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THE CRYSTAL STRUCTURE OF LENINGRADITE, $PbCu_3(VO_4)_2Cl_2$

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ABSTRACT

The crystal structure of leningradite, $PbCu_3(VO_4)_2Cl_2$, a mineral from the fumaroles of the Great fissure Tolbachik eruption, located in the Kamchatka Peninsula, Russia, has been solved by direct methods from single-crystal X-ray-diffraction data and refined to $R_1 = 0.047$ for 1235 unique reflections with $|F_o| \geq 4\sigma_F$. The mineral is orthorhombic, space group *Ibam*, *a* 9.005(7), *b* 11.046(9), *c* 9.349(7) Å, *V* 929.9(13) Å^3, $Z = 4$. The structure contains one symmetrically unique Pb position coordinated by four O and four Cl atoms. The V^{5+} cation is tetrahedrally coordinated by four O atoms. There are two symmetrically independent Cu sites in distorted octahedral [4O + 2Cl] coordination. The structure can be described in terms of fundamental chains consisting of corner-sharing CuO_4 squares and VO_4 tetrahedra. The chains are parallel to the *c* axis and are linked into a three-dimensional framework with elliptical channels occupied by the Pb^{2+} cations and Cl^- anions.

Keywords: leningradite, lead copper vanadate chloride, crystal structure, Kamchatka Peninsula, Russia.

SOMMAIRE

Nous avons résolu par méthodes directes la structure cristalline de la léningradite, $PbCu_3(VO_4)_2Cl_2$, minéral découvert dans les fumerolles de l'éruption fissurale du volcan Tolbachik, Péninsule de Kamchatka, en Russie, à partir de données en diffraction X obtenues sur monocristal et affinées jusqu'à un résidu R_1 de 0.047 en utilisant 1235 réflexions uniques pour lesquelles $|F_o| \geq 4\sigma_F$. Il s'agit d'un minéral orthorhombique, groupe spatial *Ibam*, *a* 9.005(7), *b* 11.046(9), *c* 9.349(7) Å, *V* 929.9(13) Å^3, $Z = 4$. La structure contient un atome de Pb en position symétriquement unique, coordonné par quatre atomes d'oxygène et quatre de chlor. Le cation V^{5+} possède une coordinence tétraédrique avec quatre atomes d'oxygène. Il y a deux positions symétriquement indépendantes de Cu en coordinence octaédrique difforme [4O + 2Cl]. On peut décrire la structure en termes de chaînes fondamentales de carrés CuO_4 à coins partagés et de tétraèdres VO_4. Les chaînes sont parallèles à l'axe *c* et sont interconnectées pour former une trame tri-dimensionnelle ayant des canaux elliptiques où logent les cations Pb^{2+} et les anions Cl^-.

(Traduit par la Rédaction)

Mots-clés: léningradite, vanadate chloruré de plomb et de cuivre, structure cristalline, péninsule de Kamchatka, Russie.

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Introduction

Leningradite, $PbCu_3(VO_4)_2Cl_2$, is a rare lead–copper vanadate chloride first described by Vergasova *et al.* (1990) from fumaroles of the Great fissure Tolbachik eruption (GFTE) in the Kamchatka Peninsula, Russia (Fedotov 1984). Crystals of the mineral less than 0.3 mm across occur in fumarole incrustations. Leningradite was found in close association with anglesite, hematite, P-bearing lammerite, $Cu_3[(As,P)O_4]_2$ (Filatov *et al.* 1984), and tolbachite, $CuCl_2$ (Vergasova & Filatov 1983). The mineral was named in honor of the city of Leningrad, where many studies of Tolbachik minerals have been undertaken since 1978. Though the city name was changed back to Saint Petersburg, the mineral name remains intact.

Our aim in this paper is to report results of the first determination of the structure of leningradite.

