

STRUCTURE
OF INORGANIC COMPOUNDS

Refinement of the Crystal Structure of Zn-Containing Greifensteinite

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Abstract—The crystal structure of Zn-containing greifensteinite from the Pirineus Mine (Minas Gerais, Brazil) was refined ($R = 0.045$, 562 reflections with $|F| > 2\sigma(F)$). The unit-cell parameters are $a = 15.941(3)$ Å, $b = 11.877(3)$ Å, $c = 6.625(2)$ Å, $\beta = 95.09(2)^\circ$; $V = 1249.4$ Å³; sp. gr. $C2/c$; and $Z = 2$. The idealized formula is $[\text{Mn}(\text{Fe}^{2+}, \text{Zn})_4]\text{Ca}_2\text{Be}_4(\text{PO}_4)_6(\text{OH})_4 \cdot 6\text{H}_2\text{O}$. The mineral is isostructural with the previously studied monoclinic representatives of the roscherite group from different deposits and differs from these representatives in that it contains Zn in one of two octahedral positions. © 2004 MAIK “Nauka/Interperiodica”.

Roscherite (beryllium phosphate) from the Greifenstein Rocks (Germany) was first described in [1, 2] as a monoclinic mineral (sp. gr. $C2/c$) with the formula $(\text{Ca}, \text{Mn}, \text{Fe})_3\text{Be}_3(\text{PO}_4)_3 \cdot 2\text{H}_2\text{O}$. Later on, a magnesium-rich analogue of this mineral from the Lavra da Ilha pegmatite (Minas Gerais, Brazil) [3, 4] was studied by X-ray diffraction analysis. The study of a manganese-rich specimen from the Foote Mine (North Carolina, USA) demonstrated [5] that a triclinic modification of roscherite (sp. gr. $C\bar{1}$) exists along with a monoclinic modification. Recently, the Fe^{2+} -dominant representative of the roscherite group from the Greifenstein Rocks (Saxony, Germany) [6, 7] has been approved under the name greifensteinite by the Commission on New Minerals and Mineral Names of the International Mineralogical Association. Later, we studied its triclinic magnesium-rich analogue (sp. gr. $P\bar{1}$) from the Galileia Mine (Minas Gerais, Brazil) [8]. Thus, the roscherite group includes three isostructural minerals: roscherite, zanazziite, and greifensteinite, which differ in the dom-

inating octahedral cation, and triclinic modifications of roscherite and greifensteinite.

In this study, we investigated an analogue of greifensteinite containing about 4% of ZnO, which was discovered in the Pirineus Mine (Minas Gerais, Brazil). It was of interest to study the structure of this new specimen, because an anomalously high zinc content is sometimes indicative of special structural features. The replacement of iron or manganese with zinc is untypical of some minerals (for example, minerals of the eudialyte and labuntosivite groups). The presence of zinc in a mineral of the labuntosivite group is a reliable indication that this mineral belongs to a structural type other than labuntosivite (for example, to the kuzmenkoite subgroup).

The chemical composition of the new mineral was determined by electron-microprobe (EDX) analysis. Variations in the local composition within one grain associated with growth zoning correspond to the following empirical formula:



X-ray diffraction data were collected from an irregularly shaped chip of a single crystal on a Kuma-4 CCD diffractometer. The parameters of the triclinic unit cell were determined and refined on the same diffractometer. The structural parameters and characteristics of X-ray diffraction study are given in Table 1.

The structure was refined using the atomic coordinates of greifensteinite [7] as the starting model. The cations were distributed over two independent octahedral positions, $M(1)$ and $M(2)$, taking into account the mixed atomic scattering curves for the $M(2)$ position, whereas the $M(1)$ position was assumed to be partially vacant and occupied exclusively by Mn.

