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THE CRYSTAL STRUCTURES OF LOPARITE-(Ce)

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ABSTRACT

The structures of three compositionally distinct crystals of loparite-(Ce) have been determined by single-crystal X-ray diffractometry using a CCD area detector. Niobian calcian loparite-(Ce) from the Khibina complex, in Russia, is orthorhombic [*Pbnm*; *a* 5.5108(14), *b* 5.5084(14), *c* 7.7964(20) Å]. Calcian niobian loparite-(Ce) from the Lovozero complex, also in Russia, is tetragonal [*I4/mcm*; *a* 5.5022(11), *c* 7.7967(16) Å]. Strontian calcian loparite-(Ce) from the Bearpaw Mountains, in Montana, is tetragonal [*I4/mcm*; *a* 5.5076(17), *c* 7.7767(24) Å]. None of these samples show any evidence of cation order at the *A* or *B* site. All examples of loparite-(Ce) have the general formula $(Na,Ce,Ca)_2(Ti,Nb)_2O_6$. These structural and compositional data indicate that loparite requires redefinition as a mineral species.

Keywords: loparite, perovskite, crystal structure, alkaline rocks.

SOMMAIRE

Nous avons affiné la structure de trois échantillons de loparite-(Ce) de composition distincte par diffraction X sur cristal unique en utilisant un détecteur à aire CCD. Un échantillon de loparite-(Ce) enrichie en niobium et calcium, provenant du complexe alcalin de Khibina, en Russie, est orthorhombique [*Pbnm*; *a* 5.5108(14), *b* 5.5084(14), *c* 7.7964(20) Å]. Un second, enrichi plutôt en calcium et niobium, et provenant du complexe de Lovozero, aussi en Russie, est tétragonal [*I4/mcm*; *a* 5.5022(11), *c* 7.7967(16) Å]. Un troisième échantillon, enrichi en strontium et calcium, et provenant des montagnes Bearpaw, au Montana, est tétragonal [*I4/mcm*; *a* 5.5076(17), *c* 7.7767(24) Å]. Aucun de ces échantillons ne montre de signe d'une mise en ordre des cations sur les sites *A* et *B*. Tous les échantillons de loparite-(Ce) répondent à la formule générale $(Na,Ce,Ca)_2(Ti,Nb)_2O_6$. D'après ces nouvelles données structurales et compositionnelles, la loparite requiert une redéfinition comme espèce minérale.

(Traduit par la Rédaction)

Mots-clés: loparite, pérovskite, structure cristalline, roches alcalines.

INTRODUCTION

Loparite-(Ce) was first recognized in agpaitic syenites of the Lovozero alkaline complex in 1890 by Wilhelm Ramsay, the pioneer of geological exploration of the Kola Peninsula, in Russia. Ramsay & Hackman (1894) characterized this mineral only briefly as "neues Mineral no. 1", and noted its similarity with perovskite, $CaTiO_3$. The first complete description of loparite as a new mineral species, given by Kuznetsov (1925), was based on samples from the adjacent Khibina pluton. Currently, the mineral is described in most glossaries of mineralogy (Blackburn & Dennen 1997, Gaines *et al.* 1997, Fleischer 1991) as possessing pseudocubic symmetry. Although powder-diffraction patterns of natural loparite (Haggerty & Mariano 1983, Vlasov 1966) can be indexed on a primitive cubic cell, we have previously suggested (Mitchell 1996, Chakhmouradian *et al.* 1999)

[§] *E-mail address*: rmitchel@gale.lakeheadu.ca that the actual symmetry is probably orthorhombic, as the 2.56 and 2.34 Å lines cannot be indexed on this cell. Although loparite-(Ce) has been recognized as a distinct mineral species for over 75 years, its crystal structure has not been unequivocally determined, as the mineral is typically twinned and intimately intergrown with other minerals.

The determination of crystal structures by X-ray diffraction has recently been significantly advanced by the introduction of detectors of X-rays equipped with a charged-coupled device (CCD) (Burns 1998). Previously, mineral structures were determined using serial diffractometers equipped with point detectors, thus requiring that unit cell and lattice to be known before data collection for structure solution can be initiated. The CCD-based detector, in contrast, is an area detector that collects large slices of reciprocal space simultaneously. Thus, all diffraction space is collected during a typical session of data collection, and *no assumptions regarding lattice type or unit cell are required prior to analyzing the entire dataset*. In addition, the CCD-based detector is much more sensitive to X-rays than a conventional detector. This feature permits study of very small crystals and the detection of very weak reflections. In addition, recent advances in crystallographic computing software now permit the investigation of twinned crystals. Consequently, we considered that the use of a CCD diffractometer would be ideal for the solution of the crystal structure of loparite-(Ce). In this work, we demonstrate the applicability of the technique by the successful solution of the structures of three crystals of loparite-(Ce) of differing composition.

