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PHYSICS

Crystal Structure of Belovite-(La)

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1. Belovite-(La) $Sr_3Na(La, Ce)[PO_4]_3(F, OH)$ was approved as a new mineral species by the Commission on New Minerals and Mineral Names on September 13, 1995. The description of belovite-(La) as a new mineral species was given in [1]. In this paper, we report the main results of a study of the crystal structure of belovite-La by the Rietveld method with the use of powder-diffraction data.

The belovite mineral was named in honor of an outstanding scientist (crystal chemistry) N.V. Belov; the authors of this paper belong to the scientific school that he founded. The mineral falls in the apatite $Ca_5[PO_4]_3(F, OH)$ structure type [2]; however, as distinct from the apatite and strontium-substituted apatite $(Sr, Ca)_5[PO_4]_3(F, OH)$ [3], it features a cationic ordering [4]. Correspondingly, the symmetry is reduced to the space group $P\bar{3}$ as compared to the space group $P6_3/m$ in apatite. The rare-earth elements occupy a separate site in the belovite structure. Therefore, an identifier was later added to the name of belovite to indicate the dominant rare-earth element (REE); e.g., belovite-(Ce) [5].

2. Belovite-(La) was found at two sites of the Khibin alkaline massif (Kol'skii peninsula) at the natrolite zone of pegmatite in association with microcline, aegirine, lamprophillite, pectolite, gaidonnayite, and gerasimovskite (Mt. Kukisvumchorr) and in a small-scale natrolite vein in association with analcite, murmanite, and safflorite (Mt. Eveslogchorr). The mineral forms colorless transparent crystals of prismatic habitus. The grains are brittle and do not exhibit cleavage cracks.

Chemical composition of belovite-(La) (as found at the Mt. Kukisvumchorr site) was determined with a Camebax micro-beam analyzer as including Na_2O (4.09 wt %), CaO (0.50%), SrO (40.09%), BaO (2.35%), Y_2O_3 (0.01%), La_2O_3 (13.08%), Ce_2O_3 (8.15%), Pr_2O_3 (0.30%), Nd_2O_3 (0.30%), Sm_2O_3 (0.03%), Gd_2O_3 (0.01%), ThO_2 (0.43%), SiO_2 (0.24%), P_2O_5 (28.3%), SO_3 (0.03%), F (2.04%), H_2O^+ (0.22%), and $-(O=F_2)$ (0.86%) with the total being 99.31 wt %. The measured density of the mineral was 4.19 g/cm^3. A similarity between the X-ray diffraction patterns and infrared spectra of the mineral under study and those of belovite-(Ce) confirmed the close structural consanguinity of these two minerals and made it possible to study belovite-(La) by the Rietveld method.

3. We prepared a powder sample from a single-crystalline fragment of the mineral. The acquisition of data was performed at an ADP-2 computerized X-ray powder diffractometer with the use of λCuK_α radiation and

Table 1. Belovite-(La). Parameters of the data acquisition and of the structure refinement by the Rietveld method with the use of ionic scattering curves

Unit-cell parameters	
a, Å	9.6641(1)
c, Å	7.1825(1)
V_0, Å^3	508.94(1)
The number of formula units z	2
Density ρ_{calc}, (g/cm^3)	4.15
Space group	$P\bar{3}$
The 2θ range	11°–100°
Asymmetry, 2θ	<36°
The number of Braggs' reflection spots	873
The number of the parameters to be refined	32
R_p	3.46
R_{wp}	4.45
R_{exp}	3.71
R_B	2.75
R_F	4.11
s*	1.20
DWD**	1.48
σ_x***	1.500

Notes: * $s = R_{wp}/R_{exp}$, where R_{exp} is the expected value of R_{wp}.
** DWD is the statistics by Durbin–Watson [8].
*** σ_x is a multiplier for the standard deviations calculated [9].

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Table 2. X-ray diffraction spectrum of belovite-(La)

