

MANGANESE-BEARING BERAUNITE FROM MANGUALDE, PORTUGAL: MINERAL DATA AND STRUCTURE REFINEMENT

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ABSTRACT

A Mn-bearing oxidized variety of beraunite occurs in a phosphatic nodule in a granite at Mangualde, Portugal. It forms sheaf-like aggregates of subparallel needles. The elongate prisms have a rhombic section. The prevalent forms are {301} and {301} (both closely striated) and, in cases, a very thin {001}. Mn-bearing beraunite is red, vitreous and transparent; $D_{\text{meas}} 2.99(2)$ g/cm³. Optically it is biaxial (+) with (-) elongation; orientation $Y=b$, $X:c \cong +10^\circ$; $2V_Z = 78(2)^\circ$, with medium dispersion of $2V_Z$, $r > v$, indices of refraction $\alpha_{\text{calc}} 1.768$, $\beta_{\text{meas}} 1.774$, $\gamma_{\text{calc}} 1.783$. Pleochroism $X = Y$ pale yellow, Z red-orange. Chemical analysis by ICP gives: Li₂O 0.02, Na₂O 0.15, CaO 0.17, MnO 4.23, FeO 0.01, Fe₂O₃ 49.49, P₂O₅ 31.62, H₂O 15.38, total 101.07 wt.%, leading to the formula $\text{Fe}_{3.65}^{3+}\text{Mn}_{0.54}\text{Na}_{0.04}\text{Ca}_{0.03}\text{Li}_{0.01}(\text{OH})_5(\text{PO}_4)_{4.06}(\text{OH})_{0.95}(\text{H}_2\text{O})_{4.81}$. Mn-bearing beraunite is monoclinic, space group $C2/c$, with $a 20.760(3)$, $b 5.154(1)$, $c 19.248(2)$ Å, $\beta 93.55(1)^\circ$, $V 2055.4(3)$ Å³ and $Z = 4$. The strongest reflections in an X-ray powder-diffraction pattern [d in Å (I_{obs}) (hkl)] are: 10.39(vS)(200), 9.62(vS)(002), 7.28(S)(202), 4.82(mS)(111), 3.081(S)(314). Eighteen previously unobserved reflections were recorded. The structure of the Mn-bearing beraunite has been refined to an R of 0.034 and an R_w of 0.029 for 2690 observed [$I > 3\sigma(I)$] reflections. Hydrogen bonding is proposed, based on the refined position of hydrogen atoms. Mn^{2+} partially substitutes for Fe^{3+} in Fe1 and Fe2 sites.

Keywords: Mn-bearing beraunite, phosphate, granitic pegmatite, Mangualde (Portugal), crystal structure.

SOMMAIRE

Un essai d'aiguilles subparallèles d'une variété oxydée manganifère de beraunite a été découvert dans un nodule phosphatique dans une pegmatite granitique à Mangualde (Portugal). Les prismes allongés possèdent une section rhombique, les formes {301} et {301} finement striées, et, dans certains cas, un développement très mince de {001}. La beraunite manganifère est rouge, d'aspect vitreux, et transparente; $D_{\text{mes}} 2.99(2)$. Elle est biaxe positive, avec un allongement négatif; orientation $Y=b$, $X:c \cong +10^\circ$; $2V_Z = 78(2)^\circ$, avec dispersion moyenne de $2V_Z$, $r > v$; indices de réfraction $\alpha_{\text{calc}} 1.768$, $\beta_{\text{mes}} 1.774$, $\gamma_{\text{calc}} 1.783$. Pléochroïsme $X = Y$ jaune pâle, Z rouge orangé. Une analyse chimique par plasma à induction couplée a donné: Li₂O 0.02, Na₂O 0.15, CaO 0.17, MnO 4.23, FeO 0.01, Fe₂O₃ 49.49, P₂O₅ 31.62, H₂O 15.38, total 101.07% (par poids), ce qui mène à la formule: $\text{Fe}_{3.65}^{3+}\text{Mn}_{0.54}\text{Na}_{0.04}\text{Ca}_{0.03}\text{Li}_{0.01}(\text{OH})_5(\text{PO}_4)_{4.06}(\text{OH})_{0.95}(\text{H}_2\text{O})_{4.81}$. La beraunite manganifère est monoclinique, groupe spatial $C2/c$, $a 20.760(3)$, $b 5.154(1)$, $c 19.248(2)$ Å, $\beta 93.55(1)^\circ$, $V 2055.4(3)$ Å³, Z

