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THE STRUCTURE OF $NaCa_2LuSi_2O_7F_2$, A SYNTHETIC PHASE OF THE CUSPIDINE GROUP

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ABSTRACT

Crystals of a new cuspidine-group phase $NaCa_2LuSi_2O_7F_2$ have been synthesized at 690°C and 0.12 GPa $P(H_2O)$, and the basic cuspidine-type structure confirmed by X-ray structure refinement using reflection intensities from a twinned crystal [$P2_1/a$; *a* 11.024(5), *b* 10.303(3), *c* 7.391(2) Å, β 109.40(3)°]. The site occupancies of the four *X* positions are: Ca(1): 0.155 Ca, 0.845 Na; Ca(2): 0.845 Ca, 0.155 Na; Ca(3): 0.155 Ca, 0.845 Lu; Ca(4): 0.845 Ca, 0.155 Lu. Lutetium is restricted to the Ca(3) and Ca(4) positions, and Na, to Ca(1) and Ca(2), in agreement with the predicted site-preference from bond-valence sums for the Ca positions in cuspidine ($Ca_4Si_2O_7F_2$). However, unlike the behavior of high-field-strength cations that are restricted to the smaller Ca(3) position in the mineral representatives of the cuspidine group, Lu does enter Ca(4) in synthetic Lu-cuspidine. This is because Lu^{3+} is closer in size to Ca^{2+}; when Lu occupies Ca(4), linkage of the diorthosilicate group to two edges of the $Ca(4)O_6F$ polyhedron displaces the bridging oxygen and straightens the bond angle involving the bridging oxygen.

Keywords: cuspidine group, lutetium calc-silicate, bond valence, structure refinement, site preference.

SOMMAIRE

Nous avons synthétisé des cristaux d'une composition nouvelle dans la famille de la cuspidine, $NaCa_2LuSi_2O_7F_2$, à 690°C et 0.12 GPa $P(H_2O)$, et nous avons pu en confirmer la structure-type de la cuspidine par affinement en utilisant l'intensité des réflexions obtenues sur un cristal maclé [$P2_1/a$; *a* 11.024(5), *b* 10.303(3), *c* 7.391(2) Å, β 109.40(3)°]. Les quatre positions *X* sont remplies comme suit: Ca(1): 0.155 Ca, 0.845 Na; Ca(2): 0.845 Ca, 0.155 Na; Ca(3): 0.155 Ca, 0.845 Lu; Ca(4): 0.845 Ca, 0.155 Lu. Le lutetium est uniquement présent dans les sites Ca(3) et Ca(4), et le sodium, dans les sites Ca(1) et Ca(2), comme le prédisent les valences de liaison calculées pour le pôle cuspidine, $Ca_4Si_2O_7F_2$. Toutefois, contrairement au cas des atomes à rapport élevé de charge à rayon ionique, qui semblent occuper seulement la position Ca(3) dans les exemples naturels de ce groupe, le Lu occupe définitivement la position Ca(4) dans ce matériau synthétique. Cette tendance serait due à la plus grande ressemblance des rayons ioniques de Lu^{3+} et de Ca^{2+}. Où le Lu occupe Ca(4), l'agencement de deux arêtes du polyèdre $Ca(4)O_6F$ avec le groupe bi-orthosilicate déplace l'atome d'oxygène liant les deux tétraèdres et ouvre l'angle Si–O–Si.

(Traduit par la Rédaction)

Mots-clés: groupe de la cuspidine, calc-silicate de lutetium, valences de liaison, affinement de la structure, occupation préférentielle des sites.