Experimental

The crystal of leningradite selected for data collection was mounted on a Bruker three-circle CCD- based X-ray diffractometer operated at 50 kV and 40 mA. More than a hemisphere of three-dimensional data was collected using monochromatic Mo$K\alpha$ X-radiation, with frame widths of 0.3° in ω, and with a 40 s count for each frame. The unit-cell parameters (Table 1) were refined using least-squares techniques. The unit-cell parameters determined are in good agreement with those reported previously (Vergasova *et al.* 1990). The intensity data were integrated and corrected for Lorentz, polarization, and background effects using the Bruker program Saint. A semi-empirical absorption-correction was made using 686 intense reflections. The crystal was modeled as an (100) plate, and reflections with plate-glancing angle of less than 3° were discarded from the dataset, which lowered the $R_{azimuthal}$ from 11.9 to 3.5%.

The Bruker Shelxtl Version 5 system of programs was used for determination and refinement of the crystal structure. The structure was solved by direct methods and refined to an R_1 value of 0.025, calculated for the 538 unique observed ($|F_o| \geq 4\sigma_F$) reflections. Final coordinates and displacement parameters of the atoms are given in Table 2, selected interatomic distances are in Table 3. Table 4 provides a bond-valence analysis calculated using bond-valence parameters taken from Krivovichev & Brown (2001) for the Pb^{2+}–O bonds and from Brese & O'Keeffe (1991) for other bonds. Note the low bond-valence sum for the Cl site (0.55 valence units), which is typical of anhydrous Cl-containing minerals of fumarolic origin. Calculated and observed structure-factors are available from the Depository of Unpublished Data on the MAC website [document Leningradite CM45_445].

TABLE 1. CRYSTALLOGRAPHIC DATA AND REFINEMENT PARAMETERS FOR LENINGRADITE

a (Å)	9.005(7)	Space group	*Ibam*
b (Å)	11.046(9)	F_{000}	1252
c (Å)	9.349(7)	Z	4
V (Å^3)	929.9(13)	Crystal size (mm)	0.10 × 0.06 × 0.01
Radiation	Mo$K\alpha$	μ cm^{-1}	27.295
Total reflections	1586	Maximum 2θ (°)	55.89
Unique reflections	538	R_1	0.0246
Unique $\|F_o\| \geq 4\sigma_F$	412	wR_2	0.0359
GoF	0.515	S	0.515

Note: $R_1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$; $S = \{\Sigma[w(F_o^2 - F_c^2)]/(n - p)\}^{1/2}$, where n is the number of reflections, and p is the number of refined parameters.

Results

Cation coordination

The structure of leningradite contains one symmetrically unique Pb position, located on a twofold axis. The Pb atom is coordinated by four O atoms and four Cl^- anions (Fig. 1). The coordination of the Pb^{2+} cation is rather symmetrical, which is not typical for Pb oxide chlorides (Krivovichev & Burns 2001, 2002, Pasero & Vacchiano 2000, Keller *et al.* 2001).

TABLE 2. COORDINATES AND DISPLACEMENT PARAMETERS (Å) OF ATOMS IN LENINGRADITE

Atom	x	y	z	U_{eq}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pb	½	0	¼	0.210(2)	0.0262(3)	0.0153(3)	0.0215(4)	0	0	0
Cu(1)	0	0	0	0.0142(4)	0.0176(7)	0.0146(8)	0.0104(8)	0	0	-0.0050(6)
Cu(2)	0.25095(12)	0.32837(10)	0	0.0128(3)	0.0089(5)	0.0198(6)	0.0096(5)	0	0	0.0035(4)
V	½	0.29546(14)	¼	0.0073(3)	0.0072(6)	0.0093(8)	0.0054(7)	0	0.0005(5)	0
Cl	0.3116(2)	0.0834(2)	0	0.0210(5)	0.0208(10)	0.0183(11)	0.0238(12)	0	0	0.0029(10)
O(1)	0.0981(4)	0.1107(4)	0.1354(4)	0.0126(9)	0.0123(19)	0.013(2)	0.013(2)	0.0021(17)	-0.0022(16)	-0.0034(18)
O(2)	0.3871(4)	0.2015(4)	0.1565(4)	0.0141(9)	0.017(2)	0.015(2)	0.011(2)	-0.0009(18)	-0.0032(17)	-0.0005(18)