Table 1. Structural data and characteristics of X-ray diffraction study

Characteristic	Data and conditions
Generalized chemical formula	(Fe, Mn, Zn) ₅ Ca ₂ Be ₄ (PO ₄) ₆ (OH) ₄ · 6H ₂ O
Unit-cell parameters; Å, deg	<i>a</i> = 15.941(3) <i>b</i> = 11.877(3) <i>c</i> = 6.625(2) β = 95.09(2)
Unit-cell volume, <i>V</i> , Å ³	1249.4
Space group; <i>Z</i>	<i>C</i> 2/ <i>c</i> ; 2
Calculated density ρ , g/cm ³	2.96
Absorption coefficient μ , mm ⁻¹	35.12
Molecular weight	2225.8
Diffractometer	Kuma-4 CCD
Radiation, wavelength	MoK α , 0.71073
Crystal dimensions, mm	0.25 × 0.25 × 0.125
Maximum $\sin\theta/\lambda$, Å ⁻¹	0.69
Ranges of the indices of measured reflections	-21 < <i>h</i> < 21; -16 < <i>k</i> < 15; -9 < <i>l</i> < 8
Total number of reflections	14074
Number of independent reflections	7126
Number of reflections with $ F > 2\sigma(F)$	562
<i>R</i> _{int} for equivalent reflections	0.085
Program for structure calculations	AREN [9]
<i>R</i> _{hkl} factor upon anisotropic refinement	0.046
Extinction parameter <i>E</i>	0.0000026

The hydrogen atoms of one water molecule were revealed from a difference electron-density map. The anisotropic refinement converged to an *R* factor of 4.5%. The positional and equivalent thermal parameters of the atoms corresponding to this *R* factor are given in Table 2. The interatomic distances in *M* octahedra and hydrogen-bond lengths are listed in Table 3.

The structure of Zn-containing greifensteinite, like the structures of other representatives of the roscherite group studied earlier, can be described as a three-dimensional framework consisting of tetrahedra, octahedra, and Ca seven-vertex polyhedra (figure). Be and P tetrahedra form infinite chains linked by *M* octahedra into a mixed framework. *M* octahedra, in turn, share edges to form octahedral chains. Ca atoms occupy cavities in the framework. Generally, the octahedra in the lattice sites are occupied only partially. Hence, the total number of *M* cations decreases from six to five, and the chains statistically break down into pairs of octahedra.

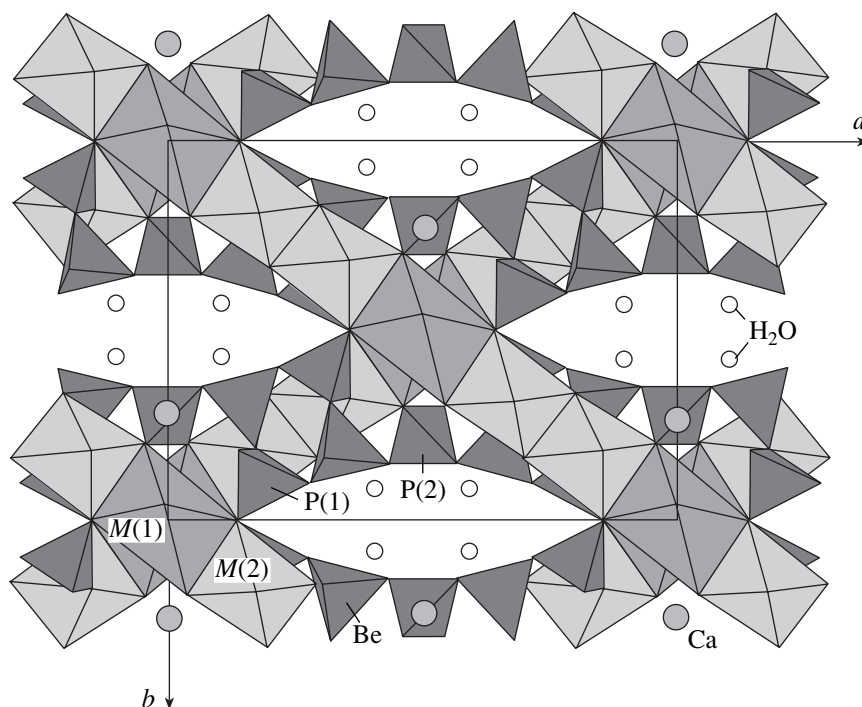
The crystal-chemical formula of the mineral can be represented as follows (*Z* = 2): [Mn_{0.68}²⁺□_{0.32}] · [(Fe²⁺, Fe³⁺)_{2.35}Zn_{0.72}Mn_{0.46}Al_{0.28}Mg_{0.19}]Ca₂Be₄(PO₄)₆ · (OH)₄(H₂O, O)₂ · 4H₂O, where the compositions of independent octahedral positions are enclosed in brackets. The Ca polyhedron is formed by four oxygen atoms and three water molecules, one of which is shared with