INTRODUCTION

The cuspidine group of minerals has the general structural formula of $X_{16}(Si_2O_7)_4(O,OH,F)_8$, where *X* denotes medium- and large-sized cations, and includes cuspidine [$Ca_{16}(Si_2O_7)_4F_8$], låvenite [$M_4(Na,Ca)_8(Zr,Nb)_4(Si_2O_7)_4O_4F_4$, where *M* represents Mn, Fe, Ca and Ti], wöhlerite [$Na_4Ca_8Zr_2(Nb,Ti)_2(Si_2O_7)_4O_4F_2(O,F)_2$], and several other exotic calc-silicate niobates and zirconates (Merlino & Perchiazzi 1988). The crystal structure of cuspidine was determined by Smirnova *et al.* (1955), who considered it to be built of chains of edge-sharing $Ca(O,F)_6$ octahedra parallel to the *c* axis, and analogous to the structures of ilvaite, epidote, and tilleyite. Subsequent refinement of the structure by Saburi *et al.* (1977) showed that the coordination numbers of the four Ca positions [Ca(1), Ca(2), Ca(3), and Ca(4)] for a bonding sphere out to 2.84 Å were actually 8, 7, 6, and 7, respectively. Also, Ca(1) and Ca(4) were found to be bonded to the bridging oxygen [O(1)] of the diorthosilicate group, $[Si_2O_7]^{6-}$. Merlino & Perchiazzi (1988) rationalized the various structures of the cuspidine group using two structural modules, an "octahedral wall" four columns

of $X(O,F)_6$ groups wide, parallel to the *c* axis and the diorthosilicate group, and derived ten different structure-types. They noted that the diorthosilicate group is connected to the walls of the octahedral groups in different ways and, in particular, it is not linked to the edges of octahedra that contain relatively small cations (Zr^{4+}, Ti^{4+}, Nb^{5+}, *etc.*). In the cuspidine structure itself, Ca(1) and Ca(2) alternate along one column of octahedra (or polyhedra), and Ca(3) and Ca(4) along another, and the diorthosilicate group is linked just to edges of the Ca(1) and Ca(4) polyhedra.

We encountered synthetic cuspidine in experiments on rare-earth-element-substituted apatite (Fleet & Pan 1994, 1995a, b). The *REE* content of synthetic cuspidine equilibrated with apatite was found to increase with increase in atomic number through the 4*f* *REE* transition-metal series, apparently showing that the smaller heavy *REE* (*HREE*) are more acceptable as substituents in the cuspidine structure than the larger light *REE* (*LREE*). Indeed, natural hiortdahlite, also a cuspidine-group mineral, is known to contain significant amounts of Y and *HREE* (*e.g.*, Merlino & Perchiazzi 1987). Also, the substitution of *REE* into cuspidine occurs according to:

$$2Ca^{2+} = Na^{1+} + REE^{3+} \quad (1)$$

but is limited in extent to the composition $NaCa_2REESi_2O_7F_2$. This suggests a structural control on incorporation of *REE*, and it was of interest to compare this control with the topological constraints recognized by Merlino & Perchiazzi (1988) for cuspidine-group structures.

Experimental

Single crystals of Lu-cuspidine were grown from a volatile-rich melt using a standard cold-seal hydrothermal reaction vessel (Fleet & Pan 1995a). In brief, the starting material was a stoichiometric mixture of tribasic calcium phosphate [$\sim Ca_{10}(PO_4)_6(OH)_2$], Lu_2O_3 (99.99 wt%), CaF_2, and SiO_2, containing the equivalent of about 50 mol% $Ca_4Lu_6(SiO_4)_6F_2$ (Lu-fluorbritholite composition). The charge consisted of 0.040 g starting mixture, 0.040 g of NaF and 0.01 cm^3 of deionized water contained in a sealed gold capsule about 4 cm in length. It was heated to 900°C at 0.17 GPa, cooled at 0.1 $deg.min^{-1}$, maintained at 690°C and 0.12 GPa for 20 hours, and quenched in air and water. The products remaining after digesting and washing in hot water were Lu-cuspidine and fluorapatite. Lu-cuspidine was in the form of elongate {110} prismatic crystals, up to 0.1 × 0.2 × 0.8 mm in size. Chemical composition was determined by electron-microprobe analysis (Table 1) using procedures reported in Pan & Fleet (1990). Powder and single-crystal X-ray-diffraction study revealed the space group to be the same as cuspidine ($P2_1/a$), and the unit cell to be analogous to that of cuspidine. Lamellar {100} twinning was evident on examination of oriented crystals with a petrographic microscope. Single-crystal X-ray precession study confirmed that all crystals are twinned by 180° rotation about the *c* axis (or reflection on {100}), and there was some diffuse diffraction intensity (streaking) along reciprocal lattice rows *h0l*, with $l \neq 2n$.