I	d_{exp}	d_{calc}	hkl	I	d_{exp}	d_{calc}	hkl
14	7.21	7.18	001	36	1.7985	1.7966	004
26	5.46	5.45	101	4	1.6524	1.6513	024
16	4.195	4.187	200	4	1.5836	1.5826	240
26	4.008	4.011	111	8	1.5636	1.5626	214
87	3.590	3.593	002	7	1.5193	1.5180	052
65	3.307	3.302	102	8	1.5117	1.5108	304
32	3.171	3.164	210	7	1.4998	1.4989	323
100	2.896	2.897	211	4	1.4733	1.4725	511
100	2.881	2.885	112	7	1.4716	1.4708	332
54	2.795	2.792	300	3	1.3214	1.3207	243
10	2.730	2.721	022	3	1.3191	1.3185	251
5	2.606	2.603	031	3	1.3096	1.3090	215
4	2.400	2.396	003	6	1.3018	1.3012	602
9	2.325	2.323	130	7	1.2818	1.2812	144
4	2.306	2.304	103	2	1.2745	1.2739	513
3	2.206	2.204	302	3	1.2572	1.2566	252
23	2.149	2.146	113	3	1.2094	1.2089	440
3	2.096	2.094	400	2	1.1956	1.1951	006
4	2.081	2.079	203	3	1.1863	1.1858	106
26	2.007	2.006	222	2	1.1632	1.1627	116
15	1.9521	1.9505	132	2	1.1514	1.1510	325
36	1.9118	1.9103	213	4	1.1357	1.1352	532
10	1.8575	1.8561	321	2	1.0738	1.0735	226
14	1.8289	1.8275	140	3	1.0650	1.0647	136
23	1.8105	1.8092	402	2	1.0401	1.0398	406

Table 3. Belovite-(La). The coordinates and the isotropic and anisotropic temperature factors (in Å^2) of basis atoms

Atom	Site	x	y	z		B_{iso}
A(1)	2(d)	1/3	2/3	0.015(2)		
A(2)	2(d)	1/3	2/3	0.512(1)		
A(3)	6(g)	0.2372(5)	−0.0195(6)	0.2449(5)		
P	6(g)	0.4023(9)	0.367(1)	0.2428(9)		2.5(2)
O(1)	6(g)	0.481(2)	0.149(2)	0.747(2)		3.4(9)
O(2)	6(g)	0.326(2)	0.265(2)	0.085(2)		4.5(8)
O(3)	6(g)	0.363(2)	0.292(2)	0.433(2)		1.9(8)
O(4)	6(g)	0.536(2)	0.111(2)	0.235(2)		3.6(5)
O(5)	2(c)	0	0	0.287(4)		2.0(1.0)
Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
A(1)	0.008(3)	0.008(3)	0.007(1)	0.004(3)	0	0
A(2)	0.0097(9)	0.0097(9)	0.0137(1)	0.0049(9)	0	0
A(3)	0.0127(9)	0.0129(9)	0.0204(7)	0.0032(9)	−0.003(1)	0.0028(7)

Notes: $T = \exp[-1/4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$

$T = \exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$

Table 4. Selected interatomic distances (in Å) and angles (in deg) in the belovite-(La) structure

A(1)-polyhedron	A(2)-polyhedron	A(3)-polyhedron
A(1)–O(1) 2.47(2) × 3	A(2) – O(1) 2.58(2) × 3	A(3)–O(1) 2.70(2)
O(2) 3.10(2) × 3	O(3) 2.79(2) × 3	O(2) 2.69(2)
O(4) 2.59(2) × 3	O(4) 2.61(2) × 3	O(2)' 2.44(2)
		O(3) 2.95(2)
		O(3)' 2.48(2)
		O(4) 2.51(2)
		O(5) 2.411(7)
The average 2.72	2.66	2.60
	P-tetrahedron	
P–O(1) 1.56(2)	O(1)–P–O(2)	105.(1)
O(2) 1.44(2)	O(1)–P–O(3)	102.(1)
O(3) 1.50(2)	O(1)–P–O(4)	109.(1)
O(4) 1.45(2)	O(2)–P–O(3)	118.(1)
	O(2)–P–O(4)	116.(1)
	O(3)–P–O(4)	106.(1)
The average 1.49		109

Table 5. Occupancies of the A(1)–A(3) sites in the belovite-(La) structure

Site	Multiplicity	REE^{3+}	Ion			
			Sr^{2+}	Na^{+}	Ca^{2+}	Ba^{2+}
A(1)	0.333	0.071(2)		0.259(2)		
A(2)	0.333	0.262(2)		0.068(2)		
A(3)	1.0		0.918(7)		0.020(7)	0.040(4)

a Ni filter; the exposure was 5 s, and the step amounted to 0.02° of 2θ. All the computations were executed with a WYRIET program (version 3.3) [6] in the context of the space group $P\bar{3}$. The basis-atom coordinates were adopted from a study [7] concerned with refining of the belovite-(Ce) structure and were used as input data in the computations. The Pearson function (six FWHMs were needed) was employed to describe the line shapes. The ionic-scattering curves were used. The belovite-(La) structure was refined in the isotropic/anisotropic approximation. The parameters of data acquisition, the results of refining, the evaluation of X-ray diffraction spectrum, atomic coordinates, isotropic/anisotropic temperature factors, the selected interatomic distances, and the occupancies of the sites are listed in Tables 1–5. Figure 1 shows the calculated and experimental X-ray diffraction spectra of belovite-(La).