PREVIOUS STUDIES OF NATURAL AND SYNTHETIC LOPARITE

Determination of the structure of loparite-(Ce) by single-crystal methods has not previously been successful, as the mineral is typically twinned (Hu *et al.* 1992). Twinning may result from growth or inversion from high-temperature cubic and tetragonal polymorphs. Samples that apparently lack twinning in thin section are characteristically twinned at the resolution of the electron microscope. It is doubtful that twin-free crystals of natural loparite-(Ce) will ever be located. Attempts to determine the structure of natural material by Rietveld methods have also not been successful owing to the large number of other phases present as inclusions, and the significant variations in composition occurring in most natural crystals.

Recently, Zubkova *et al.* (1998) claimed to have solved the crystal structure of loparite-(Ce) by single-crystal methods, and have proposed that it crystallizes as an ordered quadruple perovskite (a = 7.767 Å) in the space group $Pn3m$ (R = 4.1%). The structure proposed consists of "ordered TiO_6 and $(Ti_{0.73}Nb_{0.27})O_6$ octahedra" coupled with ordered Ca and Na but *not* Ce (and other rare-earth elements) in the interstitial sites. We consider this structural proposal to be implausible as: (1) natural loparite-(Ce) is anisotropic, (2) crypto-merohedral twinning was not considered in the structure solution, (3) too few reflections were recorded, (4) it is doubtful that ordering of the type described could actually occur (or even be recognized by standard X-ray methods), (5) ordering of the type described (if present) should result in an F-centered cubic cell or the monoclinic $C2_1/n$ space group if ordering is coupled with rotation of the TiO_6 polyhedra (Anderson *et al.* 1993, Woodward 1997).

X-ray-diffraction studies of powders of synthetic loparite, Na(*REE*)Ti_2O_6 [where *REE* represents La, Ce, Pr, *etc.*), suggest that natural loparite is probably not cubic. Rietveld refinement methods have shown that all such synthetic loparite, with the exception of $NaLaTi_2O_6$, belongs to the space group $Pnma$ (Mitchell & Chakhmouradian 1998, Chakhmouradian *et al.* 1999, Shan *et al.* 1998). On the basis of Rietveld refinement studies, Sun *et al.* (1997) considered the compound $NaLaTi_2O_6$ to be rhombohedral. In contrast, we have found that $NaLaTi_2O_6$ samples prepared by ceramic methods may loose minor variable amounts of Na during preparation, and although such compounds are close to being stoichiometric in composition, they may be orthorhombic $Pnma$ or rhombohedral $R\bar{3}c$ depending upon the amount of Na lost (Mitchell & Chakhmouradian 1998, Mitchell *et al.* 2000). However, as the *REE* occupying the A site of natural loparite are dominated by Ce, Pr and Nd (Table 1), it might be expected that their structure should be similar to those of orthorhombic $NaCe^{3+}Ti_2O_6$ and $NaNdTi_2O_6$.

EXPERIMENTAL

Three specimens of loparite-(Ce) occurring in agpaitic nepheline syenite were collected by us from: Mt. Takhtarvumchorr, Khibina alkaline complex, Russia (loparite K), Mt. Selsurt, Lovozero alkaline complex, Russia (loparite L), and Pegmatite Peak, Bearpaw Mountains, Montana (loparite BM). A brief description of localities, petrography and mineral assemblages from which the specimens originate is given in Table 1. Samples from different occurrences and parageneses were selected so that they would represent the compositional range observed in naturally occurring loparite-(Ce). All samples investigated were separated from their host syenites by standard techniques of heavy-mineral separation. Crystals chosen for study were inclusion-free, optically anisotropic and apparently not twinned (see below). The composition of the loparite crystals was determined by quantitative X-ray energy-dispersion analysis using methods described by Mitchell & Chakhmouradian (1996). Tables 2 and 3 give representative compositions and sizes of the crystals studied.