TABLE 1. CHEMICAL COMPOSITION OF Lu-CUSPIDINE IN AP27

Oxides	Average (7)	Standard deviation	Cation*
SiO_2 wt.%	24.57	0.17	1.979
P_2O_5	0.13	0.04	0.009
CaO	23.12	0.27	1.998
Lu_2O_3	41.25	0.32	1.003
Na_2O	6.48	0.04	1.012
F	7.21	0.09	1.837
O≡F	3.04		
Total	98.59	0.43	

* calculated based on 6 cations.

The crystal specimen selected for refinement of unit-cell parameters and X-ray structure analysis also is twinned in this manner. It has approximate dimensions of 0.13 × 0.11 × 0.10 mm and a calculated volume of 1.28×10^{-3} mm^3. All single-crystal measurements were made with an Enraf–Nonius CAD–4F diffractometer, using graphite-monochromatized Mo*K*α X-radiation. The unit-cell parameters [*a* 11.024(5), *b* 10.303(3), *c* 7.391(2) Å, β 109.40(3)°] were refined from 20 reflections in the 2θ range 29.7–40.3°. Intensity data were collected by θ–2θ scan with a scan angle (2θ) of 2.4° and correction for dispersion. A total of 3855 *hkl* reflections allowed by space group $P2_1/a$ out to 2θ = 55° were measured ($-14 \leq h \leq 14$, $0 \leq k \leq 13$, $-9 \leq l \leq 9$). Standard reflections were 320, 022, and 400, and no significant variation in intensity was found (R_{int} = 0.01). Background, Lorentz, polarization and absorption corrections were applied; transmission factors (calculated by Gaussian integration with a 12 × 12 × 12 grid and μ = 147.5 cm^{-1}) varied from 0.240 for $\bar{2}11$ to 0.322 for $50\bar{9}$. There were 1937 unique reflections, with 333 considered unobserved on the basis of $I < 3\sigma(I)$ [$\sigma(I) = \{I_m + 0.002^2(I_m - B)^2 + 0.005^2(I - I_m)^2\}^{1/2}$, I_m, measured intensity and B, background].

Structure refinement proceeded from the transformed positional parameters of Saburi *et al.* (1977), using the ideal formula $NaCa_2LuSi_2O_7F_2$. The value of $\Sigma w(\Delta F)^2$ was minimized ($w = 1/\sigma^2$), and unobserved reflections were given a low weight (σ = 1000). The

TABLE 2. POSITIONAL AND ISOTROPIC THERMAL PARAMETERS (Å²)

	x	y	z	B_{eq}
Ca(1)	0.4247(4)	0.1276(4)	0.8388(6)	0.67(7)
Ca(2)	0.4262(2)	0.1308(2)	0.3409(4)	0.98(4)
Ca(3)	0.30858(5)	0.40160(4)	0.52890(7)	0.50(1)
Ca(4)	0.3010(3)	0.3957(2)	0.0257(4)	1.19(4)
Si(1)	0.1276(3)	0.1775(3)	0.7198(4)	0.80(4)
Si(2)	0.1205(3)	0.1769(3)	0.1595(4)	0.85(5)
O(1)	0.1373(9)	0.1937(9)	0.9507(13)	2.66(17)
O(2)	0.1601(8)	0.0289(7)	0.6939(11)	1.53(13)
O(3)	0.1471(8)	0.0248(7)	0.2059(12)	2.00(15)
O(4)	0.2403(7)	0.2726(7)	0.7134(12)	1.47(13)
O(5)	0.2380(7)	0.2681(7)	0.2831(11)	1.55(14)
O(6)	0.9840(7)	0.2215(7)	0.5903(11)	1.44(13)
O(7)	0.9808(7)	0.2262(7)	0.1291(12)	1.61(14)
F(1)	0.1127(5)	0.4916(6)	0.4465(9)	1.13(10)
F(2)	0.1083(5)	0.4949(6)	0.9304(9)	1.36(11)

$B_{eq} = \frac{4}{3} \Sigma_i \Sigma_j \beta_{ij} a_i . a_j$

TABLE 3. SELECTED BOND DISTANCES (Å) AND ANGLES (°)