= 4. Les cinq raies les plus intenses du cliché de poudre [d en Å (I) (hkl)] sont: 10.39(vS)(200), 9.62(vS)(002), 7.28(S)(202), 4.82(mS)(111), 3.081(S)(314). De plus, 18 réflexions non décelées auparavant ont été observées. La structure de ce matériau a été affinée jusqu'à un résidu R de 0.034, $R_w = 0.029$ pour 2690 réflexions observées [$I > 3\sigma(I)$]. Nous préconisons la présence de liaisons impliquant l'hydrogène en fonction des positions affinées des atomes d'hydrogène. Le Mn^{2+} remplace une partie du Fe^{3+} dans les positions Fe1 et Fe2.

(Traduit par la Rédaction)

Mots-clés: beraunite manganifère, phosphate, pegmatite granitique, structure cristalline, Mangualde, Portugal.

INTRODUCTION

An occurrence of manganiferous beraunite was noted during a systematic study of the minerals from the granitic pegmatite of Mangualde, Viseu district, Portugal (Marzoni Fecia di Cossato & Orlandi 1987). The beraunite, identified by X-ray powder diffraction, shows 18 reflections that were not reported by Moore (1970) in his study on basic iron phosphates. Optical investigations showed also a different orientation of the indicatrix with respect to those published by Palache *et al.* (1951). Results of chemical analyses confirm that this material is quite different from classic beraunite, as described by Fanfani & Zanazzi (1967); it is here described as Mn-bearing Fe-oxidized beraunite.

OCCURRENCE

Mn-bearing beraunite occurs in altered samples of a phosphatic "nodule" included in a granite outcrop near Mangualde (Viseu district, Portugal). The matrix is an intimate mixture of frondelite, mitridatite, beraunite and an amorphous phosphate.

Around little cavities (a few millimeters to 2 cm wide) in the rock samples, the following sequence of crystallization can be observed: red, needle-like crystals of Mn-bearing beraunite with yellow stewartite and brown minerals of the jahnsite-whiteite group crystallize on intergrown, radial and fibrous aggregates of dull green frondelite, bronzy red translucent mitridatite and dark red vitreous Mn-bearing beraunite.

On the red needles, there is a dull-white crust of



FIG. 1. Red needle-like crystal of Mn-bearing beraunite encrusted by dull white prisms of strengite and yellow-green vitreous tetrahedra of pharmacosiderite. Width of field of view: 2 mm.

minute prismatic crystals of strengite. Small groups of yellow-green vitreous tetrahedra of pharmacosiderite crystallize on the latter species (Fig. 1). Such an association of minerals (all of them identified by X-ray diffraction) attests to an oxidizing environment during crystallization (Moore 1973).

PHYSICAL AND OPTICAL PROPERTIES

Mn-bearing beraunite forms sheaf-like aggregates of little needle-like individuals in subparallel association. The single crystals have an elongate prismatic shape and a rhombic section. The maximum dimensions of the crystals are about $3 \times 0.3 \times 0.1$ mm. Mn-bearing beraunite is red in color, attesting the oxidized state of the Fe (Moore 1970). The streak is yellow-orange. The luster is vitreous, and the crystals are transparent.

Forms identified by X-ray study and two-circle goniometer measurements are $\{301\}$ and $\{30\bar{1}\}$ and, rarely, $\{001\}$, which define the columnar habit of the crystals; both $\{301\}$ and $\{30\bar{1}\}$ are closely stri-

ated and associated with vicinal faces of the type $\{h0l\}$.

The density is $2.99(2)$ g/cm³, measured using Clerici solution and a torsion balance. The calculated value is 2.978 g/cm³.

Using elongate crystals tabular on $\{301\}$, we measured a moderate birefringence, and a (-) elongation. Using Na light and by comparison with liquids of known index of refraction, β is 1.774 parallel to the elongation; a value of 1.782 was determined normal to this direction.

Using the universal stage with crystals lying on $\{301\}$, we determined that the mineral is biaxial (+) and α emerges 13° (average value) with respect to the normal of the slide; the average values of $2V_Z$ are: red light $83(3)^\circ$, yellow light $78(2)^\circ$, green light $69(5)^\circ$. According to Bonatti (1942), α_{calc} is 1.768, β_{meas} is 1.774, γ_{calc} is 1.783, $2V_Z$ (meas.) is $78(2)^\circ$, $2V_Z$ (calc.) is 78.8° .

