi (BiM α), and CdS (CdL α).

The data obtained show that the main elements of mozgovaite are Pb, Bi, S and Se (the latter ranging from 0.64 to 2.23 wt%). Some samples contain minor Cd (0.42–2.01 wt%), As (0.20 wt%), Cu (0.16 wt%), Fe (0.70 wt%) and Zn (0.18 wt%). The proportion of the main elements varies noticeably, but all the analytical results are rather close to the theoretical composition PbBi₄S₇. In terms of mol% MeS (with Me representing the sum of metals), the composition of mozgovaite samples ranges from 30 to 38 mol% MeS.

Calculation of the analytical results obtained on the basis of 12 atoms, summing all the metals with Pb, As with Bi and Se with S, gave a formula close to PbBi₄(S,Se)₇, which may be considered as the ideal chemical formula of mozgovaite. The empirical chemical formula, calculated on the average result of four elec-

TABLE 2. CHEMICAL COMPOSITION OF MOZGOVAITE

No.	Pb	Cu	Cd	Fe	Zn	Bi	As	S	Se	Total
1	13.31	-	0.62	-	-	64.32	-	16.77	1.96	96.98
2	14.04	-	0.42	-	-	64.35	-	17.03	2.23	98.11
3	13.96	0.05	-	0.08	-	65.74	-	16.87	0.36	97.06
4	14.27	-	-	-	-	64.73	0.20	16.97	1.98	98.15
5	13.90	0.01	0.26	0.02	-	64.79	0.05	16.91	1.63	97.57
6	13.53	-	2.01	0.70	-	65.00	-	17.06	1.91	100.22
7	18.00	0.16	-	-	0.18	64.62	-	17.42	0.64	101.06
8	16.35	-	-	-	-	65.95	-	17.70	-	100.00

Formulae calculated on the basis of 12 atoms

1	(Pb _{0.83} Cd _{0.07}) _{20.90} Bi _{3.99} (S _{6.78} Se _{0.32}) _{7.10}
2	(Pb _{0.87} Cd _{0.03}) _{20.92} Bi _{3.99} (S _{6.79} Se _{0.30}) _{7.15}
3	(Pb _{0.88} Fe _{0.02} Cu _{0.01}) _{20.91} Bi _{4.13} (S _{6.90} Se _{0.06}) _{7.06}
4	Pb _{0.88} (Bi _{3.97} As _{0.03}) _{24.00} (S _{6.79} Se _{0.32}) _{7.11}
5	(Pb _{0.87} Cd _{0.03}) _{20.90} (Bi _{4.01} As _{0.01}) _{24.02} (S _{6.82} Se _{0.27}) _{7.09}
6	(Pb _{0.81} Cd _{0.22} Fe _{0.16} Zn _{0.17}) _{21.17} Bi _{3.89} (S _{6.79} Se _{0.30}) _{7.15}
7	(Pb _{1.09} Cu _{0.03} Zn _{0.03}) _{21.15} Bi _{3.89} (S _{6.84} Se _{0.10}) _{7.04}
8	PbBi ₄ S ₇

1–5: compositions of holotype (1993 samples from fumarole FF); 1–3: Camebax SX-50 electron microprobe; 4: ARL-SEM-Q95 electron microprobe; 5: average composition of holotype material; 6: average composition derived from three analyses of the sample from the Museum National d'Histoire Naturelle, Paris, no. 126-146, collected at Vulcano in 1923 (Zambonini *et al.* 1925); Camebax electron microprobe; 7: Sample collected in 1990 from fumarole FF, ARL-SEM-Q95 electron microprobe; 8: theoretical composition, PbBi₄S₇.

tron-microprobe analyses of type mozgovaite, is (Pb_{0.87}Cd_{0.03})_{20.90}(Bi_{4.01}As_{0.01})_{24.02}(S_{6.82}Se_{0.27})_{7.09}.

REVIEW OF COMPOSITIONAL INFORMATION ON RELATED PHASES IN THE SYSTEM Pb–Bi–S

In the system Pb–Bi–S, synthetic phases with a composition close to the ideal chemical formula of mozgovaite, PbBi₄S₇, were obtained by various authors. We will consider below the main results of these experimental investigations.