Table 2. Atomic coordinates and equivalent thermal parameters

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B</i> _{eq} , Å ²
Ca	0	0.2571(2)	0.25	2.1(1)
<i>M</i> (1)	0	0	0	2.04(1)
<i>M</i> (2)	0.1713(1)	0.1616(1)	0.9960(2)	2.26(6)
P(1)	0.1880(2)	0.1173(2)	0.4779(4)	1.9(1)
P(2)	0	0.2740(3)	0.75	1.6(2)
Be	0.333(1)	0.178(1)	0.299(2)	2.6(6)
O(1)	0.3559(5)	0.4973(6)	0.498(1)	2.4(4)
O(2)	0.2824(4)	0.0999(6)	0.450(1)	2.1(4)
O(3)	0.1454(4)	0.1823(6)	0.299(1)	1.9(4)
O(4)	0.3188(4)	0.3136(5)	0.328(1)	1.6(4)
O(5)	0.4583(4)	0.2970(6)	0.074(1)	1.9(3)
O(6)	0.4338(4)	0.1505(5)	0.342(1)	2.1(4)
OH	0.3000(4)	0.1640(6)	0.062(1)	1.9(4)
H ₂ O(1)	0.0928(5)	0.4194(6)	0.219(1)	2.5(4)
H ₂ O(2)	0	0.041(1)	0.25	3.3(6)
H(1)	0.082(1)	0.488(1)	0.179(1)	3*
H(2)	0.150(1)	0.417(1)	0.180(1)	3*

Note: *M*(1) = Mn_{1.36}; *M*(2) = Fe_{4.7}Zn_{1.44}Mn_{0.92}Mg_{0.38}Al_{0.56}; H₂O(2) = (H₂O, O).

* Isotropic thermal parameters (unrefined).



Structure of Zn-containing greifensteinite projected onto the (001) plane.

the strongly distorted $M(1)$ octahedron. According to the local bond-valence requirements [10] (Table 4), an excess of bond valences in the corresponding $H_2O(2)$ position indicates that the water molecules are partially replaced with oxygen atoms. Taking into account that the $M(1)$ position is vacant in the majority (2/3) of unit cells, we write the composition of the $H_2O(2)$ position as (H_2O, O) . Previously, we found a similar partial substitution of water molecules with OH groups in the

structure of the triclinic analogue of greifensteinite [8]. This substitution can occur also in other members of the group resulting in a decrease in the total number of H_2O molecules in the formulas of the minerals. However, this fact was not noted in the original studies.

The occurrence of Zn atoms in one of two octahedral positions is consistent with the smaller size of the $M(2)$ octahedron as compared to the $M(1)$ octahedron (interatomic distances of 2.106 and 2.194 Å, respec-

Table 3. Selected interatomic distances, Å

<i>M</i> octahedra			
$M(1)-H_2O(2)$	$1.727(3) \times 2$	$M(2)-O(1)$	2.000(7)
O(1)	$2.296(6) \times 2$	OH	2.059(7)
O(5)	$2.559(7) \times 2$	O(3)	2.099(7)
	$\langle 2.194 \rangle$	O(5)	2.133(7)
		OH	2.163(7)
		O(4)	2.183(7)
			$\langle 2.106 \rangle$
H bonds			
H(1)- $H_2O(1)$	0.87(1)	$\angle H(1)-H_2O(1)-H(2)$	97.0(1)
H(2)- $H_2O(1)$	0.97(2)	$\angle H_2O(1)-H(1)-O(6)$	166.3(5)
H(1)-H(2)	1.63(1)	$\angle H_2O(1)-H(2)-O(2)$	175.8(3)
H(1)⋯O(6)	1.94(1)		
H(2)⋯O(2)	2.09(2)		

Table 4. Bond valences according to [10]

Anion/cation	<i>M</i> (1)	<i>M</i> (2)	Ca	P(1)	P(2)	Be	Σ
O(1)	0.25	0.49		1.21			1.95
O(2)				1.21		0.52	1.73
O(3)		0.37	0.25	1.29			1.91
O(4)		0.30		1.23		0.50	2.03
O(5)	0.13	0.34	0.32		1.22		2.01
O(6)					1.21	0.50	1.71
OH		0.42				0.54	1.27
		0.31					0.27
$H_2O(1)$			0.27				2.58
$H_2O(2)$	1.19×2		0.20				

Note: The occupancy of the $M(1)$ position is 0.34; the composition of the $M(2)$ position was assumed to be Fe^{2+} .