The orientation of the indicatrix is $Y = b$, $X:c \equiv \equiv +10^\circ$ (in the obtuse angle). The dispersion is distinct, $r > v$. Pleochroism is $X = Y$ pale yellow, Z red orange.

CHEMICAL COMPOSITION

The beraunite crystals chosen for chemical analysis are needle-like and define sheaf-like aggregates. Once isolated from the associated minerals, crushed beraunite (about 200 mg) was studied by X-ray powder diffraction and then analyzed. The water content was determined (on 100 mg) by ignition to 900°C , and the other constituents were determined by means of Inductively Coupled Plasma. The ferrous/ferric ratio was obtained by titration using 50 mg of material.

The analytical results yielded: Li₂O 0.02, Na₂O 0.15, CaO 0.17, MnO 4.23, FeO 0.01, Fe₂O₃ 49.49, P₂O₅ 31.62, H₂O 15.38, total 101.07 wt.%. The chemical formula, calculated on the basis of 27 atoms of oxygen, is $\text{Fe}_{3.5}^{3+}\text{Mn}_{0.54}\text{Na}_{0.04}\text{Ca}_{0.03}\text{Li}_{0.01}(\text{OH})_5(\text{PO}_4)_{4.06}(\text{OH})_{0.95}(\text{H}_2\text{O})_{4.81}$, which is consistent with the general formula $\text{Fe}^{2+}\text{Fe}_3^{3+}(\text{OH})_5(\text{PO}_4)_4 \cdot 6\text{H}_2\text{O}$ proposed by Fanfani & Zanazzi (1967).

Beraunite from Mangualde is Mn-bearing and more oxidized than the one studied by Fanfani & Zanazzi (1967), from the Eleonore mine (Giessen, Germany). The presence of ferric iron only is consistent with the red color of the mineral (Moore 1970).

X-RAY DATA

Weissenberg photographs show that Mn-bearing beraunite is monoclinic, space group $C2/c$ or Cc . The cell parameters a 20.83(1), b 5.166(3), c 19.26(1) Å and β $93.71(17)^\circ$, were determined by means of a

least-squares refinement of powder-diffraction data (Table 1) obtained using a Gandolfi camera (diameter 114.6 mm) and $\text{FeK}\alpha$ radiation.

The powder-diffraction pattern of Mn-bearing beraunite is consistent with that of Mn-free beraunite from the Palermo mine, New Hampshire, studied by Moore (1970) (as reported in PDF 22-631). However, the Mn-bearing beraunite shows evidence of eighteen previously unobserved reflections: 6.90(vw)(202), 3.622(vw)($\bar{4}04$), 3.246(w)(510), 3.164(mw)(511), 3.126(w)($\bar{2}06$), 2.900(vw)($\bar{6}04$), 2.628(vw)(514), 2.532(vw)($\bar{5}15$), 2.347(vw)($\bar{8}04$), 2.257(vw)($\bar{4}22$), 2.044(vw)(517), 1.891(vw), 1.729(w), 1.583(vw), 1.521(vw), 1.500(vw), 1.489(vw), 1.408(w).

STRUCTURE ANALYSIS

A crystal fragment measuring $0.1 \times 0.2 \times 0.4$ mm was chosen for data collection. Intensity data were collected with an Itai Structure four-circle automatic diffractometer, using graphite-monochromated $\text{MoK}\alpha$ radiation. Collection of data was carried out with θ - 2θ scan mode up to $2\theta = 65^\circ$, h 0 to 31, k 0 to 7, l -28 to 28. No significant variation was observed in the intensity of a standard reflection, monitored every fiftieth measurement. Reflections with $I > 3\sigma(I)$ were considered observed and were used in the least-squares calculations. Data were reduced for Lorentz and polarization factors, and equivalent reflections were merged, thus obtaining a set of 2690 unique reflections. In the first stage of the refinement, no absorption correction was applied. The following unit-cell parameters were refined by a least-squares fit of 2θ values of 66 reflections ($35^\circ < 2\theta < 50^\circ$): a 20.760(3), b 5.154(1), c 19.248(2) Å, β 93.55(1)°, V 2055.4(3) Å³.

The structural refinement was carried out through the SHELX76 least-squares program (Sheldrick 1976), using the fractional coordinates from Fanfani & Zanazzi (1967) as starting values. Refinement with isotropic temperature-factors converged to an R of 0.071.

