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STRUCTURE OF INORGANIC COMPOUNDS

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Crystal Structure of Zdenekite NaPbCu₅(AsO₄)₄Cl · 5H₂O

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Received April 11, 2003

Abstract—The crystal structure of the mineral zdenekite NaPbCu₅(AsO₄)₄Cl · 5H₂O was established (Bruker SMART CCD diffractometer, synchrotron radiation, $\lambda = 0.6843$ Å, R = 0.096 for 1356 reflections). Single-crystal X-ray diffraction study demonstrated that zdenekite belongs to the monoclinic system with the unit-cell parameters a = 10.023(7) Å, b = 19.55(1) Å, c = 10.023(6) Å, $\beta = 90.02(1)^\circ$, sp. gr. $P2_1/n$, Z = 4. The structure consists of polyhedral layers parallel to the (010) plane. These layers are formed by Cuq₅ polyhedra ($\phi = 0$, Cl, H₂O) and AsO₄ tetrahedra. Distorted Na octahedra and Pb 7-vertex polyhedra and H₂O molecules coordinated to these metal atoms are located between the layers. © 2003 MAIK "Nauka/Interperiodica".

INTRODUCTION

The mineral zdenekite NaPbCu₅(AsO₄)₄Cl \cdot 5H₂O was discovered in the northern region of the Cap Garrone copper-lead mine (France). Two-thirds of this mineral consists of secondary minerals (generally, copper arsenates) [1]. More than a hundred new mineral species were first discovered in this mine. The preliminary single-crystal X-ray diffraction study of zdenekite on a precession X-ray camera (Burger method) revealed that this mineral belongs to the tetragonal system with the unit-cell parameters a = 10.066(1) Å, c =39.39(4) Å, V = 3991.41(4) Å³, Z = 8 and indicated the possible space groups $P4_122$ or $P4_322$. It was suggested that zdenekite is a tetragonal Pb-containing analogue of orthorhombic lavendulan NaCaCu₅(AsO₄)₄Cl · 5H₂O discovered in 1837 [2]. Until recently, the structure of lavendulan remained unknown. Although eight years elapsed after the discovery of zdenekite, all attempts to establish its structure failed, because X-ray diffraction patterns from its thin platelike single crystals, which are easily cleaved, were of poor quality. New possibilities of X-ray diffraction experiments associated with the use of synchrotron radiation stimulated the X-ray diffraction study of the structure of zdenekite. Here, we present the results of this investigation.

EXPERIMENTAL

X-ray diffraction data were collected from a zdenekite single crystal $0.06 \times 0.04 \times 0.01$ mm³ in size. Since it was impossible to use a standard X-ray diffractometer for collecting experimental data for zdenekite because of the small sizes and flattened shape of its crystals, the experimental set of intensities was obtained on an automated Bruker AXS SMART CCD diffractometer using synchrotron radiation ($\lambda = 0.6883$ Å) at the Daresbury Synchrotron Radiation Source Station 9.8 (UK) [3]. A total of 3068 reflections were collected in a hemisphere of reciprocal space using the ω -scan technique [4]. Based on the results of processing X-ray diffraction data, it was concluded that the crystals most likely belong to the monoclinic system (averaging of equivalent reflections yielded $R_{int} \sim 0.05$, whereas averaging within the tetragonal system gave $R_{int} \sim 0.20$), in which the unit-cell parameter b is halved. The main characteristics of the crystal and the details of X-ray-diffraction experiment are listed in Table 1. The systematic absences in the three-dimensional X-ray-diffraction data set indicate the sp. gr. $P2_1/n$. The structure was solved directly using the SHELX97 software package [5]. Simultaneously, several possible space groups were tested. The most adequate model was obtained within the sp. gr. $P2_1/n$, which confirms the validity of its choice based on systematic absences of corresponding reflections. Analysis of the model obtained and the residual electron-density map, which contained a large

