ISSN 1063-7745, *Crystallography Reports, 2007, Vol. 52, No. 2, pp. 199–202. © Pleiades Publishing, Inc., 2007.*
Original Russian Text © N.V. Zubkova, D.Yu. Pushcharovskiĭ, M. Pasero, N.V. Chukanov, S. Merlino, 2007, published in Kristallografiya, 2007, Vol. 52, No. 2, pp. 223–226.

STRUCTURE OF INORGANIC COMPOUNDS

Crystal Structure of Phosphorus-Rich Ellenbergerite

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Received July 6, 2006

Abstract—The phosphorus-rich variety of ellenbergerite $(Mg_{0.61}Ti_{0.08}\square_{0.31})_2(Mg_{0.52}Al_{0.43}\square_{0.05})_{12}[SiO_3(O_{0.29}(OH)_{0.71})]_6[(P_{0.71}Si_{0.20}\square_{0.09})O_3OH]_2(OH)_6$ was studied by X-ray diffraction and IR spectroscopy. The structure was refined in sp. gr. $P6_3mc$ to $R = 0.0248$. The structure of phosphorus-rich ellenbergerite retains the octahedral framework observed in the structures of ellenbergerite, phosphoellenbergerite, ekatite, and a series of structurally related synthetic compounds. The structure of phosphorus-rich ellenbergerite differs from the structure of ellenbergerite primarily in that the Mg and Al cations in the phosphorus-rich variety are disordered in the octahedra of the framework, thereby leading to higher symmetry, and the channels of triangular cross section are occupied predominantly by P tetrahedra.

PACS numbers: 61.10.Nz, 61.66.Fn

DOI: 10.1134/S1063774507020058

INTRODUCTION

In recent years, the group of minerals structurally similar to borosilicate dumortierite $(Al,\square)Al_6Si_3O_{12}(O_{2.25}OH_{0.75})(BO_3)$, which was discovered in 1881 [1], has been supplemented by a number of new species. In the last edition of *Strunz Mineralogical Tables* by H. Strunz and E. Nickel, magnesiodumortierite $(Mg,Ti,\square)(Al,\square)_4(Al,Mg,\square)_2Si_3O_{12.04}(OH)_{2.96}(BO_3)$ [2] and holtite $(Ta,Al,\square)Al_6(Si,Sb)_3O_{12}(O,OH,\square)_3(BO_3)$ [3] were included in this group. All discoveries of holtite in three deposits in western Australia, Khibiny, and Poland were accompanied by the description of its second variety named holtite II. The latter is characterized by a substantially lower silicon content and higher antimony and arsenic contents. The structural differences of these two modifications of holtite [holtite I $(Al,Ta,\square)(Al,\square)_6(Si,Sb,As)_3O_{13.46}(O,OH)(BO_3)$, and holtite II $(Ta,Al,\square)(Al,Sb)_2Al_2(Al,\square)_2(Si,Sb,As)_2(Sb,\square)O_{9.30}(O,OH)_{4.56}(BO_3)$] have been considered in recent publications [4–6].

In addition, a subgroup of hexagonal (primarily Mg- and Al-containing) structures has been distinguished among minerals structurally similar to orthorhombic dumortierite. In the minerals of this subgroup, BO_3 triangles and SiO_4 tetrahedra are replaced with $[PO_4]$ tetrahedra and CO_3 triangles. As a result, the isomorphous capacity of the octahedral framework of the dumortierite structure consisting of columns of Al octahedra substantially increases, and minerals characterized by a wide variety of chemical compositions can have this framework. Apart from the differences associated with the compositions of octahedral, triangular, and tetrahedral positions, the rearrangement of the framework with orthorhombic symmetry into the hexagonal framework is far from simple and evident because of the differences in the linkage of octahedra in the columns. The differences in the structure of the octahedral framework in orthorhombic and hexagonal dumortierite and structurally related minerals were considered in detail in [2]. The common feature of these structures is the presence of channels of triangular cross section in the framework formed by octahedral columns. These channels are occupied by triangular or tetrahedral anions. Owing to differences in the packing of these structural fragments, wide channels of hexagonal cross section are either present or absent in the framework, and the channels can be occupied in a radically different fashion.