At this stage an empirical correction for the absorption effects was performed through the DIFABS program by Walker & Stuart (1983). This correction reduced the internal consistency index for equivalent reflections from 8.9 to 1.5%. The refinement with anisotropic thermal parameters for all atoms converged to $R = 0.037$. In the difference Fourier map, some maxima in the expected positions for hydrogen atoms were found. The 9 hydrogen atoms were introduced in the final cycles of least-squares refinement, with isotropic thermal parameters. The final residuals were $R = 0.034$ and $R_w = 0.029$ ($w = 1/[\sigma^2(F_o) + 0.000025(F_o)^2]$) for all the 2690 observed reflections. The final positional parameters and equivalent isotropic temperature-

TABLE 1. X-RAY POWDER-DIFFRACTION DATA

Mn-BEARING BERAUNITE, Mangualde				BERAUNITE (Moore 1970)		
l_{obs}	d_{obs}	d_{calc}	hk1	d_{obs}	I/I_1	hk1
vS	10.39	10.40	200	10.40	100	200
vS	9.62	9.61	002	9.58	50	002
S	7.28	7.29	$\bar{2}02$	7.23	50	$\bar{2}02$
* vw	6.90	6.85	202	-	-	-
w	5.19	5.20	400	5.19	10	400
mS	4.82	4.83	111	4.82	60	111
m	4.44	4.46	402	4.42	50	112
w	4.08	4.08	$\bar{3}11$	4.09	20	$\bar{3}11$
m	3.757	3.753	312	3.75	30	312
* vw	3.622	3.646	404	-	-	-
m	3.481	3.496	$\bar{1}14$	3.47	30	$\bar{1}14$; 600
m	3.423	3.420	313	3.42	20	313
vw	3.330	3.328	602	3.33	10	602
* w	3.246	3.240	510	-	-	-
m	3.208	3.198	314	3.19	40	$\bar{3}14$
* mw	3.164	3.169	511	-	-	-
* w	3.126	3.118	$\bar{2}06$	-	-	-
S	3.081	3.080	314	3.08	60	314
* vw	2.900	2.899	604	-	-	-
w	2.835	2.835	513	2.835	20	513
mw	2.753	2.750	514	2.732	30	604
mw	2.715	2.718	$\bar{1}16$	2.705	30	$\bar{1}16$
* vw	2.628	2.627	514	-	-	-
w	2.579	2.583	020	2.582	30	020
* vw	2.532	2.540	515	-	-	-
w	2.489	2.490	221	2.488	20	221
w	2.429	2.420	515	2.422	20	515
* vw	2.347	2.349	804	-	-	-
w	2.315	2.313	420	2.312	25	$\bar{7}14$
* vw	2.257	2.263	422	-	-	-
w	2.235	2.236	408	2.227	20	408
vw	2.151	2.156	423	2.154	10	423
m	2.112	2.113	$\bar{3}18$	2.109	30	$\bar{3}18$
vw	2.084	2.085	912	2.082	10	$\bar{9}12$; 10.0.0
w	2.063	2.062	424	2.058	10	424
* vw	2.044	2.046	517	-	-	-
m	2.009	2.009	622	2.009	10	622
vw	1.977	1.977	518	1.972	10	518
m	1.927	1.929	624	1.923	30	624
* vw	1.891	1.892	-	-	-	-
mS	1.867	1.866	-	1.870	10	-
mw	1.828	1.829	-	1.830	10	-
vw	1.805	1.806	-	1.813	10	-
w	1.786	1.786	-	1.784	10	-
vw	1.767	1.767	-	1.767	10	-
vw	1.749	1.748	-	1.742	10	-
* w	1.729	1.728	-	-	-	-
mw	1.710	1.710	-	1.718	20	-
w	1.689	1.690	-	1.691	15	-
vw	1.661	1.660	-	1.662	10	-
vw	1.641	1.642	-	1.641	10	-
m	1.619	1.620	-	1.621	30	-
w	1.602	1.602	-	1.599	10	-
* vw	1.583	1.584	-	-	-	-
mw	1.570	1.571	-	1.570	10	-
mw	1.540	1.540	-	1.541	20	-
* vw	1.521	1.521	-	-	-	-
* vw	1.500	1.501	-	-	-	-
* vw	1.489	1.489	-	-	-	-
w	1.460	1.461	-	1.459	20	-
w	1.435	1.434	-	1.436	20	-
* w	1.408	1.409	-	-	-	-

* = previously unobserved reflection
 vS = very strong; S = strong; m = moderate;
 w = weak; vw = very weak