Formula	$NaPbCu_5(AsO_4)_4Cl \cdot 5H_2O$
Unit-cell parameters, Å	$a = 10.023(7), b = 19.55(1), c = 10.023(6), \beta = 90.02(1)^{\circ}$
Space group; Z	$P2_{1}/n; 4$
Unit-cell volume V, $Å^3$	1964.6
Calculated density ρ , g/cm ³	4.16
Measured density ρ , g/cm ³ *	4.08
Absorption coefficient μ , mm ⁻¹	20.80
Molecular weight	1229.1
F_{000}	2260
Diffractometer	Bruker AXS SMART CCD
Radiation; wavelength, Å	Synchroton radiation; 0.6843
Total number of reflections	3068
Number of reflections used in the final stage of the least-squares procedure	1356
Software package for structure solution by direct methods	SHELX97
Software package for structure refinement	JANA2000
Number of parameters in refinement	130
R _{hkl}	0.096
$\Delta \rho_{max}$, e/Å ³	3.18
$\Delta \rho_{\rm min}$, e/Å ³	-2.63

 Table 1. Main crystallographic characteristics and experimental data

* The measured density is given according to [1].

number of peaks in the vicinity of atomic positions, provided evidence for crystal twinning. The crystal structure of zdenekite was further refined using the JANA2000 program [6]. The weight coefficients of individual components, which were refined using the twin matrices [001/010/100], $[001/010/\overline{1}00]$, and $[1 \ 0 \ 0 \ / \ 0 \ 1 \ 0 \ / \ 0 \ 0 \ \overline{1}]$, are 0.30(1), 0.166(6), 0.172(6), and 0.365(7). The positions of water molecules were revealed from the difference electron-density map. The model was refined with isotropic thermal parameters, except for the lead atoms, which were refined with anisotropic thermal parameters. The thin platelike shape of the crystal hindered the application of the absorption correction. This fact, together with the poor quality of X-ray diffraction data (all reflections had diffusion tails) and a complex system of twinning, led to negative isotropic atomic thermal displacements for a number of oxygen atoms and water molecules. The coordinates of two oxygen atoms (O(15) and O(16)) and three water molecules (W(1), W(3), and W(5)), which were revealed from the residual electrondensity map, were fixed in the course of refinement. The noted reasons also led to deviations of a number of As–O distances from standard values, with the result that the positions of five oxygen atoms (O(2), O(7)), O(9), $O(\overline{11})$, and O(12)) were somewhat shifted relative to their positions in the difference electron-density map, and these positions were also fixed in the final stage of structure refinement. The average As-O dis-

tances in four nonequivalent AsO_4 tetrahedra (1.77, 1.65, 1.78, and 1.69 Å) are close to the standard values.

The coordinates and atomic thermal displacements for the cations and Cl atoms are given in Table 2. The figures were drawn with the use of the ATOMS program [7].

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The structure of zdenekite is shown in Figs. 1 and 2. It consists of heteropolyhedral layers parallel to the (010) plane. These layers are formed by $Cu\phi_5$ 5-vertex polyhedra ($\phi = O$, Cl, H₂O) and AsO₄ tetrahedra (Fig. 1). In these layers, one can distinguish clusters consisting of four edge-sharing Cuq₅ 5-vertex polyhedra linked by AsO₄ tetrahedra. In the clusters, four $Cu\phi_5$ 5-vertex polyhedra (distorted tetragonal pyramids) share a vertex occupied by the Cl atom. In all $Cu\phi_5$ 5-vertex polyhedra, the Cu–Cl distance exceeds the Cu-O distances (the average Cu-O distance and the Cu–Cl distance for four $Cu\phi_5$ 5-vertex polyhedra are 1.96 and 2.76 Å, respectively). The AsO₄ tetrahedra are linked to each cluster of four $Cu\phi_5$ 5-vertex polyhedra (four tetrahedra below and four tetrahedra above). Each tetrahedron shares two vertices with two $Cu\phi_5$ 5-vertex polyhedra of one cluster and one vertex with a $Cu\phi_5$ 5-vertex polyhedron from the adjacent cluster. The

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fourth vertex of each AsO₄ tetrahedron is linked to the fifth Cu ϕ_5 5-vertex polyhedron, which does not belong to clusters. Like the four 5-vertex polyhedra considered above, the latter copper polyhedron is also a 5-vertex polyhedron and also represents a distorted tetragonal pyramid. However, the latter copper atom is coordinated (along with four oxygen atoms) by the water molecule rather than Cl atom. The water molecule is oriented toward the interlayer space. The average Cu–O distance in this 5-vertex polyhedron is 1.93 Å. The Cu–H₂O distance is elongated to 2.26(5) Å. All the oxygen atoms in this tetragonal pyramid are located in its base and simultaneously serve as vertices of the AsO₄ tetrahedra.