The Cu(1) and Cu(2) sites are coordinated by four O^{2-} anions at the vertices of planar squares and two apical Cl^- anions, so that elongate $[CuO_4Cl_2]$ octahedra are formed (Fig. 1). Similar coordinations are typical for the mixed-ligand Cu^{2+} coordination polyhedra and have been observed, for example, at the Cu(1) site in allochalcoselite (Krivovichev *et al*. 2006), the Cu(2) site in georgbokiite (Krivovichev *et al*. 1999) and the Cu(5) site in chloromenite (Krivovichev *et al*. 1998). The octahedral $[CuO_4Cl_2]$ coordinations are distorted owing to the Jahn–Teller effect (Jahn & Teller 1937, Burns & Hawthorne 1995a, b).

There is one symmetrically independent V^{5+} cation in the structure, which is coordinated by four O atoms. The configuration and geometry of the VO_4 tetrahedron are characteristic of the structures of vanadates.

Description of the structure

The structure of leningradite is shown in Figure 2a. It can be described in terms of fundamental chains consisting of $Cu^{2+}O_4$ squares and $V^{5+}O_4$ tetrahedra. The chains are parallel to the *c* axis and are of two types. The first chain, C', is formed by the $Cu(1)O_4$ squares and VO_4 tetrahedra, whereas the second, C'', consists of the $Cu(2)O_4$ squares and VO_4 tetrahedra. The chains are arranged in such a way that a three-dimensional copper vanadate framework is formed (Fig. 2b). The framework has large elliptical channels occupied by the Pb^{2+} cations and Cl^- anions.

Discussion

The structure of leningradite provides another example of a fumarolic mineral based upon a three-dimensional metal oxide framework (copper vanadate in leningradite) with channels occupied by metal chloride species ($PbCl_2$ in leningradite). In a similar way, the structure of allochalcoselite, $Cu^+Cu^{2+}{}_5PbO_2(SeO_3)_2Cl_5$, consists of porous metal oxide layers with large cavities occupied by the $[Cu^+Cl_2]^-$ anions (Krivovichev *et al*. 2006). This "host–guest" character of some of fumarolic minerals may be the result of their formation from volcanic gases. The metal oxide species tend to organize in such a structure that allows inclusion of metal chloride species into a basic oxide matrix. It is noteworthy that in leningradite, interactions of Pb^{2+} and Cl^- ions are much stronger than the Cu^{2+}–Cl^- interactions, which are rather weak in comparison to the Cu^{2+}–O^{2-} bonds.

TABLE 3. SELECTED BOND-LENGTHS (Å) IN THE STRUCTURE OF LENINGRADITE

Pb – O(2)	2.599(4) ×4	Cu(2) – O(2)	1.948(4) ×2
Pb – Cl	3.032(2) ×4	Cu(2) – O(1)	1.976(4) ×2
		Cu(2) – Cl	2.760(3)
Cu(1) – O(1)	1.970(4) ×4	Cu(2) – Cl	2.873(3)
Cu(1) – Cl	2.953(3) ×2		
		V – O(2)	1.696(4) ×2
		V – O(1)	1.733(4) ×2

TABLE 4. BOND-VALENCE VALUES* FOR LENINGRADITE

	Pb	Cu(1)	Cu(2)	V	$\Sigma_i a$
Cl	$0.26^{4\times}$	$0.08^{2\times}$	0.12+0.09		0.55
O(1)		$0.45^{4\times}$	$0.45^{2\times}$	$1.19^{2\times}$	2.09
O(2)	$0.27^{4\times}$		$0.49^{2\times}$	$1.32^{2\times}$	2.08
$\Sigma_i c$	2.12	1.96	2.07	5.02	

* Expressed in valence units (*vu*).