Ca(1)-O(1)	2.878(8)	Si(1)-O(1)	1.682(9)
-O(2)	2.936(5)	-O(2)	1.598(8)
-O(4)	2.444(6)	-O(4)	1.596(6)
-O(6)	2.648(8)	-O(6)	1.619(4)
-O(7)	2.525(9)		
-F(1)	2.451(7)	⟨Si(1)-O⟩	1.624
-F(2)	2.308(7)		
-F(2)	2.288(6)	Si(2)-O(1)	1.624(9)
		-O(3)	1.610(8)
⟨Ca(1)-O,F⟩	2.560	-O(5)	1.615(6)
		-O(7)	1.565(4)
Ca(2)-O(5)	2.429(5)		
-O(6)	2.310(8)	⟨Si(2)-O⟩	1.604
-O(7)	2.369(8)		
-F(1)	2.271(6)	O(1)-Si(1)-O(2)	106.0(5)
-F(1)	2.315(4)	-O(4)	100.4(5)
-F(2)	2.371(6)	-O(6)	107.0(5)
		O(2)-Si(1)-O(4)	112.2(4)
⟨Ca(2)-O,F⟩	2.344	-O(6)	114.3(4)
		O(4)-Si(1)-O(6)	115.4(4)
Ca(3)-O(2)	2.220(8)		
-O(3)	2.248(8)	O(1)-Si(2)-O(3)	103.6(5)
-O(4)	2.208(8)	-O(5)	98.8(5)
-O(5)	2.204(7)	-O(7)	104.2(5)
-O(6)	2.230(4)	O(3)-Si(2)-O(5)	113.0(4)
-F(1)	2.241(3)	-O(7)	116.6(5)
		O(5)-Si(2)-O(7)	117.3(4)
⟨Ca(3)-O,F⟩	2.225		
		Si(1)-O(1)-Si(2)	164.8(7)
Ca(4)-O(1)	2.689(8)		
-O(2)	2.403(8)		
-O(3)	2.383(9)		
-O(4)	2.521(8)		
-O(5)	2.590(8)		
-O(7)	2.255(5)		
-F(2)	2.249(4)		
⟨Ca(4)-O,F⟩	2.441		

observed structure-factors were corrected for the contribution from twinning after the procedure of Fleet & Burns (1990), but with equal proportions of two twin orientations. Preliminary refinement in $P2_1/a$ with unconstrained occupancies for Ca positions showed that Na was restricted to Ca(1) and Ca(2), and Lu, to Ca(3) and Ca(4). The Na occupancy of Ca(2), and the Lu occupancy of Ca(4), were constrained to be equal by stoichiometry [substitution (1)], leaving the latter [*i.e.*, Lu in Ca(4)] as the only occupancy parameter to be varied. The final refinement was made in $P2_1/a$ using all reflections out to $2\theta = 55°$ and 136 variable parameters, and converged to $R = 0.041$, $R_w = 0.050$ [for reflections with $I \geq 3\sigma(I)$, $S = 1.817$, $\Delta\rho = -1.04$ to $0.87\ e\text{Å}^{-3}$, [both near Ca(3)]. The Lu occupancy of Ca(4) was 0.155(1), and the isotropic-extinction parameter for type-I extinction (g; Coppens & Hamilton 1970) was $1.74(16) \times 10^{-4}$. The twin proportion was not refined. Scattering factors for neutral atomic species and f′,f″ were taken, respectively, from Tables 2.2B and 2.3.1 of the International Tables for X-ray Crystallography (1974). All computations were carried out with DATAP77 and LINEX77 (State University of New York at Buffalo). Final parameters are given in Table 2; a table of anisotropic thermal parameters and a list of observed and calculated structure-factors are available from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2. Selected interatomic distances and bond angles are given in Table 3.

Discussion

The composition of the Lu-cuspidine presently investigated corresponds to the ideal end-member complement of cations, within error of analysis (Table 1). The substitution of *REE* into synthetic cuspidine compositions prepared similarly to AP27 occurs according to the exchange reaction (1), and increases with *REE* content and atomic number (Fleet & Pan 1995b; work in progress). In general, the *LREE* are not readily accommodated in the cuspidine structure, but the substitution of P for Si according to:

$$Ca^{2+} + Si^{4+} = Na^{+} + P^{5+} \quad (2)$$

may be very extensive.