Table 2 demonstrates that each sample of loparite shows some variation in composition with respect to major and minor components. This intragranular varia-

TABLE 1. DESCRIPTION OF SAMPLES

Sample	Locality	Rock type	Major minerals	Characteristic accessory minerals
Loparite K	Mt. Takhtarvumchorr SW part of the Khibina alkaline complex, Russia	Lens-shaped pegmatite in coarse-grained leucocratic nepheline syenite (khibinite)	Nepheline[a], microcline, arfvedsonite, aenigmatite, aegirine	Eudialyte, lamprophyllite, titanite, ilmenite
Loparite L	Mt. Selsurt N part of the Lovozero alkaline complex, Russia	Foyaite unit in the differentiated series	Nepheline[a], microcline, albite, eudialyte	Apatite, aegirine, eudialyte, monazite-(Ce)
Loparite BM	Pegmatite Peak Rocky Boy stock, west part of the Bearpaw Mtns alkaline complex, Montana	Lens-shaped pegmatite in nepheline syenite	Nepheline[a], microcline aegirine, lamprophyllite	Crichtonite, titanite, zircon, strontiochevkinite, ilmenite, thorite

[a] Nepheline is partly or completely altered to an aggregate of secondary minerals (natrolite, muscovite, gibbsite, analcime).

tion is relatively minor and does not exceed a few mole percent of any end-member component. In all samples, the proportion of the loparite component ($Na_{1/2}Ce_{1/2}TiO_3$) outweighs that of other perovskite-type end-members, *i.e.* tausonite ($SrTiO_3$), lueshite ($NaNbO_3$), and perovskite ($CaTiO_3$). However, the variation in composition among the different samples is very significant. In terms of nomenclature of the perovskite group suggested by Mitchell (1996), loparite K should be regarded as niobian calcian loparite-(Ce), loparite L as calcian niobian loparite-(Ce), and loparite BM as strontian calcian loparite-(Ce).

Single crystals of loparite-(Ce) were fixed with epoxy glue onto thin glass rods and mounted on a Bruker PLATFORM 3-circle goniometer equipped with a 1K SMART CCD detector with a crystal-to-detector distance of 5 cm.

The data were collected using monochromatic Mo*K*α X-radiation (λ = 0.71073 Å) and frame widths of 0.3°ω. Either a sphere or more than a hemisphere of three-dimensional data were collected over the interval $3° \leq 2\theta \leq 56.6°$ and analyzed to locate peaks for the determination of unit-cell dimensions by least-squares techniques. The number of reflections used to determine the unit-cell parameters for loparite samples K, L and BM were 553, 560 and 301, respectively. Data-collection parameters are listed in Table 3. The three-dimensional data were reduced and corrected for Lorentz, polarization, and background effects using the Bruker program SAINT. An empirical absorption-correction was applied to all data on the basis of the intensities of

TABLE 2. REPRESENTATIVE COMPOSITIONS OF LOPARITE

Wt.%	Loparite K		Loparite L		Loparite BM	
Na_2O	9.81	9.50	7.99	8.25	5.65	5.15
La_2O_3	9.28	8.81	8.61	8.41	9.60	8.91
Ce_2O_3	16.42	15.97	18.26	17.45	14.65	13.04
Pr_2O_3	1.22	1.11	1.94	2.17	n.d.	0.37
Nd_2O3	2.78	3.04	4.20	4.34	2.86	2.58
CaO	2.91	2.96	4.44	4.09	2.62	2.27
SrO	2.12	1.99	2.56	2.88	16.06	18.57
ThO_2	0.97	0.95	0.58	0.60	1.93	2.08
TiO_2	35.30	35.13	41.42	38.92	42.22	42.68
Nb_2O_5	17.93	18.64	7.49	11.31	4.16	3.64
Ta_2O_5	0.86	0.91	0.94	1.24	0.46	0.51
Fe_2O_3[a]	0.01	0.01	0.22	0.29	0.08	0.15
Total	99.61	99.02	98.65	99.95	100.29	99.95
Structural formulae based on 3 atoms of oxygen						
Na	0.546	0.529	0.447	0.459	0.322	0.295
La	0.098	0.093	0.092	0.089	0.104	0.097
Ce	0.172	0.168	0.193	0.183	0.158	0.141
Pr	0.013	0.012	0.020	0.023	0.000	0.004
Nd	0.028	0.031	0.043	0.044	0.030	0.027
Ca	0.089	0.091	0.137	0.126	0.083	0.072
Sr	0.035	0.033	0.043	0.048	0.274	0.318
Th	0..006	0.006	0.004	0.004	0.013	0.014
ΣA	0.987	0.963	0.979	0.976	0.984	0.968
Ti	0.762	0.759	0.898	0.840	0.934	0.947
Nb	0.233	0.242	0.098	0.147	0.055	0.049
Ta	0.007	0.007	0.007	0.010	0.004	0.004
Fe^{3+}	0.000	0.000	0.005	0.006	0.002	0.003
ΣB	1.002	1.008	1.008	1.003	0.995	1.003
Mol.% end members						
Loparite[b]	61.42	57.01	69.35	60.61	52.07	48.66
$SrTiO_3$	3.54	3.38	4.34	4.80	27.10	31.95
$NaNbO_3$	23.98	25.37	10.66	15.66	5.84	5.29
$CaTiO_3$	8.96	9.28	13.92	12.59	8.17	7.21
$Th_{1/2}TiO_3$	1.27	1.26	0.77	0.79	2.55	2.81
$Ce_{2/3}TiO_3$	0.83	3.70	0.96	5.55	4.27	4.08