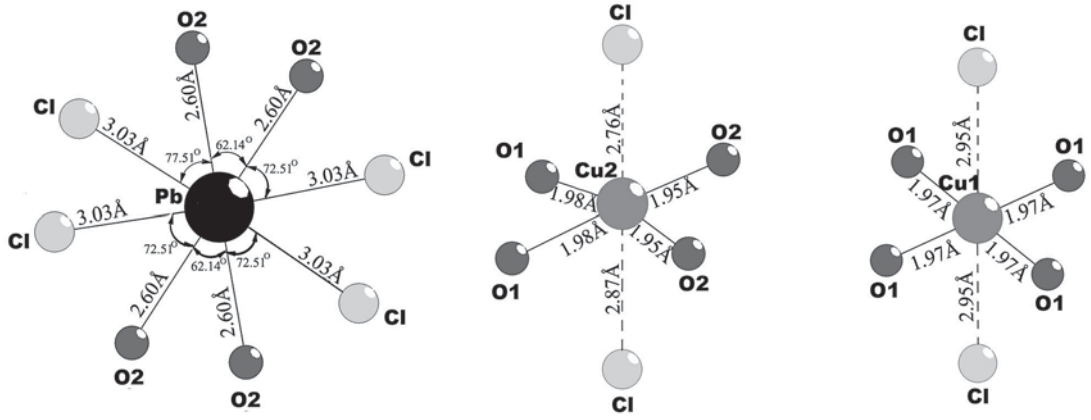

FIG. 1. Coordination of cations in the structure of leningradite.

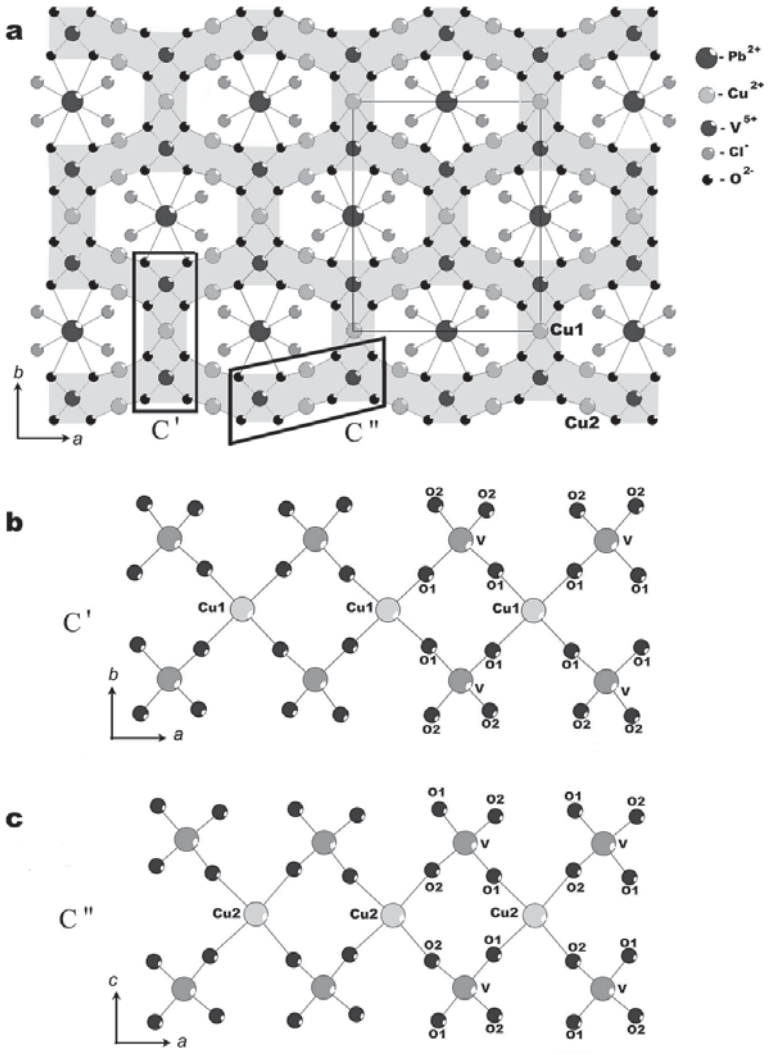

FIG. 2. The crystal structure of leningradite projected along the *c* axis. The three-dimensional metal oxide framework consisting of CuO_4 squares and VO_4 tetrahedra is highlighted; sections of the C' and C'' chains are shown (a). C' (b) and C'' (c) chains of CuO_4 squares and VO_4 tetrahedra are projected along the *c* and *b* axes, respectively.

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