Among the rather new minerals belonging to this group, let us mention ellenbergerite, $(Mg,Ti,\square)_2Mg_6Al_6Si_8O_{28}(OH)_{10}$ with sp. gr. $P6_3$ from the Dora Maira crystalline massif (western Italian Alps) [7]. In the octahedral framework of this mineral, Mg and Al cations are ordered. Almost simultaneously with the discovery of ellenbergerite, new magnesium phosphate $CaMg_5(CO_3)(PO_4)_3(OH)$ was found in the serpentine–magnesite deposit in the Modum area (southern Norway) as inclusions in heneuite and characterized [8]. More recently, a structural study [9] demonstrated that this mineral is a magnesium phosphate analog of ellenbergerite, in which tetrahedra in the triangular channels of the octahedral framework are partially replaced with triangular [CO_3] anions. The composition of the mineral is described by the formula $Mg_{12}(Mg,Fe,\square)_2(PO_4)_6[(HPO_4)_{1.24}(CO_3)_{0.76}](OH)_6$, and the mineral belongs to sp. gr. $P6_3mc$. The channels of hexagonal cross section are occupied by [PO_4] and [PO_3OH] tetrahedra and a small amount of [AsO_4] tetrahedra.

The mineral ekatite, $(Fe^{3+},Fe^{2+},Zn)_{12}[AsO_3]_6[AsO_3,HOSiO_3]_2(OH)_6$, which was discovered in the Tsumeb deposit (Namibia), is also structurally related to ellenbergerite. This mineral is characterized by the framework consisting of (Fe,Zn) octahedra. As opposed to the above-described mineral, the channels of hexagonal cross section in the latter mineral are occupied by pyramidal AsO_3 groups, and the channels of triangular cross section contain similar AsO_3 groups randomly replaced with SiO_3OH tetrahedra [10].

Another group of minerals, which is similar to ellenbergerite but characterized by the absence of channels of hexagonal section, includes the natural and synthetic holtedahlites $Mg_{12}(PO_3OH,CO_3)(PO_4)_5(OH,O)_6$ and $Mg_{12}(PO_3OH)(PO_4)_5(OH,O)_6$, respectively, [11] and satterlyite $(Fe^{2+},Mg,Mn)_{12}(PO_3OH)(PO_4)_5(OH,O)_6$ [12].

It should be noted that specimens containing up to 16 wt % P_2O_5, which corresponds to 2.4 phosphorus atoms per formula unit, were mentioned in the first description of ellenbergerite. The isomorphism scheme $Al^{[VI]} + Si^{[IV]} \longleftrightarrow Mg^{[VI]} + P^{[IV]}$ with the transition from sp. gr. $P6_3$ to sp. gr. $P6_3mc$ was suggested for these specimens [7]. The main aim of the present study was to establish the structure of the phosphorus-containing variety of ellenbergerite.

EXPERIMENTAL

We discovered both varieties of ellenbergerite in one association, which includes also pyrope, quartz, talc, magnesiostaurolite, and rutile. The phosphorus-poor variety is from purple to violet in color and is characterized (electron-probe X-ray microanalysis) by the empirical formula $Mg_{6.6}Al_{5.9}Zr_{0.2}Ti_{0.3}Si_{7.95}P_{0.05}(O,OH)_{38}$. The phosphorus-rich variety of ellenbergerite is characterized by a lighter pink color. The components in this mineral vary in the ranges described by the following formula: $Mg_{7.5-7.8}Al_{5.0-5.2}Fe_{0-0.1}Ti_{0.1-0.25}Si_{6.4-6.7}P_{1.3-1.6}(O,OH)_{38}$.

The IR spectrum of the phosphorus-rich variety shows bands in the range of 3300–3600 cm^{-1} and at 800 cm^{-1} (O–H stretching and bending vibrations, respectively), at 1040 and 586 cm^{-1} (stretching and bending vibrations of PO_4 tetrahedra, respectively), and at 925 and 472 cm^{-1} (stretching and bending vibrations of SiO_4 tetrahedra, respectively).

The coexistence of these two phases in one system (and even in a close association), the absence of miner-

Table 1. Principal crystallographic characteristics and X-ray diffraction data for phosphorus-rich ellenbergerite