According to [8], the Cu²⁺ ϕ_5 tetragonal pyramids differ in the displacement of the copper atom with respect to the square base. This displacement can be characterized by the O–Cu–O angles formed by the O atoms located in the bases of the pyramids. With regard to these values, the fifth CuO₄H₂O 5-vertex polyhedron is somewhat different from the other four CuO₄Cl 5-vertex polyhedra, because the O–Cu–O angles in the former 5-vertex polyhedron are closer to 180°. This circumstance allows us to consider the copper atom in this 5-vertex polyhedron as located virtually in the plane of the square base.

Potassium atoms are located in distorted octahedra and lead atoms are located in 7-vertex polyhedra (the average Na-O and Pb-O distances are 2.35 and 2.52 Å, respectively). These polyhedra and the water molecules coordinated to these metal atoms are located in the interlayer space (Fig. 2). It should be noted that each layer in the zdenekite structure can be described within the tetragonal symmetry with the sp. gr. P4, which is consistent with the preliminary data on this mineral obtained by the photographic method [1]. However, the adjacent polyhedral layers are shifted upon their rotation about the twofold screw axis relative to each other. which leads to lowering of the zdenekite symmetry to monoclinic. The structural formula of zdenekite is in complete agreement with its idealized composition reported previously [1].

The correctness of the proposed structural model is additionally supported by the calculations of the valence balance for anions (Table 3). The deviations of the interatomic distances from standard values did not allow us to calculate the local valence balance. However, the formal valence balance for the O^{2-} anions seems to be quite reasonable. The exception is the Cl⁻ anion, which forms elongated bonds with four surrounding copper atoms. The latter circumstance must be taken into account to correctly estimate the valence balance. This is why the formal valence balance for the chloride anion is overestimated, and this value is not given in Table 3.

The formation of mixed layers consisting of $[Cu\phi_5]$ tetragonal pyramids and $[AsO_4]$ tetrahedra in the struc-

Table 2. Coordinates of the basis atoms and thermal displacements for the cations and Cl⁻ anion in the crystal structure of zdenekite

Atom	x	У	z	U _{iso}
Pb	0.362(1)	0.5891(4)	0.2160(9)	0.050(2)*
As(1)	0.152(2)	0.8361(6)	0.919(1)	0.007(3)
As(2)	0.148(3)	0.8473(9)	0.503(2)	0.050(5)
As(3)	0.066(1)	0.6598(7)	0.424(1)	0.006(3)
As(4)	0.060(1)	0.6641(7)	0.010(1)	0.009(4)
Cu(1)	0.128(1)	0.7151(5)	0.714(1)	0.001(3)
Cu(2)	-0.138(2)	0.7838(7)	0.989(1)	0.010(4)
Cu(3)	0.081(2)	0.794(1)	0.207(2)	0.035(6)
Cu(4)	0.364(2)	0.7094(8)	0.946(1)	0.017(4)
Cu(5)	-0.143(3)	0.5931(5)	0.215(2)	0.027(3)
Na	-0.135(7)	0.604(2)	0.707(6)	0.027(9)
Cl	0.634(5)	0.367(1)	0.289(4)	0.026(5)
O(1)	0.235(4)	0.671(2)	0.372(5)	0.001
O(2)	0.271	0.164	0.460	0.001
O(3)	0.541(3)	0.854(2)	0.096(3)	0.001
O(4)	-0.013(5)	0.739(3)	0.375(5)	0.001
O(5)	-0.022(3)	0.826(2)	0.901(4)	0.001
O(6)	0.014(4)	0.657(2)	0.834(4)	0.001
O(7)	0.820	0.160	0.918	0.001
O(8)	0.211(4)	0.770(2)	0.580(5)	0.001
O(9)	0.780	0.241	0.148	0.001
O(10)	0.235(5)	0.909(2)	0.563(5)	0.001
O(11)	0.820	0.157	0.660	0.001
O(12)	0.502	0.090	0.430	0.001
O(13)	0.002(4)	0.863(3)	0.537(5)	0.001
O(14)	0.204(6)	0.916(3)	0.828(6)	0.001
O(15)	-0.008	0.723	0.081	0.001
O(16)	-0.044	0.597	0.364	0.001
W (1)	0.206	0.504	0.148	0.001
W(2)	-0.172(5)	0.479(3)	0.233(8)	0.001
<i>W</i> (3)	-0.142	0.538	0.558	0.001
W(4)	0.035(8)	0.994(4)	0.657(7)	0.001
W(5)	0.390	0.522	0.412	0.001