Craig (1967) was the first to recognize the existence of a synthetic phase, designated as phase V, stable from 680° to 730°C, with a composition close to PbBi₄S₇ (~35 mol% PbS). Soon thereafter, Otto & Strunz (1968), on the basis of structural investigations of the products of their syntheses in the system PbS–Bi₂S₃, showed that phase V consists of compounds of different symmetries, some of them monoclinic, the others orthorhombic, but they gave no information on their compositions. Salanci & Moh (1969) showed that phase V has an extensive range of compositions. Considering the substitution Pb→Bi in the structure of PbS, they gave for phase V the general formula Pb_{1-x}Bi_{2x/3}S•2Bi₂S₃ (0 ≤ x ≤ 0.266), i.e., PbBi₄S₇ for x = 0.

Salanci & Moh (1969) noted also that PbS-rich and Bi₂S₃ rich-samples differ in the X-ray powder patterns, and suggested that phase V consists of more than one compound. This finding was confirmed in the synthesis of Takéuchi and co-workers (1974, 1979), Sugaki *et al.* (1974) and Tilley & Wright (1986).

Takéuchi *et al.* (1974, 1979) designated as V-1 the monoclinic Bi-rich variety of phase V, as V-2 the orthorhombic Pb-rich member, and as V-3 the orthorhombic intermediate. These phases have in common $a \approx 13.3$ Å and $c \approx 4.03$ Å, but differ in b periodicities. Phases V-1, V-2 and V-3 thus constitute a homologous series of compounds derived through the mechanism of trochochemical cell-twinning (Takéuchi *et al.* 1979, Takéuchi 1997), and related to pavonite and lillianite their structures (Makovicky 1981). The structures of these three compounds consist of two kinds of slabs built of octahedra, and differ in the sequences of twins.

Two new ordered sequences of twins, phases V-4 and V-5, as well as regular intergrowths of different phases (V-2 with V-3, V-3 with V-4), have been observed using transmission electron microscopy (TEM) (Colaïtis *et al.* 1981). Many other sequences and disordered materials have been described in rapidly quenched samples using high-resolution transmission electron microscopy (HRTEM) (Tilley & Wright 1986).

The compositional range of phase V as given by various authors varies quite importantly. In their experimental study of the system Pb-Bi-S, Salanci & Moh (1969) obtained the compositional field for the phase V from ~34 mol% PbS up to ~26 mol% PbS. Sugaki *et al.* (1974) reported that the synthetic phase V that they obtained in their experiments has compositions ranging from ~35 mol% PbS to ~31 mol% PbS. According to data calculated by Takéuchi (1997) on the basis of crystal-chemical considerations, the spectrum of chemical composition for phase V ranges from ~33 mol% PbS for the Bi-rich end member (subphase V-1) to ~40 mol% PbS for the Pb-rich end member (subphase V-2).

X-RAY POWDER-DIFFRACTION DATA

X-ray powder-diffraction data for the holotype of mozgovaite were obtained using a Gandolfi camera (diameter 57.3 mm) with unfiltered Fe-radiation (β -lines were filtered out by calculation) on material extracted from the polished section after electron-microprobe analysis (anal. 1 in Table 2). The data obtained are given in Table 3, and compared with those published for synthetic phases. In general, the X-ray powder-diffraction data for mozgovaite are in agreement with those for synthetic phases. In particular, the reflections of the mineral under consideration correspond to the strong reflections of the synthetic phases. The fewer reflections obtained for mozgovaite may be explained by its less perfect order, its nonstoichiometric nature, the presence of some additional elements, and the limits of the Gandolfi technique. In any case, the strongest reflection, corresponding to a d value of 3.80 Å, may be used as a first diagnostic indicator of this mineral.

The cell parameters of mozgovaite, calculated from the X-ray powder data according to the indexing of Sugaki *et al.* (1974), are: a 13.18(6), b 37.4(2), c 4.05(3)

Å. They agree with the reported data for synthetic orthorhombic phase V-2 (space group *Bbmm*, $Z = 6$): a 13.3, b 36.8, c 4.03 Å (Takéuchi *et al.* 1974), and refined by Tilley & Wright (1986): a 13.278, b 36.768, c 4.034 Å.

