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The crystal structure of a rare earth bearing leucophanite: $(Ca,RE)CaNa_2Be_2Si_4O_{12}(F,O)_2$

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Dedicated to Prof. Dr. F. Liebau on the occasion of his 65 birthday

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Triclinic leucophanite / Crystal structure / Rare earths in leucophanite

Summary. The orthorhombic symmetry $P2_12_12_1$ of leucophanite $CaNaBeSi_2O_6F$ is lowered to triclinic $P1$ ($a = 7.417$ Å, $b = 7.398$ Å, $c = 9.986$ Å, $\alpha = 90°$, $\beta = 90°$, $\gamma = 90°$, $Z = 4$) by the presence of rare earths, which replace calcium (roughly one RE atom for each 16 calcium sites) in two of the four sites equivalent in the orthorhombic unit cell. Because of the strong difference in number of electrons between calcium and rare earths, the intensities of the reflections show a clear triclinic symmetry, whereas the lattice dimensions, atomic coordinates, bond distances and angles are practically unaffected by the above replacement and retain the orthorhombic symmetry.

Introduction

The crystal structure of leucophanite $CaNaBeSi_2O_6F$ was determined by Cannillo, Giuseppetti and Tazzoli (1967) with X-ray data obtained by the Weissenberg method. The structure is analogous to that of melilite (Warren, 1930; Smith, 1953), but the ordering of the pairs Ca/Na, Si/Be and O/F produces both the doubling of the c edge and the lowering of the symmetry from the space group $P\bar{4}2_1m$ to $P2_12_12_1$. Actually the authors suggested that the true symmetry could be still lower, i.e. $P1$, because of slight differ-

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ences observed in the intensities of the equivalent reflections, and the presence of three forbidden *h*00 reflections with *h* odd. However, in a successive paper, Cannillo, Giuseppetti and Tazzoli (1969), after a new collection of experimental data, confirmed the orthorhombic symmetry and suggested that the observed anomalies had to be imputed to double reflection effects.

More recently, the structural arrangement in orthorhombic leucophanite was confirmed by Grice and Hawthorne (1989).

The specimen from Mt. Saint Hilaire (Quebec, Canada), here studied, has a really triclinic *P*1 symmetry in the intensities of the reflections: it follows from the presence of rare earths, that replace partially calcium in an ordered way.

A rare earths microprobe analysis with a WDS-EMP CAMEBAX apparatus gave nearly $RE_2O_3 = 3\%$ (mean of the measurements in 27 points of the specimen), with Ce, Nd, La, Pr in order of decreasing amount.

Experimental details

Table 1 reports the main X-ray experimental and refinement data. The intensities of all reflections within $\theta = 2-30°$ were collected; they were preliminarily used to calculate some statistics to evidence the possible equivalence of groups of the measured reflections according to different point symmetries. Obviously, the best equivalence was observed between *hkl* and $\overline{hkl}$: the low R_{sym} indicated a good precision in the measurements, in particular because the very small differences between the centrosymmetrical reflections had to be imputed not only to the experimental errors, but also to the anomalous dispersion. Higher R_{sym}'s were calculated for three possible monoclinic symmetries and for the orthorhombic symmetry: apart from the triclinic symmetry, the second best result was obtained for point symmetry $1\,2/m\,1$.

The refinement of the crystal structure with the set of 6288 observed reflections started in the space group *P*1 from the atomic parameters reported in the paper by Cannillo et al. (1967): 48 atomic positions were calculated from the coordinates of the 12 atoms in the orthorhombic leucophanite, on the basis of the four equivalent positions in the space group $P2_12_12_1$.

During the first least squares cycles of refinement it was observed that the differences *F*(obs) − *F*(calc) for those *hkl* and *khl* reflection pairs, which had notably differing structure amplitudes, were systematically negative for the most intense reflection and positive for the less intense reflection. This evidence indicated that the specimen was actually a (110) twin formed by two individuals with differing sizes. The formation of this twin follows from the "tetragonal" topology derived from the melilite structure.