[a] Total Fe expressed as Fe_2O_3; [b] loparite = $Na_{1/2}Ce_{1/2}TiO_3$
n.d. not detected

TABLE 3. CELL DIMENSIONS AND MISCELLANEOUS DATA FOR THE LOPARITE CRYSTALS STUDIED BY CCD X-RAY DIFFRACTOMETRY

Sample	K	L	BM
a(Å)	5.5108(14)	5.5022(11)	5.5076(17)
b(Å)	5.5084(14)	5.5022(11)	5.5076(17)
c(Å)	7.7964(20)	7.7967(16)	7.7767(24)
V(Å^3)	236.67	236.04	235.90
Space group	*Pbnm*	*I4/mcm*	*I4/mcm*
a_p(Å)	3.897	3.893	3.892
μ(mm^{-1})	12.79	12.82	12.83
D_{calc}(g/cm^3)	4.980	4.994	4.997
Crystal size (mm)	0.02 x 0.14 x 0.12	0.18 x 0.16 x 0.02	0.18 x 0.16 x 0.02
Count time/frame	10 seconds	10 seconds	10 seconds
Collection time	11 hours	11 hours	5 hours
Total reflections	2825	2819	1477
Unique reflections	346	95	94
$\|F_o\| \geq 4\sigma_F$	128	71	51
Final R(%) obs. refl.	3.36	2.57	2.89
Final R(%) all data	7.95	7.20	6.53
Diff.Fourier peaks	0.10 - 0.86	0.10 - 0.40	0.04 - 0.47 (e/Å^3)

$R = \sum(|F_o|-|F_c|)/\sum|F_o|$: a_p = pseudocubic cell parameter $[(V/4)^{1/3}]$: Sample K, Mt. Takhtarvumchorr, Khibina (Russia); sample L, Mt. Selsurt, Lovozero (Russia); sample BM, Pegmatite Peak, Montana (U.S.A.).

equivalent reflections, and the crystal shape was modeled as an ellipse. The total number of observations and unique reflections used in the crystal-structure determinations are listed in Table 3. Observed and calculated structure-factors are available from the Depositary of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2, Canada.

Structure Solution and Refinement

Scattering factors for neutral atoms, together with anomalous-dispersion corrections, were taken from *International Tables for X-Ray Crystallography*, Vol. IV (Ibers & Hamilton 1974). The Bruker SHELXTL Version 5 system of programs was used for the determination and refinement of the crystal structures.

Loparite K

Systematic absences and reflection statistics indicated that the crystal investigated does not possess cubic or tetragonal symmetry. It was found possible to refine the structure to an agreement factor (*R* value) of approximately 6% in both the cubic space groups $Fm\bar{3}m$ and *F*432 because of the existence of a pseudocubic subcell in perovskite-group compounds. We found no evidence for the existence of an *I*-centered cubic lattice in these data. Refinement in the tetragonal space-groups *P*4/*mbm* or *I*4/*mcm*, which are commonly adopted by perovskite-group compounds (Woodward 1997), resulted in *R* values of 5.92 and 5.54% for *P*4/*mbm* and *I*4/*mcm*, respectively. In the space group *P*4/*mbm* there were 38 *b*-glide violations. Refinement in the space group *Cmcm* gave an *R* value of 5.5%. Unacceptably high anisotropic-displacement parameters for oxygen were obtained for all of these space groups.

The final model chosen was based upon the space group *Pbnm*, the non-standard setting of the space group *Pnma* (#62), which is commonly adopted by ABO_3 perovskite-group compounds such as $CaTiO_3$ (Sasaki *et al.* 1987). Refinement in space group *Pbnm* resulted in an *R* value of 4.36%, together with poorly behaved displacement-parameters for the O atoms. However, many of the F_{obs} were substantially greater than their corresponding F_{calc}, suggesting that the crystal is twinned. As the *a* and *b* unit cell parameters are similar, we assumed that the twinning involved the matrix [010/100/00$\bar{1}$], which we incorporated into the model using the methods of Jameson (1982) and Herbst-Irmer & Sheldrick (1998). This improved the refinement to an *R* value of 3.36% and resulted in reasonable displacement-parameters for all atoms. Our final model included refined positional parameters, anisotropic displacement-parameters and a correction for extinction. In the final cycle of refinement, the average parameter shift/esd was 0.000 and the maximum peaks in the final difference-Fourier maps were less than 0.86 e/Å^3.

