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MINERALOGY

The Pseudobrookite Group: Crystal Chemical Features of the Armalcolite Fe^{2+} Analogue

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Abstract—The crystal structure of a potentially new mineral, the Fe^{2+}-dominant analogue of armalcolite with the idealized formula $Fe^{2+}Ti_2O_5$ has been solved. The sample studied originates from a pneumatolytic association related to the lamproite complex of SE Spain. The mineral is orthorhombic, space group *Cmcm*, the unit-cell parameters are $a = 3.7325(1)$ Å, $b = 9.7649(4)$ Å, $c = 9.9902(3)$ Å, $V = 364.12(2)$ Å^3. The crystal-chemical formula $^{M1}(\mathrm{Mg}_{0.19}\mathrm{Fe}^{2+}_{0.25}\mathrm{Fe}^{3+}_{0.26}\mathrm{Ti}_{0.30})^{2.86+}[^{M2}(\mathrm{Ti}_{0.65}\mathrm{Fe}^{3+}_{0.27}\mathrm{Fe}^{2+}_{0.08})^{3.57+}]_2\mathrm{O}_5$ ($Z = 4$) is in good agreement with the chemical composition of the mineral.

Keywords: double oxides, pseudobrookite group, armalcolite Fe^{2+} analogue, X-ray structural analysis, cation ordering, lamproite, Aljorra, Spain

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Double oxides related to the structural type of pseudobrookite, namely, pseudobrookite $(Fe^{3+}, Fe^{2+})(Ti, Fe^{3+})_2O_5$ and armalcolite $(Mg, Fe^{2+})Ti_2O_5$, are quite typical minerals of high-temperature, low-pressure formations, including titanium-enriched basalts, andesites, rhyolites, lamproites, and some types of lunar rocks [1–3]. Similar phases of technogenic origin from slags and combustion products of dumps containing brown coal were described [4, 5]. The results of the synthesis of compounds of this type are given in several publications [1, 6]. Studies of natural double oxides related to the structure type of pseudobrookite are also interesting due to the well-balanced anisotropy of thermal expansion, which makes them suitable as thermistors, electrically conductive, optical and magnetic materials, catalysts, photocatalysts, cheap thermally stable filters for diesel engines, heat-resistant pigments of paints, plastics, rubber, energy-saving materials (cooling pigments), and heat-resistant ceramics with a low coefficient of thermal expansion. The nature of the cationic order/disorder and the actual composition of these minerals, including the valence state of Fe, determine their main crystal chemical features and affect their thermal stability.

In the crystal structure of the pseudobrookite minerals with the general formula $M(1)M(2)_2O_5$, the M cations (Mg^{2+}, Fe^{2+}, Fe^{3+}, and Ti^{4+}) occupy two independent positions $M(1)$ and $M(2)$ (Wykoff positions 4*c* and 8*f*, respectively) [5, 7]. These cations have octahedral coordination. As a rule, their positions, are characterized by mixed occupation, with Ti always dominating in the $M(2)$ position, and Fe^{3+} (in pseudobrookite) or Mg (in armalcolite) dominating in the $M(1)$ position. Oxygen atoms occupy three independent positions. All the atomic positions in the structure are special. The octahedra are linked via common edges into triads, where the central octahedron is filled with $M(1)$ cation, and the outer octahedra are filled with $M(2)$ cations. Being connected through the common vertices of the $M(2)O_6$ octahedra, the triads form chains elongated along the *c*-axis (Figs. 2, 3). The chains are joined together via common edges and vertices of the octahedra to form a three-dimensional pseudo-framework.

According to the Mössbauer spectroscopy and neutron diffraction studies, the $M(2)$ position in the synthetic Fe^{2+} analogue of armalcolite $Fe^{2+}Ti_2O_5$ at high synthesis temperatures (above 1700°C) is completely occupied by Ti atoms, while in the products of lower temperature synthesis (at 1200°C and below)

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Fig. 1. Crystals of Fe^{2+}-dominant analogue of (*1*) armalcolite in association with (*2*) enstatite and (*3*) sanidine. The image width is 3 mm. Photo by Marco Burkhardt.