Table 1. X-ray crystal and refinement data.

X-ray single crystal diffractometer Philips PW 1100
Radiation: Mo$K\alpha$ monochromatized on graphite

Formula unit (Ca,RE)$CaNa_2Be_2Si_4O_{12}(F,O)_2$

Unit cell dimensions (Å):

a	7.417(4)	
b	7.398(4)	
c	9.986(4)	
α (°)	90.00(2)	
β (°)	90.00(2)	
γ (°)	90.00(2)	
Volume (Å^3)	547.9	
Space group	$P1$	Z 2

Crystal dimensions (mm) $0.14 \times 0.23 \times 0.41$

Scan: mode ω, width 2.1°, speed 0.035°/s, range 2–30°
Mean variation in three standard reflections 3.6%
Absorption correction after North et al. (1968)

Measured reflections ($\pm h$, $\pm k$, $\pm l$)	6431
Observed reflections ($I/\sigma(I) \geqslant 10$)	6288

Statistics obtained by averaging the F_o's according to different symmetries;
$R_{\mathrm{sym}} = \Sigma|F(hkl) - mF|/\Sigma F(hkl)$:

symmetry	averaged reflections	R_{sym}
$\bar{1}$	$mF = [F(hkl) + F(\overline{hkl})]/2$	0.013
$1\ 2/m\ 1$	$mF = [F(hkl) + F(h\bar{k}l) + F(\overline{hkl}) + F(\bar{h}k\bar{l})]/4$	0.026
$1\ 1\ 2/m$	$mF = [F(hkl) + F(hk\bar{l}) + F(\overline{hkl}) + F(\overline{hk}l)]/4$	0.036
$2/m\ 1\ 1$	$mF = [F(hkl) + F(\bar{h}kl) + F(\overline{hkl}) + F(h\overline{kl})]/4$	0.038
mmm	$mF = [F(hkl) + F(\bar{h}kl) + F(h\bar{k}l) + F(hk\bar{l}) +$ $+ F(\overline{hkl}) + F(h\overline{kl}) + F(\bar{h}k\bar{l}) + F(\overline{hk}l)]/8$	0.041

Refinements:

Ratio between the (110) twin individuals	0.732/0.268
R (obs) space group $P1$	0.013
R (meas)	0.014
R (obs) neglecting the anomalous dispersion	0.017
R (obs) space group $P12_11$	0.028
R (obs) space group $P2_12_12_1$	0.045

A particular least squares computer program was prepared; it was able to refine the fractions of the two twin individuals, besides the usual atomic parameters. The refinement converged after some cycles of least squares. During the least squares cycles, the occupancy (x) of an atomic species was varied against that (y) of a second species ($x + y = 1$), for the sites involved in isomorphous replacements. On the basis of crystal chemical considerations, both general and peculiar to the structure of leucophanite (see next section), the atomic pairs were: Ca^{2+} against Ce^{3+} (Ca sites), Na^+ against

Table 2. Site occupancies, atomic coordinates (× 10^4), equivalent isotropic temperature factors (× 10^4), and deviations from the mean monoclinic (*Dvm*) and orthorhombic (*Dvo*) positions.