The structure of synthetic Lu-cuspidine is basically the same as that of natural cuspidine (Fig. 1; Saburi *et al.* 1977, Merlino & Perchiazzi 1988). We note that in the cuspidine structure, Ca(1) and Ca(2) are coordinated to three atoms of F compared to just one F in the coordination polyhedra of Ca(3) and Ca(4). The coordination of F with Ca is tetrahedral, and similar to that of F in fluorite. In Lu-cuspidine, the coordination numbers of Ca(1), Ca(2), Ca(3), and Ca(4) out to an arbitarily set limit of 2.94 Å are 8, 6, 6, and 7, respectively. An interesting feature of the cuspidine structure

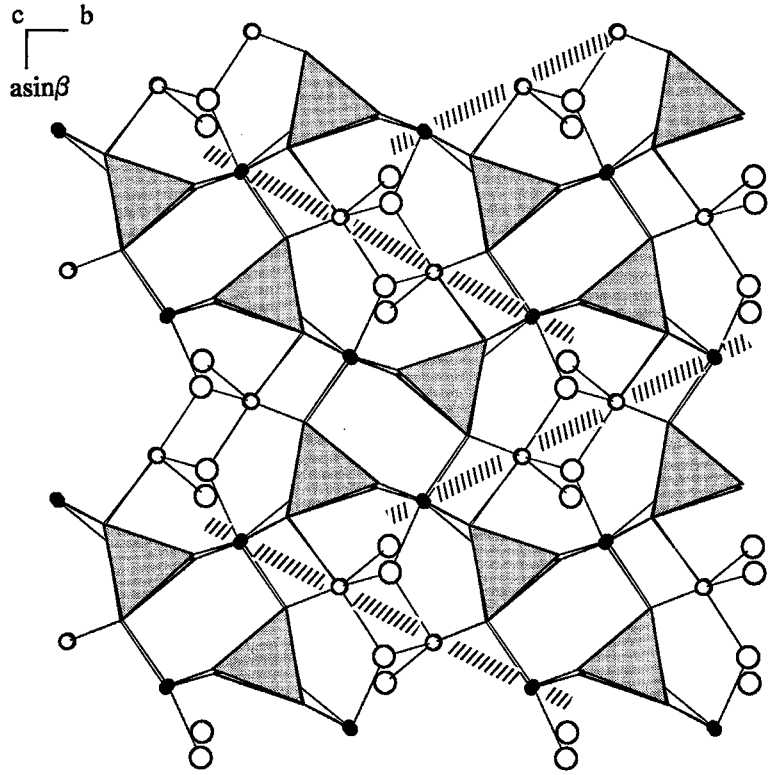

FIG. 1. Structure of Lu-cuspidine, with the two structural modules of cuspidine (polyhedral wall and diorthosilicate group) viewed in projection: Ca(1) and Ca(2) are small open circles; Ca(3) and Ca(4) are small filled circles; four walls of polyhedra are hatched.

is the bonding interaction between Ca(1) and Ca(4) and the bridging oxygen [O(1)] of the diorthosilicate group; Ca(1)–O(1) and Ca(4)–O(1) are 2.499 and 2.656 Å in cuspidine, and 2.878 and 2.689 Å in Lu-cuspidine, respectively. It is the additional bond to O(1) that distorts the Ca(1) and Ca(4) polyhedra from the ideal octahedral configuration assumed in the structural synthesis of Merlino & Perchiazzi (1998). When the long Ca(1)–O(2) distance is ignored, the coordination numbers of the $X(O,F)_n$ polyhedra in Lu-cuspidine are 7, 6, 6, and 7, respectively. The two columns of alternating Ca(3)–Ca(4) polyhedra are on the outside edges of the wall of $X(O,F)_n$ polyhedra (Fig. 1); Ca(4) thus links two diorthosilicate groups, through the two pairs of nonbridging oxygen atoms O(2)–O(3) and O(4)–O(5) (Fig. 2), and therefore has a more important role in defining structural topology than Ca(1) (*cf.* Merlino & Perchiazzi 1988).