Table 5. Structural data for minerals of the roscherite group

No.	Mineral	Unit-cell parameters; Å, deg	Sp. gr.	Formula	Mn : Fe : Mg	Reference
1	Roscherite*	$a = 15.90, b = 11.88, c = 6.69$ $\beta = 94.7$	$C2/c$	$(\text{Mn, Fe})_5\text{Ca}_2\text{Be}_4(\text{PO}_4)_6(\text{OH})_4 \cdot 6\text{H}_2\text{O}$	0.85 : 0.14 : 0.01	[2]
2	Zanazziite	$a = 15.874, b = 11.854, c = 6.605$ $\beta = 95.21$	$C2/c$	$(\text{Mg, Fe})_5\text{Ca}_2\text{Be}_4(\text{PO}_4)_6(\text{OH})_{3.4} \cdot 6.6\text{H}_2\text{O}$	0.05 : 0.33 : 0.62	[4]
3	Greifensteinite	$a = 15.903, b = 11.885, c = 6.677$ $\beta = 94.68$	$C2/c$	$(\text{Fe, Mn})_5\text{Ca}_2\text{Be}_4(\text{PO}_4)_6(\text{OH})_4 \cdot 6\text{H}_2\text{O}$	0.16 : 0.74 : 0.09	[7]
4	Zn-containing greifensteinite	$a = 15.941, b = 11.877, c = 6.625$ $\beta = 95.09$	$C2/c$	$(\text{Fe, Mn, Zn})_5\text{Ca}_2\text{Be}_4(\text{PO}_4)_6(\text{OH})_4 \cdot 6\text{H}_2\text{O}$	0.31 : 0.64 : 0.05	This study
5	Triclinic roscherite	$a = 15.921, b = 11.965, c = 6.741$ $\alpha = 91.04, \beta = 94.21, \gamma = 89.59$	$C\bar{1}$	$(\text{Mn, Fe})_5\text{Ca}_2\text{Be}_4(\text{PO}_4)_6(\text{OH})_4 \cdot 6\text{H}_2\text{O}$	0.90 : 0.09 : 0.01	[5]
6	Triclinic greifensteinite	$a = 9.883, b = 9.879, c = 6.668$ $\alpha = 86.93, \beta = 85.60, \gamma = 73.53$	$P\bar{1}$	$(\text{Fe, Mg})_5\text{Ca}_2\text{Be}_4(\text{PO}_4)_6(\text{OH})_4 \cdot 6\text{H}_2\text{O}$	0.04 : 0.51 : 0.45	[8]

Note: For uniformity, the unit-cell parameters a and b for triclinic greifensteinite are interchanged.

* The structure was not studied.

tively). An analogous regular and compact Zn octahedron is observed, for example, in the alsakharovite-Zn structure ($\text{Zn-O} = 2.04\text{--}2.26$ Å; aver., 2.14 Å) [11, 12]. The idealized formula of the mineral can be written as $[\text{Mn}(\text{Fe}^{2+}, \text{Zn})_4]\text{Ca}_2\text{Be}_4(\text{PO}_4)_6(\text{OH})_4 \cdot 6\text{H}_2\text{O}$.

Minerals of the roscherite group from different deposits differ in the cation content in octahedral positions, with the compositions in tetrahedral positions being invariant (Table 5). For example, Mg atoms predominate in the zanazziite structure (three of five atoms), whereas Mn and Fe cations predominate in roscherite and greifensteinite, respectively. In monoclinic minerals of the roscherite group, there is only one key ("specimen-forming") octahedral position (eightfold $M(2)$ position), whereas the second position (at the inversion center) tends to be vacant (greifensteinite) or contains the same dominating cation as that in the major position (zanazziite). In the triclinic mineral, three positions (except for the vacant one) are of importance from the viewpoint of classification [8].

To summarize, the mineral under study retains the structural type of the monoclinic representatives of the roscherite group and differs from them in that Zn atoms are present in the eightfold octahedral position.

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