Atom	Site population	*x*	*y*	*z*	U_{eq}	*Dvm* (Å)	*Dvo* (Å)
Ca *a*	Ca 0.92, RE 0.08	1037(0)	−1711(0)	96(0)	98(1)	0.007	0.002
Ca *b*	Ca 0.82, RE 0.18	−1030(1)	3306(1)	4904(1)	106	0.007	0.013
Ca *c*	Ca 0.98, RE 0.02	3963	1720	−4903	116	0.003	0.007
Ca *d*	Ca 0.98, RE 0.02	−3968	−3282	−100	107	0.003	0.006
Na *a*	Na 0.93, Ca 0.07	742(2)	−1473(2)	4973(1)	204(4)	0.005	0.018
Na *b*	Na 0.98, Ca 0.02	−734	3526	34	202	0.005	0.011
Na *c*	Na 0.87, Ca 0.13	4279	1481	−27	207	0.017	0.007
Na *d*	Na 0.98, Ca 0.02	−4315	−3515	−4952	228	0.017	0.030
Si1 *a*	Si 1.	−2583(1)	131(1)	−2508(1)	64(2)	0.003	0.003
Si1 *b*	Si 1.	2575	−4870	−2492	63	0.003	0.005
Si1 *c*	Si 1.	−2415	−125	2490	66	0.004	0.005
Si1 *d*	Si 1.	2419	4873	2503	67	0.004	0.004
Si2 *a*	Si 1.	1077(1)	1504(1)	−2256(1)	64(2)	0.004	0.004
Si2 *b*	Si 0.94 Be 0.06	−1086	−3492	−2741	51	0.004	0.006
Si2 *c*	Si 0.97 Be 0.03	3922	−1499	2737	54	0.003	0.005
Si2 *d*	Si 0.94 Be 0.06	−3918	3502	2258	57	0.003	0.003
Be *a*	Be 0.97 Si 0.03	1109(4)	1313(4)	2803(3)	78(7)	0.005	0.010
Be *b*	Be 0.94 Si 0.06	−1095	−3686	2197	100	0.005	0.002
Be *c*	Be 0.98 Si 0.02	3905	−1310	−2199	64	0.004	0.002
Be *d*	Be 0.96 Si 0.04	−3916	3692	−2803	76	0.004	0.009
O1 *a*		2420(2)	63(2)	−1610(2)	94(5)	0.004	0.005
O1 *b*		−2431	−4934	−3393	99	0.004	0.009
O1 *c*		2581	−51	3387	91	0.003	0.007
O1 *d*		−2581	4950	1606	93	0.003	0.007
O2 *a*		1031(2)	1594(2)	−3844(2)	104(5)	0.007	0.015
O2 *b*		−1048	−3410	−1156	98	0.007	0.004

O2 *c*		3948	−1582	1148	98	0.006	0.007
O2 *d*		−3936	3419	3845	99	0.006	0.012
O3 *a*		−1638(2)	−1508(2)	−3394(2)	98(5)	0.003	0.004
O3 *b*		1631	3488	−1606	100	0.003	0.006
O3 *c*		−3359	1515	1609	96	0.003	0.004
O3 *d*		3360	−3488	3385	99	0.003	0.006
O4 *a*		−1620(2)	−1692(2)	1531(2)	105(5)	0.004	0.011
O4 *b*		1622	3308	3462	99	0.004	0.009
O4 *c*		−3357	1703	−3468	97	0.002	0.009
O4 *d*		3355	−3301	−1536	94	0.002	0.010
O5 *a*		−881(2)	742(2)	3435(2)	96	0.002	0.006
O5 *b*		886	−4258	1563	93	0.002	0.007
O5 *c*		−4121	−732	−1576	92	0.005	0.009
O5 *d*		4110	4263	−3428	94	0.005	0.005
O6 *a*		−918(2)	1010(2)	−1605(2)	100(5)	0.004	0.007
O6 *b*		909	−3993	−3393	100	0.004	0.010
O6 *c*		−4071	−1024	3383	98	0.005	0.012
O6 *d*		4079	3977	1609	104	0.005	0.006
F *a*	F 0.94 O 0.06	1033(2)	1282(2)	1224(2)	145(4)	0.005	0.005
F *b*	F 0.79 O 0.21	−1020	−3716	3775	132	0.005	0.009
F *c*	F 0.87 O 0.13	3957	−1294	−3771	131	0.006	0.010
F *d*	F 0.86 O 0.14	−3971	3711	−1228	136	0.006	0.003
Mean deviation from the monoclinic coordinates (Å)						0.005	
Mean deviation from the orthorhombic coordinates							0.008

Note: Numbers in parentheses are e.s.d.'s referred to the last digit: they are equal for sites equivalent in the orthorhombic symmetry Standard deviations in occupancies of sites are: 0.001 for Ca, 0.003 for Na, Si2 and Be, 0.02 for F.