The adopted *Pbnm* model involves 29 refinable parameters, whereas the tetragonal structure-models involve 14 and 24 refinable parameters for the space groups *I*4/*mcm* and *P*4/*mbm*, respectively. The method of Hamilton (1965) using these parameters and 346 observations indicates that the better structural model is the space group *Pbnm* at the 95% confidence level.

Loparite L

The refinement strategy for loparite L followed that given above. Refinement in the space groups $Fm\bar{3}m$, *F*432 and *Pbnm* gave *R* values of 3.53, 3.66 and 3.71%, respectively. However, because of the similarity within experimental error of the *a* and *b* cell dimensions, we considered that the crystal might possess tetragonal symmetry. The structure was not refined in the space group *P*4/*mbm*, owing to significant *b*-glide violations, which are unrelated to twinning, but gave an acceptable refinement in the space group *I*4/*mcm*. In this space group, the *R* value was reduced to 2.57%, and the displacement parameters for all atoms were found to be acceptable. In the final cycle of refinement, the average parameter shift/esd was 0.000, and the maximum peaks in the final difference-Fourier maps were less than 0.40 e/Å^3. Note that the slightly higher *R* value in the space group *Pbnm* relative to the higher-symmetry space group *I*4/*mcm* results from merging of equivalent reflections prior to refinement. Using the criteria of Hamilton (1965), the space group *I*4/*mcm* (#140) is the better model at the 95% confidence level.

Loparite BM

Loparite BM was refined according to the strategy outlined above. Refinement in the space groups $Fm\bar{3}m$, *F*432 and *Pbnm* gave *R* values of 1.52, 1.56 and 3.62%, respectively. Refinement in the space group *P*4/*mbm* did not converge owing to *b*-glide violations. Refinement in *I*4/*mcm* gave an *R* value of 2.89%. The refinements in the cubic space-groups give low *R* values, but cannot be correct because the crystals are optically anisotropic. Therefore, we consider that loparite BM belongs to the space group *I4/mcm*. Note that the final *R* values obtained from the cubic and tetragonal structures are not strictly comparable because symmetry-equivalent reflections are averaged before the refinements. The cubic structures each involved 39 unique observed reflections, whereas the tetragonal structure was refined on the basis of 76 unique observed reflections, likely accounting for the lower *R* values obtained for the cubic structures. In the final cycle of refinement in this space group, the average parameter shift/esd was 0.000, and the maximum peaks in the final difference-Fourier maps were less than 0.47 e/Å^3. The excellent fit to the cubic space-groups arises from the very small deviation from the ideal cubic structure shown by this Sr-rich loparite (see below).

TABLE 4. FINAL ATOMIC PARAMETERS FOR LOPARITE

	x	y	z	sof	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
Loparite K											
Ce	-0.0034(1)	0.5003(5)	0.25	0.159(2)	0.0179(4)						
Na	-0.0034(1)	0.5003(5)	0.25	0.341(2)	0.0179(4)						
Ti	0	0	0	0.417(5)	0.0097(9)	0.0142(11)	0.0112(5)	-0.0013(13)	0	0.0019(11)	0.0117(4)
Nb	0	0	0	0.083(5)	0.0097(9)	0.0142(11)	0.0112(5)	-0.0013(13	0	0.0019(11)	0.0117(4)
O(1)	0.0508(8)	-0.0016(24)	0.25	0.5	0.0242(24)	0.0622(41)	0.0166(20)	0	0	-0.0033(69)	0.0344(13)
O(2)	0.428(8)	0.2510(34)	-0.0181(5)	1.0	0.0610(52)	0.0530(57)	0.0652(28)	0.0149(53)	-0.0049(85)	-0.0435(21)	0.0597(15)
LopariteL											
Ce	0	0.5	0.25	0.046(2)	0.0196(9)	0.0196(9)	0.0200(10)	0	0	0	0.0197(9)
Na	0	0.5	0.25	0.079(2)	0.0196(9)	0.0196(9)	0.0200(10)	0	0	0	0.0197(9)
Ti	0	0	0	0.114(5)	0.0127(11)	0.0127(11)	0.0113(12)	0	0	0	0.0122(10)
Nb	0	0	0	0.011(5)	0.0127(11)	0.0127(11)	0.0113(12)	0	0	0	0.0122(10)
O(1)	0	0	0.25	0.125	0.0856(47)	0.0856(47)	0.0210(50)	0	0	0	0.0641(31)
O(2)	0.2828(6)	0.7828(6)	0	0.25	0.0261(18)	0.0261(18)	0.0792(39)	0	0	0.0053(21)	0.0438(19)
LopariteBM											
Ce,Sr	0	0.5	0.25	0.058(2)	0.0146(7)	0.0146(7)	0.0114(8)	0	0	0	0.0136(6)
Na	0	0.5	0.25	0.067(2)	0.0146(7)	0.0146(7)	0.0114(8)	0	0	0	0.0136(6)
Ti,Nb	0	0	0	0.125	0.0075(10)	0.0075(10)	0.0067(12)	0	0	0	0.0073(9)
O(1)	0	0	0.25	0.125	0.0554(53)	0.0554(53)	0.0106(46)	0	0	0	0.0404(36)
O(2)	0.2684(11)	0.7684(11)	0	0.25	0.0169(31)	0.0169(31)	0.0480(49)	0	0	0.0019(30)	0.0273(27)