4. We refined the occupancies of the sites A(1) = 2(d), A(2) = 2(d), and A(3) = 6(g), where heavy cations, namely, REE^{3+}, Sr^{2+}, Ca^{2+}, Ba^{2+}, and Na^{+}, reside. Among the rare-earth elements (REEs), La and Ce are dominant; therefore, the *f*-curve for La^{3+} was used in the refining. The temperature factors were calculated to anisotropic approximation for the sites A(1)–A(3); this resulted in a decrease in the *R*-factors. Analysis of the occupancies of the sites reveals that A(1) = $REE^{3+}_{0.213}Na^{+}_{0.777}$, A(2) = $REE^{3+}_{0.786}Na^{+}_{0.204}$, and A(3) = $Sr^{2+}_{0.918}Ba^{2+}_{0.04}Ca^{2+}_{0.02}$; this is indicative of cationic ordering in the structure of belovite-(La) (Table 5) and makes it possible to separate out the A(2) site as occupied predominantly by lanthanum.

5. The belovite-(La) mineral belongs to the widely occurring type of $Ca_5(PO_4)_3F$ apatite (Fig. 2). The P-tetrahedrons bind the A(1)–A(3) polyhedrons into a unified crystal framework. While there are two independent sites for Ca (space group $P6_3/m$) in apatite, one of the sites in belovite (space group $P\bar{3}$) is separated into two sites of the same symmetry owing to cationic ordering; i.e., the sites A(1) and A(2) differ only in the *z*-coordinate (Table 3). The prevalence of La at the site A(2) made it possible to treat this mineral as a new mineral species. Interatomic distances in the A(2)