Unfortunately the small quantity of material does not allow us to carry out any single-crystal X-ray study.

On the basis of the cell parameters obtained, and considering $Z = 6$ for the given formula, the calculated density for mozgovaite is 6.26(6) g/cm³.

DISCUSSION

Relationships of mozgovaite with synthetic phases

On the basis of the chemical and X-ray data, we consider mozgovaite to be closely related to synthetic phase V. The empirical chemical formula calculated on the basis of electron-microprobe data is $(\text{Pb}_{0.87}\text{Cd}_{0.03})_{\Sigma 0.90}(\text{Bi}_{4.01}\text{As}_{0.01})_{\Sigma 4.02}(\text{S}_{6.82}\text{Se}_{0.27})_{\Sigma 7.09}$, which corresponds to ~31 mol% PbS. This composition is in the field of the synthetic phase V obtained by Salanci & Moh (1969) and Sugaki *et al.* (1974) in their experimental work.

The presence in the system Cd-Bi-S of some compounds structurally related to the synthetic phase V (Coe *et al.* 1997) explains also the presence of small amounts of cadmium in most of the mozgovaite samples, presumably as a consequence of structural incorporation.

X-ray powder-diffraction data obtained for mozgovaite are in agreement with the main reflections of the synthetic phase V (Table 3). The unit-cell parameters of mozgovaite, calculated on the basis of the indexing given by Sugaki *et al.* (1974) for the phase $\text{Pb}_{1.07}\text{Bi}_{3.96}\text{S}_7$, agree with those reported by various authors for the subphase V-2 (Sugaki *et al.* 1974, Tilley & Wright 1986). However, the X-ray powder data available in literature resemble each other and do not permit a definitive identification of mozgovaite with a particular subphase. To define the true structure of mozgovaite, it will be necessary to carry out a single-crystal study, but unfortunately the dimensions of the crystals available do not permit such investigations.

Like the synthetic homologue, mozgovaite forms at a high temperature, as confirmed by the value of 607°C directly measured in the fumarole where the type mozgovaite was found. Moreover, it is not excluded that the quick cooling of the sample may give rise to crystals departing from the fully ordered structure, and thus consisting of a disordered intergrowth of variously ordered areas. It is not excluded that the range occupied by synthetic phase V consists of many very similar chemical and structural compounds that commonly are disordered, especially in samples rapidly quenched from the melt (Tilley & Wright 1986). This feature is typical of nonstoichiometric compounds and may explain some differences in the X-ray-diffraction spectra of mozgovaite and synthetic phase V.