TABLE 2. Mn-BEARING BERAUNITE: POSITIONAL AND THERMAL PARAMETERS

Site	x	y	z	U* eq
Fe1	0.0	0.0	0.0	0.0131(2)
Fe2	0.25	0.25	0.0	0.0093(2)
Fe3	0.04363(2)	0.27055(10)	0.17228(2)	0.0110(1)
Fe4	0.10754(2)	0.03252(10)	0.41240(2)	0.0107(1)
P1	0.10480(4)	0.47752(17)	0.02599(4)	0.0081(2)
P2	0.40746(4)	0.03940(18)	0.18244(4)	0.0092(2)
O1	0.1772(1)	0.4856(5)	0.0154(1)	0.0126(6)
O2	0.4273(1)	0.2454(5)	0.0185(1)	0.0119(6)
O3	0.4242(1)	0.2402(5)	0.4996(1)	0.0145(7)
O4	0.0925(1)	0.4392(5)	0.1020(1)	0.0189(8)
O5	0.4794(1)	0.0458(5)	0.1684(1)	0.0141(6)
O6	0.1017(1)	0.4779(5)	0.2410(1)	0.0157(7)
O7	0.3788(1)	0.3087(4)	0.1655(1)	0.0124(7)
O8	0.1299(1)	0.3414(5)	0.3643(1)	0.0134(7)
O9	0.0076(1)	0.0464(6)	0.3965(1)	0.0168(7)
O10	0.1912(1)	0.0172(6)	0.4622(1)	0.0145(7)
O11	0.0	0.1035(8)	0.25	0.0173(11)
O12	0.3857(2)	0.4728(6)	0.3214(2)	0.0245(9)
O13	0.2471(1)	0.0839(6)	0.0977(1)	0.0187(8)
O14	0.2310(2)	0.3490(8)	0.2156(2)	0.0387(13)
H1	0.009(4)	0.950(15)	0.388(4)	0.17(4)
H2	0.191(2)	0.117(9)	0.476(2)	0.04(2)
H3	-0.002(6)	0.978(9)	0.235(6)	0.14(3)
H4	0.127(4)	0.907(16)	0.154(4)	0.14(4)
H5	0.113(3)	0.909(14)	0.215(4)	0.12(3)
H6	0.289(3)	0.974(12)	0.111(3)	0.10(2)
H7	0.241(2)	0.161(9)	0.126(2)	0.03(2)
H8	0.252(2)	0.957(10)	0.276(3)	0.04(2)
H9	0.191(3)	0.386(13)	0.218(3)	0.09(3)

* U_{iso} for hydrogen atoms. Refined site-occupancies for the octahedral sites: Fe1: Fe₈₀Mn₂₀; Fe2: Mn₁₀₀; Fe3 and Fe4: Fe₁₀₀. E.S.D. values are given in parentheses and refer to the last digit.

TABLE 3. Mn-BEARING BERAUNITE: SELECTED BOND-DISTANCES (Å)

Fe1 - O2	2.048(2)	Fe2 - O1	1.975(2)
- O3	2.066(2)	- O10	1.951(3)
- O9	2.022(2)	- O13	2.070(2)
Average	2.045	Average	1.999
Fe3 - O4	1.945(2)	Fe4 - O2	2.145(2)
- O5	1.945(2)	- O3	2.194(2)
- O6	2.036(2)	- O7	1.927(2)
- O9	2.011(2)	- O8	1.913(2)
- O11	1.992(2)	- O9	2.080(2)
- O12	2.121(4)	- O10	1.933(2)
Average	2.008	Average	2.032
P1 - O1	1.530(2)	P2 - O5	1.534(2)
- O2	1.558(2)	- O6	1.531(2)
- O3	1.549(3)	- O7	1.537(2)
- O4	1.514(2)	- O8	1.538(2)
Average	1.538	Average	1.535
O9 - H1	0.52(8)	O9 - H1 ... O5	2.886(4)
O10 - H2	0.58(5)	O10 - H2 ... O1	2.781(4)
O11 - H3	0.70(7)	O11 - H3 ... O5	3.290(4)
O12 - H4	0.64(8)	O12 - H4 ... O13	3.299(5)
O12 - H5	0.77(7)	O12 - H5 ... O7	3.112(4)
O13 - H6	1.05(6)	O13 - H6 ... O8	2.896(3)
O13 - H7	0.69(4)	O13 - H7 ... O14	2.687(5)
O14 - H8	0.67(5)	O14 - H8 ... O14	2.981(5)
O14 - H9	0.86(6)	O14 - H9 ... O6	2.837(5)

factors are given in Table 2. Selected bond-distances are given in Table 3. Observed and calculated structure-factors and anisotropic temperature-factors have been submitted to the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Canada K1A 0S2.