The four sites labelled *a*, *b*, *c*, *d* derive from the unique site in the orthorhombic leucophanite; they correspond to the equivalent positions: $x\ y\ z$, $-x\ 1/2+y\ 1/2-z$, $1/2-x\ -y\ 1/2+z$, $1/2+x\ 1/2-y\ -z$.

Ca^{2+} (Na sites), Si against Be (sites Si2 and Be), and O against F (sites O2 and F). A mixed curve obtained by equal fractions of the scattering factors for O and O^{2-} (Tokonami, 1965) was used for the remaining O sites. To prevent correlations between the scale factor, the occupancies and the temperature factors of sites, the refinement proceeded by alternate cycles, in which either the occupancies or the positional and temperature parameters of each site were varied; no site occupancy was refined together with the scale factor. No weight function was applied during the refinement.

To test the reliability of the triclinic symmetry, three further refinements were carried out using always the same set of 6288 observed reflections, respectively in the same space group $P1$ (without considering the anomalous dispersion) and in space groups $P12_11$ and $P2_12_12_1$. The R factors concerning these refinements are in Table 1: all of them were larger than that obtained in the first triclinic refinement.

As the two last worse results could be imputed to the reduction of the number of the atomic positions, a further test of the internal coherency of the triclinic experimental data was carried out: a new set of structure amplitudes was prepared by means of random permutations of the F_o's within each group of the reflections which are equivalent in the orthorhombic symmetry. The refinement with these data in space group $P1$ gave $R = 0.045$, *i.e.* the same R obtained from the refinement in space group $P2_12_12_1$, and equal RE contents in all Ca sites.

Some other determinations were carried out to clear the nature of the twinning, which was undetectable under the polarizing microscope. The specimen used for the previous collection of data was broken into two fragments, having volume ratio nearly 3:1. Two complete sets of X-ray intensities were collected from these fragments, and they were used for two separate structure refinements under the same conditions of the previous refinement.

All results were practically identical to those obtained from the original specimen, except for the twin fractions, which from 0.732/0.268 in the original specimen were changed into respectively 0.680/0.320 for the largest fragment, and 0.884/0.116 for the other.

Incidentally, the separate determination of the lattice parameters of the original specimen and of the two fragments having three differing ratios between the (110) twin individuals, allowed to extrapolate more accurate a and b lattice parameters (Table 1).

Table 2 reports the atomic coordinates and U_{eq} isotropic temperature factors. Bond distances and angles are in Table 3.[1]

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[1] The list of the anisotropical temperature factors and the list of observed and calculated structure amplitudes can be ordered from the Fachinformationszentrum Energie-Physik-Mathematik GmbH, D-7514 Eggenstein-Leopoldshafen 2 FRG. Please quote reference CSD 56113.

Table 3. Bond distances (Å) and angles (°).