Ti atoms are distributed between two cation sites [6]. However, it is not clear from the work cited whether the synthesized compounds were in a state of thermodynamic equilibrium under the conditions of their synthesis or not.

Isomorphic substitutions and some crystal chemical features of the pseudobrookite group minerals from the Spanish lamproites were considered in [8]. In particular, it was shown that chemical composition of the minerals varies in the ranges $Mg_{0.2-0.7}Fe^{2+}_{0-0.6}Fe^{3+}_{0.2-1.6}Ti_{1.2-1.9}O_5$, and the basic scheme of isomorphic substitution corresponds to $Ti^{4+} + 3Fe^{2+} \leftrightarrow 2Mg^{2+} + 2Fe^{3+}$. However, the distribution of Fe^{2+}/Fe^{3+} ions over the positions of the crystal structure was not discussed.

In this work, we studied the crystal structure of the mineral, the composition of which corresponds to an intermediate member of the three-component system of solid solutions pseudobrookite–armalcolite–Fe^{2+}-analogue of armalcolite (the latter, in which the end member corresponds to the formula $Fe^{2+}Ti_2O_5$, has no mineralogical name). Samples were collected in an abandoned building stone quarry near the village of Los Nietos (Aljorra municipality, autonomous region Murcia, southeast Spain). The studied sample consists of fragments of cavernous lamproite containing phenocrysts of serpentinized forsterite [9, 10]. The pneumatolite association is represented by sanidine, pyroxene, fluorophlogopite, and pseudobrookite group minerals, the crystals of which grow on the walls of miarol cavities. The Fe-analogue of armalcolite forms brown board-like crystals up to 3 mm long elongated along (010) and flattened along (100).

The chemical composition of the mineral was determined by means of a Tescan Vega-II XMU scanning electron microscope (EDS mode, accelerating voltage 20 kV, current 400 pA, electron probe diameter 160 nm) equipped with the system for recording X-ray radiation and calculating the sample composition INCA Energy 450. MgO and pure Ti and Fe were used as standards (preliminary measurements showed that the contents of the other elements are below the detection limit of the electron probe method). The crystal studied is rather homogeneous in composition. The composition is (mean values for three local analyses; limits are given in parentheses; all iron is given in the form of FeO, wt %): MgO 3.40 (3.01–3.75), FeO 37.87 (37.20–38.04), TiO_2 55.74 (55.20–56.38), total 97.01. The empirical formula calculated on three cations and five oxygen atoms is: $Mg_{0.19}Fe^{2+}_{0.41}Fe^{3+}_{0.80}Ti_{1.60}O_5$. The

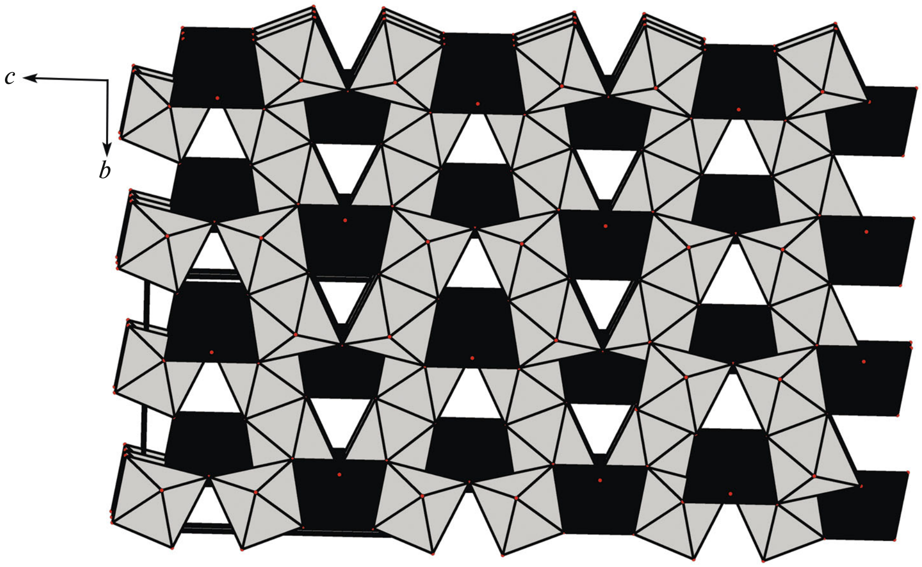

Fig. 2. Armalcolite crystal structure along the *a* axis. Black octahedra, $M1O_6$; gray octahedra, $M2O_6$.

coefficients of Fe^{2+} and Fe^{3+} were determined considering the bond valence balance and correspond to 12.83 wt % FeO and 27.83 wt % Fe_2O_3. The final analysis sum equals 99.80 wt %, which indirectly confirms the approach used.