DISCUSSION

Our refinement confirms the main features of the crystal structure of beraunite (Fanfani & Zanazzi 1967). The increased number of observed reflections allowed us to obtain lower standard deviations on coordinates and distances; moreover, it was possible to locate and refine the positions of the hydrogen atoms which, in the refinement carried out by Fanfani & Zanazzi (1967), were only assumed to be present for crystal-chemical reasons. Actually, a bond-valence summation (Table 4), computed according to Brown & Wu (1976), and assuming 100% Fe occupancy in the octahedral sites, clearly indicates that O9, O10 and O11 are hydroxyl groups, and O12, O13 and O14 belong to water molecules

[the contribution of the hydrogen bonds in the electrostatic valence-balance calculations was computed according to Lippincott & Schroeder (1955)]. The proposed scheme of hydrogen bonds is reported in Table 3. We can observe that O14 does not belong to any polyhedron and is involved in the system of water molecules only. All the hydrogen bonds seem to be acceptable, with O - H ... O angles ranging from 117° to 174°; the difficulties in the refinement of the positions of the hydrogen atoms, resulting in some "incorrect" distances and angles, are due to the presence of atoms with much higher scattering power.

We refined the occupancies of iron and manganese in the octahedral sites (*cf.* Table 2), but the values obtained have little or no meaning, because of the very similar scattering power of these two atoms. However, some hypotheses may be put forward, if one considers the mean *M-O* distances in Mn-bearing beraunite with respect to those in "normal" beraunite:

1) The lack of Jahn-Teller distortion in the octahedral sites indicates that all manganese in Mn-bearing beraunite probably is in the reduced state;

TABLE 4. ELECTROSTATIC VALENCE SUMMATION FOR Mn-BEARING BERAUNITE

	Fe1	Fe2	Fe3	Fe4	P1	P2	$\Sigma c'_v$	corr. for H bonds	Σc_v
01		0.551			1.285		1.836	+0.174	2.010
02	0.449			0.343	1.196		1.988		1.988
03	0.427			0.302	1.222		1.951		1.951
04			0.601		1.352		1.953		1.953
05			0.605			1.264	1.869	+0.177	2.046
06			0.466			1.273	1.739	+0.153	1.892
07				0.635		1.259	1.894	+0.078	1.972
08				0.661		1.254	1.915	+0.131	2.046
09	0.483		0.499	0.412			1.394	-0.135	1.259
010		0.594		0.625			1.219	-0.174	1.045
011			0.526				1.052	-0.042	1.010
012			0.370				0.370	-0.118	0.252
013		0.423					0.423	+0.040 -0.347	0.116
014							0	+0.216 -0.153	0.063
Σa_v	2.718	3.136	3.067	2.978	5.055	5.050			

likewise, the occurrence of Mn^{2+} and Fe^{3+} in several phosphate minerals from granitic pegmatites was pointed out by Moore (1973).

2) Mn^{2+} seems to be located in Fe1 and Fe2 sites, because the mean $M-O$ distances in Fe3 and Fe4 octahedra are very close to the corresponding distances in beraunite (2.008 and 2.00 Å in Fe3, and 2.032 and 2.03 Å in Fe4, respectively, whereas the mean $M-O$ distances increases from 2.02 to 2.045 Å in Fe1, and from 1.97 to 1.999 Å in Fe2.

3) The bond-valence summations display a greater deviation from the theoretical value of 3 v.u. in the octahedral site Fe1, which has a Σa_v of 2.718 v.u.; this could indicate major partial substitution of Mn^{2+} for Fe^{3+} in this site; moreover, from the crystal-chemical viewpoint, Fe1 seems to be the preferred site for such a substitution, with a consequent increase in the volume of the coordination polyhedron; in fact, the Fe1 octahedron shares two of its faces with two opposite Fe3 octahedra, and the $Fe^{3+} - Mn^{2+}$ substitution allows the Fe1-Fe3 distance to be increased, which represents an energetically favored configuration.

On the basis of the chemical and single-crystal X-ray data, we cannot consider the Mn-bearing beraunite as a new mineralogical species. The beraunite from Mangualde represents a Mn-rich variety of beraunite, in which Mn^{2+} plays the same role as Fe^{2+} in "normal" beraunite.

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