* The parameter U_{iso} for the Pb atom was calculated based on anisotropic thermal displacements.

ture of zdenekite corresponds to a Cu/As ratio of 1.25 [9]. Mixed layers consisting of Cu polyhedra and As tetrahedra were found in a large group of minerals, among which are pushcharovskite CuAsO₃(OH) \cdot 1.5H₂O [10], geminite Cu(AsO₃OH) \cdot H₂O [11], yvonite Cu(AsO₃OH) \cdot 2H₂O [12], and fluckite CaMn(AsO₃OH)₂ \cdot 2H₂O [13]. The largest distance between the adjacent mixed layers



Fig. 1. Polyhedral layer in the structure of zdenekite projected onto the (010) plane [7]. The copper polyhedra and AsO_4 tetrahedra are dark-gray and light-gray, respectively. The Pb and Na atoms are represented by large gray and black circles, respectively. The water molecules are indicated by small gray circles.



Fig. 2. Crystal structure of zdenekite projected along the [001] direction. For notations, see Fig. 1.

(10.90 Å) was found in pushcharovskite, whereas these distances in the other aforementioned minerals are in the range 7.613–7.822 Å. Like in pushcharovskite, the polyhedral layers and interlayer spaces are rather bulky in the structure of zdenekite. Hence, the distances between these layers are rather large (~9.78 Å).

Until recently, none of the representatives of the lavendulan group have been structurally studied. In addition to the parent mineral lavendulan, this group includes zdenekite and sampleite NaCaCu₅(PO₄)₄Cl · $5H_2O$. As in the case of lavendulan, the orthorhombic symmetry has been suggested initially for sampleite.

	Na	Pb	As(1)	As(2)	As(3)	As(4)	Cu(1)	Cu(2)	Cu(3)	Cu(4)	Cu(5)	Σ
O(1)		0.29			1.25			0.40				1.94
O(2)		0.29				1.25				0.40		1.94
O(3)	0.17				1.25		0.40		1			1.82
O(4)					1.25				0.40	0.40		2.05
O(5)		0.29	1.25					0.40				1.94
O(6)	0.17					1.25	0.40					1.82
O(7)	0.17		1.25						0.40			1.82
O(8)				1.25			0.40	0.40				2.05
O(9)			1.25				0.40			0.40		2.05
O(10)				1.25							0.40	1.65
O (11)	0.17			1.25					0.40			1.82
O(12)						1.25					0.40	1.65
O(13)		0.29		1.25						0.40		1.94
O(14)			1.25								0.40	1.65
O(15)						1.25		0.40	0.40			2.05
O(16)					1.25						0.40	1.65
W (1)	0.17	0.29										0.46
W(2)											0.40	0.40
<i>W</i> (3)	0.17											0.17
<i>W</i> (4)		0.29										0.29
W(5)		0.29										0.29

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Table 3. Formal valence balance for the anions in the structure of zdenekite

However, in the course of studying zdenekite, it was discovered that the crystal structures of lavendulan and one of the forms of sampleite also belong to the monoclinic system with the sp. gr. $P2_1/n$ and have structures similar to that of zdenekite (unpublished data by G. Giester, P. Williams, and U. Kolitsch). In addition, according to the data of these researchers, another polymorph of sampleite exists, whose structure was established within the sp. gr. $P2_1/c$. Correspondingly, the latter structure is characterized by another alternation of the polyhedral layers. The "tails" of diffraction reflections of zdenekite extended along the [010] direction are indicative of possible violation of the alternation of the polyhedral layers in the zdenekite structure, which suggests that this mineral is characterized by a more complex polytypism.

ACKNOWLEDGMENTS

We are grateful to G. Giester, P. Williams, and U. Kolitsch for providing us with the unpublished data on the structures of lavendulan and sampleite.

This study was supported by the Russian Foundation for Basic Research (project no. 03-05-64054) and the program "Universities of Russia."

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Translated by T. Safonova