The XRD pattern obtained on a "Rigaku" R-AXIS Rapid II diffractometer equipped with cylindrical IP detector (monochromatic Co$K\alpha$ radiation, Debye-Scherrer geometry, d = 127.4 mm, exposure time of 15 min), confirms that the mineral studied belongs to the pseudobrookite structure type. The lattice parameters determined are as follows: a = 3.7331(6) Å, b = 9.768(1) Å, c = 9.991(1) Å, and V = 364.3(1) Å^3.

A three-dimensional set of diffraction reflections was obtained from a single crystal with dimensions of 0.17 × 0.11 × 0.08 mm at room temperature using a single crystal Xcalibur S CCD diffractometer on MoKα radiation (λ = 0.71073 Å) for a full sphere of reciprocal space in the interval of θ angles from 4.08° up to 30.40°. The experimental data were processed by means of the CrysAlis v. 1.171.39.46 software.

The parameters of the orthorhombic unit cell refined using 1710 reflections are a = 3.7325 (1) Å, b = 9.7649 (4) Å, c = 9.9902 (3) Å, V = 364.12 (2) Å^3, and Z = 4. The crystal structure was determined by direct methods within the *Cmcm* space group and refined in the anisotropic approximation of thermal displacements of atoms using the SHELX-97 software package [11]. The final R-factor was 0.0183 for 301 independent reflections with $I > 2\sigma(I)$. The coordinates of atoms and the parameters of their thermal displacements are listed in Table 1.

The most likely distribution of cations in the sample corresponds to the structural formula $^{M(1)}(Fe_{0.51}Mg_{0.19}Ti_{0.30})^{M(2)}(Ti_{0.65}Fe_{0.35})_2O_5$. The M(2) octahedron is more distorted than the M(1) octahedron. The M(1)–O bond lengths are in the range 1.930(2)–2.156(2) Å, and the M(2)–O bond lengths are in the range 1.858(2)–2.176(2) Å. The average bond lengths in the $M(1)O_6$ and $M(2)O_6$ octahedra are 2.032 and 2.000 Å, respectively.

Table 2 shows the results of calculations of the bond valence sums for various compositions: the first block of Table 2 corresponds to the final composition, refined using the data of electron probe analysis, the second and third correspond to the boundaries of the refinement range, in which the R factor has an almost constant minimum value, close to 0.018. Since the $Fe^{2+} : Fe^{3+}$ ratio in the M(1) and M(2) positions was initially unknown, the average value R_o = 1.712 Å was used in calculations of the bond valence sum.

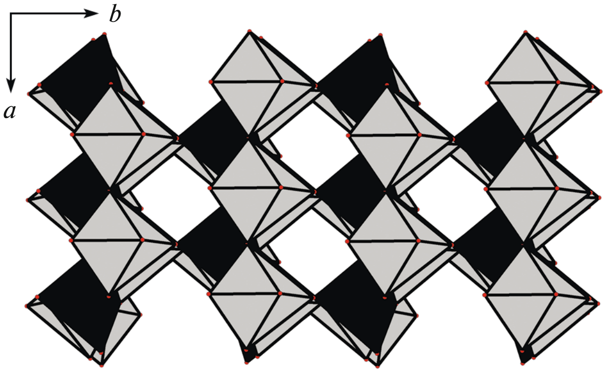

Fig. 3. Armalcolite crystal structure along the c axis. Black octahedra, $M1O_6$; gray octahedra, $M2O_6$.