Formula	$(Mg_{0.61}Ti_{0.08}\square_{0.31})_2(Mg_{0.52}Al_{0.43}\square_{0.05})_{12}[SiO_3(O_{0.29}(OH)_{0.71})]_6[(P_{0.71}Si_{0.20}\square_{0.09})O_3OH]_2(OH)_6$
Crystal system	Hexagonal
Sp. gr., Z	$P6_3mc$; 1
Unit-cell parameters, Å	$a = 12.476(9)$, $c = 4.9766(6)$
V, Å^3	670.8(7)
ρ_{calcd}, g/cm^3	2.897
μ, mm^{-1}	0.970
Molecular weight	1170.51
F_{000}	586
Crystal dimensions, mm	0.15 × 0.20 × 0.25
Diffractometer	Ital Structures
Radiation; wavelength, Å	MoK_α; 0.71073
Minimum, maximum θ, deg	3.27, 27.45
Scan ranges	$0 \le h \le 15$; $-15 \le k \le 12$; $-6 \le l \le 6$
Total number of reflections	3317
Number of reflections with $I > 2\sigma(I)$	1659
Number of independent reflections with $I > 2\sigma(I)$ [R_{ind}]	376 [0.0399]
Number of parameters in refinement	70
$R_F/wR(F^2)$	0.0248/0.0552
$\Delta\rho_{max}/\Delta\rho_{min}$, e/Å^3	0.282/–0.371

als of intermediate composition, and the similarity of the compositions of both phases to the compositions of their analogs determined in [7] are indicative of the absence of continuous isomorphism between ellenbergerite and its phosphorus-rich "variety" and suggest that the latter is a new mineral type. To verify this suggestion, we studied the crystal structure of this mineral.

A single crystal of the dimensions 0.15 × 0.20 × 0.25 mm was selected for the structural study. The crystallographic characteristics and the X-ray data collection and refinement statistics are given in Table 1.

The hexagonal unit-cell parameters of phosphorus-rich ellenbergerite ($a = 12.476(9)$ Å, $c = 4.9766(6)$ Å) were determined by the least-squares refinement with the use of the angular parameters of 18 reflections in the range $18° \le 2\theta \le 23°$. The unit-cell parameters determined for this mineral are very similar to those reported for ellenbergerite [7], phosphoellenbergerite [9], ekatite [10], and a large group of synthetic compounds [13–18]. The systematic absences in the three-dimensional X-ray diffraction data set indicated sp. gr. $P6_3mc$. The ψ-scan absorption correction for phosphorus-rich ellenbergerite was applied.

All calculations were performed using the SHELX97 program package [19]. The structure of phosphorus-rich ellenbergerite was solved by direct methods and refined anisotropically in sp. gr. $P6_3mc$ to $R = 0.0248$. The refinement gave the following structural formula for this compound: $(Mg_{0.61}Ti_{0.08}\square_{0.31})_2(Mg_{0.52}Al_{0.43}\square_{0.05})_{12} \cdot [SiO_3(O_{0.29}(OH)_{0.71})]_6[(P_{0.71}Si_{0.20}\square_{0.09})O_3OH]_2(OH)_6$. This formula is consistent with the compositions estimated by electron-probe X-ray microanalysis. The cation distribution was established on the basis of the refinement of the electron contents of the cation positions and the charge balance with allowance for the requirement of the electroneutrality of the chemical formula. To verify the validity of the chosen space group, which is indicative of the disordered distribution of Mg and Al cations in the octahedral framework of the structure, we performed the refinement in sp. gr. $P6_3$ determined for ellenbergerite [7]. In this case, lowering of the symmetry did not reduce the final R factors and two crystallographically nonequivalent octahedra were characterized by very similar cation–oxygen distances, unlike the ellenbergerite structure characterized by the ordered distribution of Mg and Al and substantially different distances in the corresponding polyhedra [7]. The final coordinates of the basic atoms and the atomic displacement parameters for phosphorus-rich ellenbergerite are given in Table 2. The structural data for phosphorus-rich ellenbergerite were deposited in the Inorganic Crystal Structure Database (ICSD), reference number 417393.

Table 2. Atomic coordinates and atomic displacement parameters for the crystal structure of phosphorus-rich ellenbergerite

Atom	x	y	z	U_{eq}^*
$M(1)$	0.42509(12)	0.34570(10)	−0.0028(3)	0.0105(4)
$M(2)$	0.0	0.0	0.1908(9)	0.0178(13)
$T(1)$	0.6667	0.3333	0.7804(7)	0.0092(8)
$T(2)$	0.31018(13)	0.15509(7)	0.4785(4)	0.0127(4)
O(1)	0.2797(3)	0.3494(3)	0.1476(6)	0.0175(7)
O(2)	0.3834(5)	0.1917(2)	0.1928(9)	0.0234(10)
O(3)	0.1595(4)	0.0797(2)	0.4325(8)	0.0197(10)
O(4)	0.4762(2)	0.5238(2)	0.8111(10)	0.0190(12)
O(5)	0.4030(2)	0.5970(2)	0.3847(10)	0.0267(11)
O(6)	0.3333	0.6667	0.9538(19)	0.040(3)
H(1)	0.448(3)	0.552(3)	0.936(14)	0.06(3)**
H(2)***	0.303(5)	0.607(11)	0.82(2)	0.010**

* The parameters U_{eq} were calculated from the corresponding anisotropic displacement parameters.