sof: site-occupancy factor.

The final R values for the all of the converged datasets are given in Table 3, and final atomic-position parameters and anisotropic-displacement parameters, in Table 4. Selected interatomic distances and bond angles are listed in Table 5.

DISCUSSION

Loparite K

Loparite K gave an acceptable refinement of the crystal structure (Table 3) in the space group *Pbnm* (#62) and is thus considered to have a structure similar to that of $CaTiO_3$ (Sasaki *et al.* 1987, Buttner & Maslen 1992), and the large number of ABO_3 perovskite-group compounds that adopt the $GdFeO_3$ structure (Hyde & Anderson 1989). Compounds of this structure-type consist of a framework of *B*-site cations that are octahedrally coordinated by atoms of oxygen. Larger *A*-site cations are surrounded by twelve atoms of oxygen in cubo-octahedral coordination within this framework. The $GdFeO_3$ structure differs from that of the ideal cubic perovskite structure in that the octahedra are rotated about more than than one pseudocubic Cartesian axes. The rotation, and consequent reduction in symmetry, result from the presence in the *A* site of cations that are smaller than required to maintain the ideal geometry of this site. The rotation or tilting of octahedra in perovskite-group compounds has been extensively discussed by Glazer (1972), Woodward (1997) and Howard & Stokes (1998).

Tables 4 and 5 indicate that loparite K consists of a framework of tilted and distorted $(Ti,Nb)O_6$ polyhedra with the larger rare-earth element, Na and Ca cations occupying distorted 12-fold-coordinated sites within this framework. The latter may be regarded as distorted $(Na,Ce,Ca)O_{12}$ polyhedra. No evidence was found for ordering of the cations in either of the structural sites.

The $(Ti,Nb)O_6$ polyhedra exhibit a similar style of distortion to that found for $CaTiO_3$ (Table 5), which is characterized by relatively short Ti–O(2) bonds (*i.e.*, compression) along the semi-minor axis [designated O(2)B] of the equatorial plane of the polyhedron (Table 5). However, the amount of distortion is greater than that found in $CaTiO_3$ (Table 5). Thus, the Ti–O(2) bonds in loparite K and $CaTiO_3$ are shortened or ex-

TABLE 5. LOPARITE K, L, BM AND $CaTiO_3$ PEROVSKITE: INTERATOMIC DISTANCES (Å) AND ANGLES (°)

	K	PER*		L	BM
Ti - O(1) x 2	1.969(1)	1.953	Ti - O(1) x 2	1.949(4)	1.944(1)
Ti - O(2)A x 2	1.977(14)	1.959	Ti - O(2) x 4	1.962(7)	1.953(1)
Ti - O(2)B x 2	1.929(14)	1.958			
(Na,Ce) - O1	2.495(5)		(Na,Ce) - (O2) x 4	2.580(31)	2.652(6)
(Na,Ce) - O2 x 2	2.625(10)		(Na,Ce) - (O1) x 4	2.751(5)	2.754(6)
(Na,Ce) - O2 x 2	2.672(10)		(Na,Ce) - (O2) x 4	2.940(35)	2.855(6)
(Na,Ce) - O1	2.760(15)				
(Na,Ce) - O1	2.780(15)				
(Na,Ce) - O2 x 2	2.845(10)				
(Na,Ce) - O2 x 2	2.887(10)				
(Na,Ce) - O1	3.016(5)				
Bond Angles					
Ti-O(1)-Ti	163.7(.26)	156.9	Ti - O(1) - Ti	180.0	180.0
Ti-O(2)A-Ti	171.5(.26)	155.8	Ti - O(2) - Ti	165.1(.27)	171.5(.5)
O(2)A-Ti-O(2)B	89.7(.03)	89.4			
O(1)-Ti-O(2)A	88.0(.32)	89.6			
O(1)-Ti-O(2)B	88.7(.32)	89.3			
Tilt Angles					
[001]	1.6	5.5	Ti - O(2) - Ti	7.45	4.30
[010]	1.7	8.4		-	-
[111]	2.9	10.0		-	-
Polyhedra Volumes (Å^3)					
V_B	10.01	9.99		10.00	9.88
V_A	49.32	46.17		49.06	49.09
V_A/V_B	4.93	4.62		4.91	4.97
Polyhedron Distortion					
ΔAO_{12}	2.570	-		2.844	0.906
ΔBO_6	0.115	0.002		0.009	0.005