From a comparison of the data given in Table 2, it can be seen that the optimal composition corresponds to the empirical formula calculated from the electron probe data: for this composition, the bond valence sum on all cations of the formula calculated for Z = 4 is strictly equal to the theoretical value of the total charge on these cations (+10 in a charge-balanced formula with five oxygen atoms), while other options give overestimated values of the bond valence sums.

The charge balanced crystal chemical formula determined on the assumption that the mean M(2) cation charge equals the bond valence sum at this position corresponds to

$$^{M1}(Mg_{0.19}Fe^{2+}_{0.25}Fe^{3+}_{0.26}Ti_{0.30})^{2.86+}$$
$$[^{M2}(Ti_{0.65}Fe^{3+}_{0.27}Fe^{2+}_{0.08})^{3.57+}]_2O_5.$$

In this formula the mean charge of the M(1) cations (+2.86) is equal to the bond valence sum at this

Table 1. Atomic positions (x, y, z), thermal displacement parameter ($U_{экв}$, Å^2), multiplicity (Q), and the site occupancy factor (s.o.f.)

Position	x	y	z	U_{eq}	Q	s.o.f.
M(1)	0	0.18945(6)	0.75	0.0072(2)	4	$Fe_{0.51}Mg_{0.19}Ti_{0.30}$
M(2)	0	0.13558(4)	0.43583(4)	0.0067(1)	8	$Ti_{0.65(1)}Fe_{0.35(1)}$
O(1)	0	0.3112(2)	0.5699(2)	0.0088(4)	8	1
O(2)	0.5	0.2654(3)	0.75	0.0092(5)	4	1
O(3)	0	0.0472(2)	0.6158(2)	0.0101(4)	8	1

Table 2. Bond valence sums [14] (net and crystal chemical formula are given in each case)

$Fe_{1.21}Mg_{0.19}Ti_{1.60}O_5$
$(Fe_{0.51}Mg_{0.19}Ti_{0.30})(Ti_{0.65}Fe_{0.35})_2O_5$

	O(1)	O(2)	O(3)	Σ
M(1)	$0.34^{\rightarrow x2}$	$0.49^{\rightarrow x2}$ $\downarrow x2$	$0.60^{\rightarrow x2}$	2.86
M(2)	$0.67^{\rightarrow x2}$ $\downarrow x2$ 0.37	0.46 $\downarrow x2$	0.82 0.58	3.57
Σ	2.05	1.90	2.00	

$Fe_{1.14}Mg_{0.2}Ti_{1.66}O_5$
$(Fe_{0.5}Mg_{0.2}Ti_{0.3})(Ti_{0.68}Fe_{0.32})_2O_5$

	O(1)	O(2)	O(3)	Σ
M(1)	$0.34^{\rightarrow x2}$	$0.49^{\rightarrow x2}$ $\downarrow x2$	$0.60^{\rightarrow x2}$	2.86
M(2)	$0.68^{\rightarrow x2}$ $\downarrow x2$ 0.38	0.46 $\downarrow x2$	0.83 0.59	3.62
Σ	2.08	1.90	2.02	

$Fe_{0.86}Mg_{0.2}Ti_{1.94}O_5$
$(Fe_{0.4}Mg_{0.2}Ti_{0.4})(Ti_{0.77}Fe_{0.23})_2O_5$

	O(1)	O(2)	O(3)	Σ
M(1)	$0.35^{\rightarrow x2}$	$0.50^{\rightarrow x2}$ $\downarrow x2$	$0.61^{\rightarrow x2}$	2.92
M(2)	$0.70^{\rightarrow x2}$ $\downarrow x2$ 0.38	0.47 $\downarrow x2$	0.85 0.60	3.70
Σ	2.13	1.94	2.06	

position (+2.86), which confirms the correctness of the structural data obtained.

The Ti distribution between the *M*(1) and *M*(2) positions in the natural Fe analogue of armalcolite is in good agreement with the literature data on three synthetic samples of $Fe^{2+}Ti_2O_5$ with a pseudobrookite structure and the

$$^{M(1)}(Fe^{2+}_{0.68}Ti_{0.32})^{M(2)}(Ti_{0.84}Fe^{2+}_{0.16})_2,$$
$$^{M(1)}(Fe^{2+}_{0.72}Ti_{0.28})^{M(2)}(Ti_{0.86}Fe^{2+}_{0.14})_2, \text{ and}$$
$$^{M(1)}(Fe^{2+}_{0.81}Ti_{0.19})^{M(2)}(Ti_{0.905}Fe^{2+}_{0.095})_2$$

crystal chemical formulas [1]. In all cases the Ti atoms are distributed between the *M*(1) and *M*(2) positions, dominating in the latter.