	Si1 *a*	Si1 *b*	Si1 *c*	Si1 *d*
–O3	*a* 1.656	*b* 1.659	*c* 1.654	*d* 1.653
–O4	*c* 1.612	*d* 1.611	*a* 1.615	*b* 1.614
–O5	*c* 1.605	*d* 1.607	*a* 1.612	*b* 1.608
–O6	*a* 1.662	*b* 1.661	*c* 1.657	*d* 1.659
Mean	1.634	1.634	1.635	1.634
TQE	1.0019	1.0019	1.0018	1.0018
O3–Si1–O4	*ac* 111.2	*bd* 111.3	*ca* 111.5	*db* 111.4
O5	*ac* 108.6	*bd* 108.5	*ca* 108.6	*db* 108.5
O6	*aa* 105.2	*bb* 105.1	*cc* 105.5	*dd* 105.5
O4–Si1–O6	*cc* 112.2	*dd* 112.2	*aa* 112.0	*bb* 112.0
O6	*ca* 107.8	*db* 107.9	*ac* 107.5	*bd* 107.7
O5–Si1–O6				
	Si2 *a*	Si2 *b*	Si2 *c*	Si2 *d*
–O1	*a* 1.595	*b* 1.599	*c* 1.600	*d* 1.599
–O2	*a* 1.587	*b* 1.584	*c* 1.588	*d* 1.586
–O3	*b* 1.656	*a* 1.657	*d* 1.661	*c* 1.659
–O6	*a* 1.658	*b* 1.659	*c* 1.660	*d* 1.659
Mean	1.624	1.625	1.627	1.626
TQE	1.0052	1.0052	1.0048	1.0050
O1–Si2–O2	*aa* 116.5	*bb* 116.3	*cc* 116.1	*dd* 116.0
–O3	*ab* 106.2	*ba* 106.1	*cd* 106.2	*dc* 106.2
–O6	*aa* 104.6	*bb* 104.3	*cc* 104.9	*dd* 104.7
O2–Si2–O3	*ab* 111.1	*ba* 111.3	*cd* 111.0	*dc* 111.0
–O6	*aa* 112.5	*bb* 112.7	*cc* 112.7	*dd* 113.1
O3–Si2–O6	*ba* 105.2	*ab* 105.3	*dc* 105.1	*cd* 105.0
	Be *a*	Be *b*	Be *c*	Be *d*
–O1	*c* 1.597	*d* 1.606	*a* 1.610	*b* 1.610
–O4	*b* 1.660	*a* 1.665	*d* 1.666	*c* 1.666
–O5	*a* 1.660	*b* 1.655	*c* 1.647	*d* 1.647
–F	*a* 1.578	*b* 1.577	*c* 1.571	*d* 1.574
Mean	1.624	1.626	1.623	1.624
TQE	1.0035	1.0038	1.0035	1.0036
O1–Be–O4	*cb* 105.1	*da* 104.5	*ad* 104.2	*bc* 104.0
–O5	*ca* 108.0	*db* 107.9	*ac* 107.8	*bd* 107.9
–F	*ca* 112.4	*db* 112.5	*ac* 112.2	*bd* 112.2
O4–Be–O5	*ba* 106.2	*ab* 106.4	*dc* 107.3	*cd* 107.3
–F	*ba* 114.6	*ab* 114.8	*dc* 114.2	*cd* 114.4
O5–Be–F	*aa* 110.1	*bb* 110.3	*cc* 110.7	*dd* 110.7
	Ca *a*	Ca *b*	Ca *c*	Ca *d*
–O1	*a* 2.383	*b* 2.381	*c* 2.384	*d* 2.381
–O2	*b* 2.353	*a* 2.346	*d* 2.361	*c* 2.350
–O2	*c* 2.403	*d* 2.402	*a* 2.420	*b* 2.411
–O4	*a* 2.436	*b* 2.438	*c* 2.451	*d* 2.449
–O5	*b* 2.389	*a* 2.401	*d* 2.391	*c* 2.397
–F	*a* 2.484	*b* 2.475	*c* 2.499	*d* 2.493

Table 3 (Continued)