* PER = $CaTiO_3$ (Buttner & Maslen 1992); Tilt angles for loparite - K and perovskite calculated from cell parameters using equations given by Megaw (1973) and Zhao *et al.* (1993). Tilt angle [001] for loparite - L and loparite - BM calculated from bond angles. Polyhedral volumes calculated using IVTON software (Balić Žunić & Vicković 1996). Polyhedron distortion Δ calculated from bond lengths by the method of Shannon (1976).

tended by 1.23% or 0.31%, respectively, relative to the Ti–O bond (1.953 Å) of the ideal TiO_6 polyhedron in cubic $SrTiO_3$ (*a* 3.9050 Å; Galasso 1969, Mitchell & Chakhmouradian 1999). The $(Ti,Nb)O_6$ polyhedra are also unlike those occurring in $CaTiO_3$, which are characterized by apical Ti–O(1) shortening relative to the metal–oxygen bonds in the equatorial plane (Table 5).

The *B*-site polyhedron in loparite K and $CaTiO_3$ differ in volume (V_B) (Table 5). As expected for these relatively Nb-poor titanates, the mean (Ti,Nb)–O bond length of 1.958 Å is similar to that of the Ti–O bond (1.953 Å) of an ideal TiO_6 polyhedron in cubic $SrTiO_3$, but significantly less than the metal–oxygen bonds (1.985 Å) in Nb-rich titanates such as the mineral latrappite (Mitchell *et al.* 1998).

The *A*-site cations occupy a highly distorted site and are coordinated by 12 atoms of oxygen. Consequently, *A*–O bond lengths (Table 4) deviate significantly from the ideal Sr–O bond length in cubic $SrTiO_3$ (2.761 Å). In contrast, *A*-site cations in $CaTiO_3$ perovskite are considered, on the basis of bond-valence calculations, to be coordinated within the first coordination sphere by only 10 atoms of oxygen, as some Ti atoms lie in closer to the *A* cation than the remaining O(2) oxygen atoms. This situation results from the greater degree of rotation of the TiO_6 octahedra in this compound (see below). The volume (V_A) of the AO_{12} polyhedron in loparite K is close to that of SrO_{12} in $SrTiO_3$ (49.62 $Å^3$). The ratio V_A/V_B is 4.93, and close to the ideal value of 5 (Thomas 1996), suggesting that rotation angles of the BO_6 polyhedra are not as large as observed in many *Pbnm* perovskite-group compounds.

Table 5 shows that Ti–O(1)–Ti and Ti–O(2)A–Ti bond angles are less than 180°, demonstrating that the $(Ti,Nb)O_6$ polyhedra are rotated. Although these polyhedra are distorted, the rotation scheme according to Howard & Stokes (1998) would correspond to $a^+b^-b^-$ in Glazer's (1972) notation. The amount of tilting is considerably less than that observed in $CaTiO_3$, as the *A* site is occupied by cations (Na^+) larger than Ca^{2+}. The structural parameter θ_3 of Thomas (1998) also provides a measure of deviation from ideal cubic symmetry (θ_3 = 7.35° for V_A/V_B = 5.0); it is 7.74° (*cf.* $CaTiO_3$; θ_3 = 12.34°).