As expected, cleavage in cuspidine is determined by the configuration and structural role of the diorthosilicate group. The perfect {110} and good {010} and {001} cleavages in Lu-cuspidine are readily attributable to planes cutting the weaker (Ca,Na,Lu)–(O,F) bonds (Fig. 1).

The site occupancies of the four *X* cation positions were determined to be: Ca(1): 0.155 Ca, 0.845 Na; Ca(2): 0.845 Ca, 0.155 Na; Ca(3): 0.155 Ca, 0.845 Lu; Ca(4): 0.845 Ca, 0.155 Lu. We interpret this result as positional disorder of Ca and Na on Ca(1) and Ca(2), and of Ca and Lu on Ca(3) and Ca(4). As discussed below, the ideally ordered structure, with Ca(1) occupied by Na, Ca(2) by Ca, Ca(3) by Lu, and Ca(4) by Ca, is favored on stereochemical grounds. The extent of disorder should increase with *k*T, but this effect has not been investigated.

Standard deviations of bond distances are higher for Lu-cuspidine (Table 3) than for cuspidine (Saburi *et al.* 1977) by factors of about 3. This reflects both the positional disorder in Lu-cuspidine and the use of a twinned crystal for the collection of reflection intensities. The relatively coarse-scale {100} twinning is evidently a product of crystal growth. Although approximately equal proportions of the two twin orientations are present, we doubt that the twinning

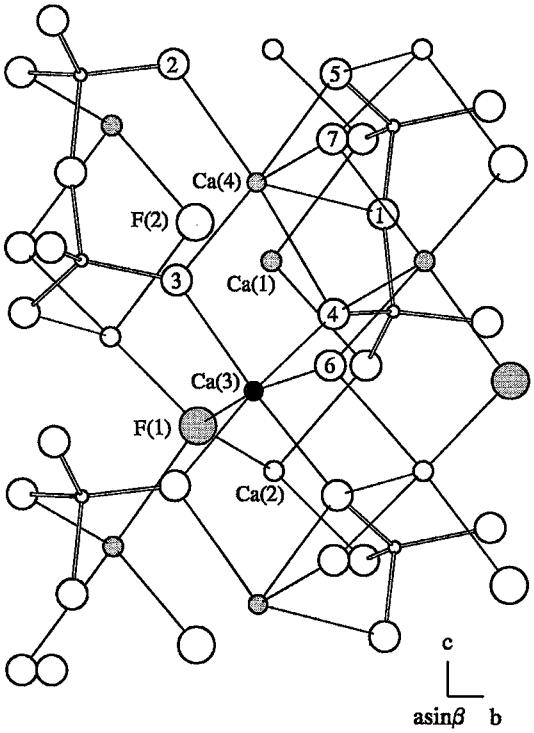

FIG. 2. Partial stereochemical environment of *X* positions in structure of Lu-cuspidine: Lu preferentially occupies Ca(3), and Na, Ca(1).

results from structural transformation associated with local ordering of *X* cations. We emphasize that the {100} twinning would not simulate the observed disordering of *X* cations, and equal proportion of the two twin orientations would be inconsistent with the observed partial disorder of *X* cations.

The positional disorder involving the *X* cations, and particularly occupancy of Ca(4) by Lu, distorts and displaces the diorthosilicate group; this is manifest in larger values of B_{eq} for oxygen atoms and Si (Table 2) relative to ordered silicate structures. The high value of B_{eq} for the bridging oxygen O(1), in particular, reflects displacement in response to the linking of the diorthosilicate group to two relatively short edges of the LuO_6F polyhedron. The bond angle at the bridging (br) oxygen is high (164.8°; Table 3) and inconsistent with the mean Si–$O(1)_{br}$ bond distance, compared with other silicate structures (Hill & Gibbs 1979), but this discrepancy is attributable to constraints imposed by the structural topology (Saburi *et al.* 1977) and the positional disorder (Liebau 1985). The Si(2)–O(7) distance is short (1.565 Å) because O(7) is bonded predominantly to Ca and Na (Table 3) in addition to Si(2).