	Ca *a*	Ca *b*	Ca *c*	Ca *d*
−O4	*d* 2.645	*c* 2.651	*b* 2.657	*a* 2.659
−O6	*a* 3.007	*b* 2.992	*c* 3.029	*d* 3.020
Mean	2.512	2.511	2.524	2.520
Mean*	2.408	2.407	2.418	2.414
	Na *a*	Na *b*	Na *c*	Na *d*
−O1	*c* 2.340	*d* 2.334	*a* 2.345	*b* 2.341
−O2	*a* 2.567	*b* 2.570	*c* 2.563	*d* 2.582
−O3	*a* 2.404	*b* 2.400	*c* 2.396	*d* 2.394
−O5	*a* 2.548	*b* 2.542	*c* 2.546	*d* 2.527
−O6	*b* 2.480	*a* 2.483	*d* 2.470	*c* 2.488
−F	*b* 2.428	*a* 2.426	*d* 2.418	*c* 2.394
−F	*c* 2.698	*d* 2.715	*a* 2.716	*b* 2.759
−O3	*d* 2.917	*c* 2.912	*b* 2.924	*a* 2.927
Mean	2.548	2.548	2.547	2.552
Mean*	2.461	2.459	2.456	2.454

Estimated standard deviations in distances: 0.002 (0.003 for Be−O).
Estimated standard deviations in angles: 0.1 (0.2 for O−Be−O).
TQE tetrahedral quadratic elongation after Robinson et al. (1971).
The letters *a b c d* written before the distances and angles complete the labels of the oxygens or fluorines.
* Mean of the six shortest distances.

Discussion

The crystal structure of leucophanite may be briefly described as follows: two layers of Si−O and Be−O tetrahedra parallel to (001) are arranged in the unit cell. The Si1 tetrahedron shares its vertices with two Si2 and two Be tetrahedra, whereas both latter tetrahedra share only three vertices: two with two Si1 tetrahedra and the third with either the Be tetrahedron (Si2) or the Si2 tetrahedron (Be). The unshared fourth vertex of the Si2 tetrahedron is occupied by O2, and that of the Be tetrahedron by F. All atoms of the two layers of tetrahedra are nearly superposed along the [001] direction, in which Si1−Si1 and Si2−Be tetrahedra alternate. Also Ca and Na atoms, which lie in holes between the layers of tetrahedra, alternate in the same direction.

The refinement of the site occupancies showed that, at differing extent, only two sites (Ca *a* and Ca *b*) out of the four Ca sites are involved in an appreciable replacement of rare earths for calcium: actually the most significant enrichment in RE is presented particularly by one of such position (0.18 for Ca *b* against 0.08 for Ca *a*). This RE amount is higher than that obtained from the microprobe analysis (see in the Introduction) and it corresponds to 4.8% RE_2O_3.

The increase of positive charge due to the presence of trivalent rare earths replacing divalent calcium is balanced by the substitution of some oxygen for fluorine in sites F (Table 2): no replacement of fluorine for oxygen was instead observed for sites O2, homologous to the F sites. Only very small substitutions of beryllium for silicon (Si2 sites), or silicon for beryllium (Be sites), or calcium for sodium (Na sites) resulted from the refinement of the crystal structure.

The shifts of the actual atomic positions from those coherent with an orthorhombic symmetry are very low. The last column of Table 2 shows that they are at most about one-two hundredths of angstrom: the departures of the atomic positions from those of the monoclinic $P12_11$ symmetry (penultimate column of Table 2) are still lower, *i.e.* some thousandths of angstrom. The last evidence agrees with the result of the statistics on the equivalences between the structure factors (Table 1).

It is evident that the triclinic symmetry shown by the intensities of the reflections is mostly due to the strong differences in the scattering factors of the isomorphous atoms (Ca and RE), rather than to the shifts of the atomic sites. Consistently, also the bond distances and angles are very similar within each group of four atoms coming from the unique site in the orthorhombic leucophanite, although the mean Ca—O distances involving sites Ca *a* and Ca *b* (*i.e.* the sites partially occupied by the rare earths) seem to be slightly shorter than those of Ca *c* and Ca *d* (Table 3).

The remarkable variations in the fractions of the twin-individuals for the three crystal fragments show that the twin domains are fairly large. On the other hand, the identical results for the occupancies of the rare earths in sites Ca *a* and Ca *b* indicate an equally diffuse replacement of RE for Ca in these sites, in the rough proportion of one RE atom per four unit cells (or for each 16 Ca sites).

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