Calculation of tilt angles from cell parameters according to equations given by Megaw (1973) also suggests significantly less tilting in loparite K ([111] tilt = 2.9°) than in the $CaTiO_3$ perovskite structure ([111] tilt = 10.0°). This observation is in keeping with the [111] tilts calculated from cell-dimension data for other synthetic (2.5–6.0°; Mitchell & Chakhmouradian 1998, Chakhmouradian *et al.* 1999) and natural loparite from the Sarambi alkaline complex (4.4°; Haggerty & Mariano 1983). Calculation of tilt angles from bond angles using the equations of Zhao *et al.* (1993) is not possible as cos[001] > 1. We suggest that this is related to the small degree of tilting and the observation that *a* > *b*, and is thus unlike most *Pbnm* perovskite-group compounds, where *a* < *b*. Other orthorhombic perovskite-group phases with *a* > *b* include $LaCrO_3$ (Khattak & Cox 1977), $LaGaO_3$ (Geller *et al.* 1974) and $SmAlO_3$ (Yoshikawa *et al.*1998). Perovskite-group phases with such "reversed" unit-cell parameters occur at compositions or intensive parameters close to phase transitions. This observation suggests that loparite K is structurally close to being tetragonal, and that a slight change in its composition, *e.g.*, changes in Na or Sr content, would result in a change in symmetry.

Loparite L and loparite BM

Both of these loparite samples belong to the tetragonal space-group $I4/mcm$, which is derived from the cubic aristotype $Pm\bar{3}m$ space-group by a single antiphase rotation of the TiO_6 polyhedra about the *c* axis, *i.e.*, tilt scheme $a^\circ a^\circ c^-$ (Howard & Stokes 1998). The amount of rotation and degree of distortion of the TiO_6 polyhedra (Table 5) are correlated with composition, with the Sr-rich loparite BM exhibiting only a slight deviation from cubic symmetry. Thus Ti–O(2) bonds in loparite BM show no compression or elongation relative to those (1.953 Å) in the ideal TiO_6 polyhedron of $SrTiO_3$, whereas these bonds in loparite L exhibit only minor distortion (0.46%). Ti–O(1) bonds show 0.46% and 0.20% compression in loparite BM and loparite L, respectively, relative to these bonds in $SrTiO_3$.

The *A*-site cations occupy AO_{12} polyhedra that are significantly less distorted than those found in loparite K (Table 5). As a consequence of the greater proportion of Sr in loparite BM relative to loparite L, its V_A/V_B value (4.97) is close to the ideal value (5) found for $SrTiO_3$.

Implications regarding mineral nomenclature

It is evident on the basis of data presented in this work that loparite requires redefinition as a mineral species, as we have demonstrated that diverse samples of loparite-(Ce) belong to either orthorhombic or tetragonal space-groups at room temperature. The space group adopted by natural loparite is a function of composition. Loparite BM is essentially a member of the solid-solution series between tausonite and loparite (approximately 35–40 mol.% tausonite). Our determination of the space group of the natural material as $I4/mcm$ is in agreement with high-temperature (>1100°C) experimental studies of the system $NaLaTi_2O_6$ – $SrTiO_3$ (Mitchell *et al.* 2000), which show that intermediate members of this solid-solution series containing 30–70 mol.% $SrTiO_3$ belong to the space group $I4/mcm$.

Loparite L also is tetragonal, although it differs substantially in composition from loparite BM, and is essentially a ternary solid-solution in the system loparite – lueshite – perovskite. Although the mineral composition is dominated by the loparite component (Table 2), it unfortunately does not correspond in composition to the synthetic end-member $NaCeTi_2O_6$, which we consider to possess orthorhombic symmetry (see above). We consider that this difference in symmetry must be due to the presence of other cations in the *A* and *B* sites. Loparite K, which corresponds closely in composition to the holotype material described by Kuznetsov (1925), is orthorhombic. Loparite L is similar in composition to loparite K, and the transition to the orthorhombic structure in the lueshite – loparite series is probably driven by entry of Na into the *A* site.

As a final point, the current IMA definition of loparite gives the general formula $(Ce,Na,Ca)_2(Ti,Nb)_2O_6$ (Blackburn & Dennen 1997). In contrast, we have found that all loparite (including that from the type locality) so far examined (Mitchell & Chakhmouradian 1996, Chakhmouradian & Mitchell 1998) has Na > Ce, and that the total *REE* never exceed Na.

CONCLUSION

This study of the structure of loparite-(Ce) crystals originating from three different localities conclusively demonstrates that depending upon its composition, the mineral crystallizes in either the space group *Pbnm* or *I*4/*mcm*. These structures are derived from the ideal perovskite structure by tilting and distortion of the $(Ti,Nb)O_6$ polyhedra. None of the *A*- or *B*-site cations are ordered. The *Pbnm* structure of Sr-poor Nb-rich loparite is similar to that of $CaTiO_3$ perovskite, which crystallizes in the same space-group but differs with respect to amount of tilting of the TiO_6 polyhedra. In contrast, calcian niobian loparite and strontian calcian loparite both crystallize in the space group *I*4/*mcm*, and show only minor deviation form cubic symmetry owing to the higher proportion of large cations in these minerals. The name "loparite" requires redefinition as a mineral species.

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