TABLE 3. X-RAY POWDER-DIFFRACTION DATA FOR MOZGOVAITE AND SYNTHETIC COMPOUNDS IN THE REGION OF PHASE V

I				II		III		IV		V	
d_{obs}	I/I_0	hkl	d_{cal}	d_{obs}	I/I_0	d_{obs}	I/I_0	d_{obs}	I/I_0	d_{obs}	I/I_0
				6.15	20	6.099	W	6.044	W	5.783	W
				4.96	12	4.911	M	5.002	W	5.070	VW
										4.974	W
				3.87	10	3.861	W	3.857	W	3.846	M
										3.827	M
3.80	10	280	3.81	3.79	100	3.816	W	3.796	VS	3.783	M
			3.79			3.768	VS	3.746	W	3.766	M
3.67	0.5	131	3.70	3.69	18	3.682	M	3.675	W		
								3.601	W		
3.58	3	141	3.58	3.57	6			3.526	W	3.563	M
				3.46	8			3.456	M		
3.40	2	151	3.44	3.43	10	3.419	M	3.434	W		
								3.399	W		
								3.338	M	3.323	M
3.30	3	400	3.29	3.314	25	3.308	S	3.317	M	3.307	M
				3.278	13	3.267	M	3.244	W		
3.11	2	430	3.18	3.210	3	3.190	W	3.195	W	3.194	VW
				2.986	35	2.979	W	3.008	W		
						2.967	M	2.975	M	2.968	S
2.95	4B	321	2.94	2.954	20	2.942	M	2.945	VW		
2.92	2	331	2.90	2.908	8	2.893	M	2.920	W	2.926	M
				2.842	4	2.832	W	2.867	W	2.837	VW
2.81	2	191	2.83	2.816	6	2.799	W			2.823	M
			2.80								
2.75	0.5	351	2.77	2.773	25	2.758	S	2.766	W	2.725	M
				2.690	5	2.678	W	2.717	VW		
				2.469	3					2.561	W
				2.442	18	2.435	W	2.421	W	2.415	VW
										2.404	W
										2.387	W
2.34	4B	0.16.0	2.34	2.303	50	2.291	W			2.317	W
				2.233	3						
				2.232	3					2.232	M
2.19	0.5B	531	2.18	2.175	15	2.178	W	2.172	W	2.147	M
				2.157	7	2.167	W	2.157	W		
				2.121	7	2.111	W	2.115	S		
				2.086	10	2.082	M				
2.04	1	571	2.04	2.050	7			2.073	M	2.043	M
				2.024	17	2.021	S	2.009	W	2.014	M
										2.005	W
				1.998	20	1.987	M	1.987	W	1.999	W
				1.973							
				1.968						1.968	M
						1.946	M			1.945	M
1.917	2B					1.895	W	1.931	W		
1.892	1					1.884	W	1.886	W		
1.862	1										
1.826	0.5										
1.795	0.5					1.782	S	1.773	S	1.783	M
1.767	1									1.777	M
										1.731	W
						1.725	M	1.715	M	1.720	M

- I. Mozgovaite, type material from Vulcano. B: broad. Indexed on the basis of an orthorhombic cell (Sugaki *et al.* 1974). Calculated unit-cell parameters: a 13.18(6), b 37.4(2), c 4.05(3) Å.
- II. Synthetic $Pb_{1.07}Bi_{3.98}S_7$: a 13.27, b 36.84, c 4.04 Å (Sugaki *et al.* 1974).
- III. Synthetic phase V-2 (Tilley & Wright 1986): a 13.278, b 36.768, c 4.034 Å.
- IV. Synthetic phase V-3 (Tilley & Wright 1986): a 13.366, b 59.542, c 4.060 Å.
- V. Synthetic phase V-1 (Tilley & Wright 1986): a 13.461, b 12.371, c 4.028 Å, γ 99.19°.

Comparison of mozgovaite with other natural Bi-rich lead sulfosalts

A sulfosalts with composition very close to that of mozgovaite was first described by Zambonini *et al.* (1924) from a fumarolic condensate at La Fossa crater, and named cannizzarite. Further investigations of "cannizzarite" samples from different museums showed them to be a mixture of bismuthinite with Pb–Bi sulfosalts. Cannizzarite was redefined as a new compound with a composite unit-cell (Graham *et al.* 1953), but with an undefined chemical composition. Matzat (1979) resolved the complex, incommensurate crystal-structure of cannizzarite, and proposed a formula close to $Pb_{46}Bi_{54}S_{127}$; this formula was refined later through electron-microprobe analysis (Mozgova *et al.* 1985, 1989). In any case, the sulfosalts actually named cannizzarite has a Pb/Bi ratio considerably higher than stoichiometric $PbBi_4S_7$.

Another occurrence of a natural sulfosalts with a composition close to $PbBi_4S_7$ was reported by Kostov (1958) from scheelite-bearing quartz veins from the metamorphic complex in the central Rhodope Mountains near Narechenski Bani, Bulgaria (Breskovska *et al.* 1986). For this mineral, the name bonchevite was proposed. As for cannizzarite, the history of investigation of bonchevite is very complicated (Kupčik *et al.* 1969, Godovikov 1972), and some characteristics ascribed to bonchevite, among which its X-ray powder pattern, were later attributed to other sulfosalts (*i.e.*, pekoite, according to Birch & Mumme 1985).

In any case, the X-ray powder diagram of bonchevite is quite different from that of synthetic phase V, and consequently bonchevite was not considered the natural analogue of phase V (Otto & Strunz 1968, Sugaki *et al.* 1974). Similarly, the X-ray data of mozgovaite, the natural analogue of phase V, and bonchevite are clearly distinct.

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