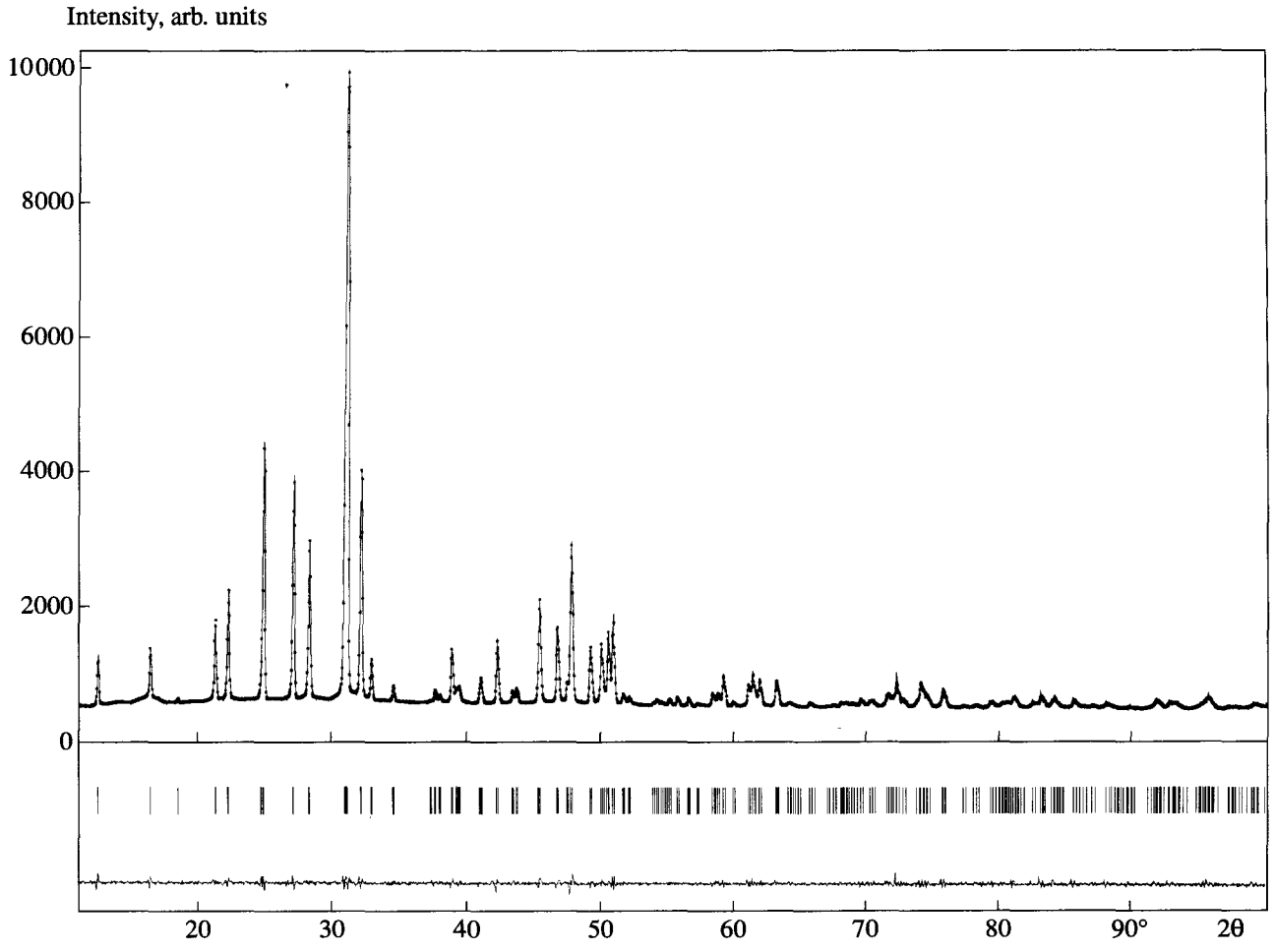

Fig. 1. The experimental (points) and theoretical (solid line) X-ray diffraction spectra of belovite-(La).

polyhedron are quite comparable to those reported in [7] for belovite-(Ce). Only the distance from A(2) to O(3) increases to 2.79 Å as compared to the similar distance (2.69 Å) in belovite-(Ce) [7]. Correspondingly, the distance between P and O(3) in the P-tetrahedron is shortened to 1.50 Å as compared to 1.55 Å reported in [7]. The A(1) polyhedron features a large spread in interatomic distances; namely, six distances [to the O(1) and O(4) sites] vary from 2.47 to 2.59 Å, whereas the further three distances [from A(1) to O(3)] are equal to 3.10 Å. In fact, the A(1) polyhedron is a regular octahedron. The A(3) seven-coordinated polyhedron is virtually no different from the similar polyhedrons in the structures of apatite and belovite-(Ce).

In the structure of belovite-(La), the P-tetrahedron features the shortened average interatomic distance (1.49 Å) as compared to 1.54 Å in belovite-(Ce). Chemical analysis indicated that belovite-La contains a quantity of fluorine. By analogy with the structure of apatite, the atoms of F are likely to reside at the O(5) site together with atoms of O.

Thus, the refinement of the crystal structure of belovite-(La) demonstrated that the structure of this mineral is a derivative of the apatite structure type with reduction of the symmetry from $P6_3/m$ to $P\bar{3}$ due to cationic ordering.

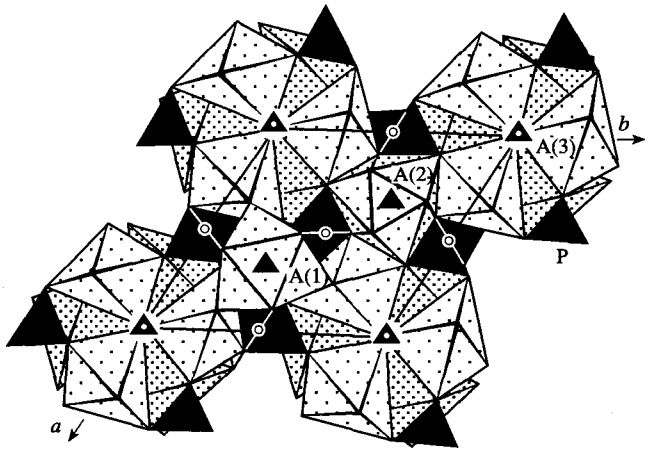

Fig. 2. Projection of the crystal structure of belovite-(La) on the *xy*-plane.

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REFERENCES

1. Pekov, I.V., Kulikova, I.M., Kabalov, Yu. K., *et al.*, *Zap. Vseross. Mineral. O-va*, 1996, vol. 125, no. 3, pp. 101–103.
2. Beevers, S.A., *Mineral. Mag.*, 1946, vol. 27, p. 254.
3. Klevtsova, R.F., *Zh. Strukt. Khim.*, 1964, vol. 5, no. 2, pp. 318–320.
4. Klevtsova, R.F. and Borisov, S.V., *Zh. Strukt. Khim.*, 1964, vol. 5, no. 2, pp. 151–153.
5. Miyawaki, R. and Nakai, I., *Crystal Structure of Rare Earth Minerals. Handbook Phys. Chem. RE*, Nagoya: Rare Earth Soc. Japan, 1993, vol. 16.
6. Schneider, J., Profile Refinement on IBM PCs, *Proc. IUCr Int. Workshop on the Rietveld Method*, Petten, 1989, p. 71.
7. Nadezhdina, T.N., Pushcharovskii, D.Yu., and Khomyakov, A.P., *Mineralog. Zh.*, 1987, vol. 9, no. 2, pp. 45–48.
8. Hill, R.G. and Flack, H.D., *J. Appl. Crystallogr.*, 1991, vol. 20, pp. 356–361.
9. Berar, J.-F. and Lelann, P., *J. Appl. Crystallogr.*, 1991, vol. 24, pp. 1–5.

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