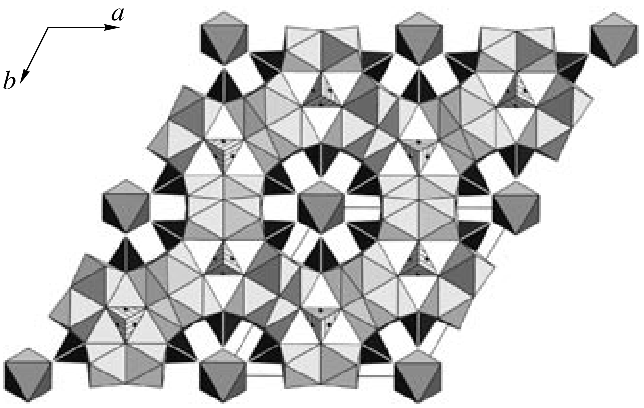
** Isotropic displacement parameters.

*** H(2) = 0.33H.

Note: $M(1) = 0.52(2)Mg + 0.426(17)Al$, $M(2) = 0.61(2)Mg + 0.082(12)Ti$, $T(1) = 0.71(3)P + 0.20(4)Si$, $T(2) = Si$.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The projection of the crystal structure of phosphorus-rich ellenbergerite along the [001] direction is shown in the figure drawn with the use of the DIAMOND2 program. The structure of phosphorus-rich ellenbergerite retains the octahedral framework found in the structures of ellenbergerite, phosphoellenbergerite, ekatite, and a number of structurally related synthetic compounds. The structure of phosphorus-rich ellenbergerite differs from ellenbergerite primarily in



Crystal structure of phosphorus-rich ellenbergerite projected along the [001] direction. The (Mg,Al) and (Mg,Ti) polyhedra are light gray and dark gray, respectively, the Si tetrahedra are filled, and the (P,Si) tetrahedra are diagonally hatched. The H atoms are indicated by small filled circles.

that Mg and Al cations in the phosphorus-rich variety are disordered in the octahedra of the framework and the channels of triangular cross section are occupied predominantly by P tetrahedra. Like the framework in the structures of the above-mentioned compounds, the framework in phosphorus-rich ellenbergerite is composed of columns formed by face- and edge-sharing octahedra. Four (Mg,Al)–O distances vary from 1.954(4) to 1.984(3) Å. Two (Mg,Al)–O(4)=OH bonds are elongated (2.145(4) and 2.188(4) Å). Wide channels of hexagonal cross section are occupied by chains of face-sharing octahedra, which are randomly (by ~69%) filled by Mg and Ti. The (Mg,Ti)–O(3) distances vary from 2.101(5) to 2.150(5) Å. In the magnesiodumortierite structure, the octahedra in this chain are filled in a similar fashion [2]. The (Mg,Ti) octahedra are linked to the walls of the octahedral framework through Si tetrahedra (the average Si–O distance is 1.625 Å).

The narrower channels of triangular cross section are occupied by the $[(P_{0.71}Si_{0.20}\square_{0.09})O_3OH]$ tetrahedra (the average (P,Si)–O distance is 1.601 Å). By analogy with ellenbergerite and other structurally related compounds, the H atom in the OH group involved in this tetrahedron would occupy the special position 2*b*. However, this hydrogen atom, H(2), in phosphorus-rich ellenbergerite is shifted to the position 6*c*, the occupancy of the corresponding position being 1/3.

Calculations of the local balance of valence forces of the anions [20] demonstrated that the structure of phosphorus-rich ellenbergerite contains not only two positions of OH groups, which have been revealed earlier for a large group of structurally similar compounds and confirmed by IR spectroscopic data (bands at 3300–3600 cm^{-1}), but also the OH group in the O(3) position, where it partially replaces the oxygen atom (the sum of valence forces of the O(3) atom is 1.40).

ACKNOWLEDGMENTS

This study was supported by the Russian Foundation for Basic Research (project no. 06-05-64024-a), the joint Russian–Italian project “Crystal Structures and Topology of Rare and New Minerals,” and the Federal Program for Support of Prominent Scientists and Leading Scientific Schools (grant nos. MK-4479.2006.5 and NSh-4964.2006.5).

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Translated by T. Safonova