In conclusion, let us discuss the status of the Mg–Fe–Ti oxide studied in this work as a mineral species. Currently, two criteria are used to determine the dominant cation in the position of the crystal structure [12, 13]. According to the criterion of the average charge, the species-defining component is the one the charge of which is most close to the average charge of the cations in the position considered. For the *M*(1) site composed of $Mg_{0.19}Fe^{2+}_{0.25}Fe^{3+}_{0.26}Ti_{0.30}$, the average charge (+2.86) is close to three and, therefore, the Fe^{3+} cation should be considered as a species-forming cation in this mineral and, thus, the mineral should be considered as a pseudobrookite variety. On the other hand, according to valence-dominance rule, the mineral studied is $^{M(1)}M^{2+}$ dominant (the sums of two-, three-, and tetravalent cations in the *M*(1) position are 0.44, 0.26, and 0.30, respectively) with the dominance of the Fe^{2+} cation, which should be considered as a species-defining one. The resulting contradiction shows that the currently accepted principles of identifying mineral species need to be clarified.

We consider the criterion of prevailing valence as preferable in this case, since it leads to the idealized formula $Fe^{2+}Ti_2O_5$, which, in terms of titanium content (two atoms per formula unit), is closer to the empirical formula (1.6 atoms per formula unit) than the idealized formula of pseudobrookite $Fe^{3+}_2TiO_5$. However, the final decision on the status of the mineral studied can be made only after the rules for the definition of mineral species in such cases have been formulated.

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REFERENCES

1. J. F. W. Bowles, Am. Mineral. **73**, 1377–1383 (1988).
2. A. T. Anderson, T. E. Bunch, E. N. Cameron, S. E. Haggerty, F. R. Boyd, L. W. Finger, O. B. James, K. Keil, M. Prinz, P. Ramdohr, and A. El Goresy, Geochim. Cosmochim. Acta **34** (Suppl. 1), 55–63 (1970).
3. A. K. Pedersen, Contrib. Mineral. Petrol. **77**, 307–324 (1981).
4. V. V. Lapin, N. N. Kurtzeva, and O. P. Ostrogorskaya, Dokl. Akad. Nauk SSSR **109**, 824–827 (1956).
5. E. V. Sokolova, Yu. K. Egorov-Tismenko, and T. Nishanbaev, Vestn. Mosk. Univ., Ser. 4. Geol., No. 3, 82–86 (1991).

6. R. G. Teller, M. R. Antonio, A. E. Grau, M. Gueguin, and E. Kostiner, J. Solid State Chem. **88** (2), 334–350 (1990).
7. M. Shiojiri, S. Sekimoto, T. Maeda, Y. Ikeda, and K. Iwauchi, Phys. Status Solidi A **84**, 55–64 (1984).
8. M. F. Brigatti, S. Contini, S. Caperdi, and L. Poppi, Eur. J. Mineral. **5**, 73–84 (1993).
9. M. J. Pellicer, Estud. Geol. (Madrid, Spain) **29**, 99–106 (1973).
10. S. Contini, G. Venturelli, L. Toscani, S. Capedri, and M. Barbieri, Mineral. Mag. **57**, 203–216 (1993).
11. G. M. Sheldrick, Acta Crystallogr. A **64**, 112–122 (2008).
12. F. Bosi, F. Hatert, U. Hålenius, M. Pasero, R. Miyawaku, and S. Mills, Mineral. Mag. **83**, 627–632 (2019).
13. F. Bosi, C. Biagioni, and R. Oberti, Minerals **9** (10), 591 (2019). https://doi.org/10.3390/min9100591
14. O. C. Gagné and F. C. Hawthorne, Acta Crystallogr. **71**, 562–578 (2015).

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