We have elsewhere (Fleet & Pan 1994, 1995a, b) emphasized the utility of bond valence (Brown 1981; Hawthorne 1992) in predicting the site preference of *REE* in apatite and calc-silicates. In the structure of cuspidine, Ca(3) and Ca(4) are underbonded (Table 4), and therefore we expect trivalent *REE* to substitute into them in preference to Ca(1) and Ca(2), which is in agreement with the observed site-occupancies. In Lu-cuspidine, both cation and ligand bond-valences, calculated for the disordered structure, are in much better agreement with the formal valences (Table 4).

Of course, in estimating the site preferences of *X* cations, balancing of bond valence has to be combined with the constraints imposed by the structural topology, particularly in respect to the linking of the diorthosilicate group to edges of $X(O,F)_n$ polyhedra. Merlino & Perchiazzi (1988) have demonstrated that spatial accommodation is an important factor in determining the site preference of *X* cations in cuspidine-group minerals. Although high-valence cations should prefer Ca(3) and Ca(4) on the basis of bond valence alone, the high-field-strength cations are too small for Ca(4) (Table 5), resulting in O(2)–O(3) and O(4)–O(5) edges that are too small to be readily accommodated by the diorthosilicate group. High-field-strength cations are therefore restricted to the smaller Ca(3) position. On the other hand, Lu^{3+} is closer in size to Ca^{2+} (Table 5), and the destabilization energy associated with its occupancy of Ca(4) appears to be of the same order of magnitude as *k*T, giving the site preference Ca(3) > Ca(4).

An additional factor destabilizing high-valence cations in Ca(4) is the bond-valence requirement of the bridging oxygen [O(1)]. The long bridging Si–O(1) distances require valence balancing by Ca^{2+}; high-

TABLE 4. COMPARISON OF BOND DISTANCE (Å) AND BOND VALENCE FOR CUSPIDINE AND Lu-CUSPIDINE

	Cuspidine[1]			Lu-Cuspidine			
	CN	Distance	s^2	CN	Distance	s	Ca Na Lu[3]
Ca(1)	8	2.481	1.917	8	2.560	1.122	15 85 0
Ca(2)	7	2.405	1.955	6	2.344	1.713	85 15 0
Ca(3)	6	2.364	1.844	6	2.225	2.908	15 0 85
Ca(4)	7	2.450	1.837	7	2.441	1.928	85 0 15
Si(1)		1.618	4.147		1.624	4.089	
Si(2)		1.620	4.115		1.604	4.314	
O(1)			2.250			2.105	
O(2)			1.830			1.956	
O(3)			1.789			1.832	
O(4)			1.966			2.032	
O(5)			1.926			2.024	
O(6)			1.972			1.980	
O(7)			1.934			2.062	
F(1)			1.057			1.097	
F(2)			1.091			0.985	

1. Bond distances from Saburi et al. (1977). 2. Bond valence (s) calculated after Brown (1981). 3. Site occupancies x10^2.

TABLE 5. EFFECTIVE IONIC RADII (Å) FOR SOME X CATIONS IN THE CUSPIDINE GROUP[1]

Cation\CN	6	7	8
Na^{1+}	1.02	1.12	1.18
Ca^{2+}	1.00	1.06	1.12
Lu^{3+}	0.861		0.977
Zr^{4+}	0.72	0.78	0.84
Nb^{5+}	0.64	0.69	0.74
Ti^{4+}	0.605		0.74
La^{3+}	1.032	1.10	1.160

1. Data from Shannon (1976)

valence cations overcompensate the bond valence of O(1), and Na^{1+} undercompensates it. Hence, when Lu^{3+} occupies Ca(4), the accommodation of O(2)–O(3) and O(4)–O(5) distances moves O(1) away from Ca(4) and toward Ca(1), which is presumably simultaneously occupied by Ca. This largely accounts for the straightening of the bridging-oxygen bond angle in the average structure. From this reconstruction, the positionally disordered Na–Ca and Lu–Ca cations may not be randomly distributed within the two types of columns of $X(O,F)_n$ polyhedra. Rather, domain ordering of normal structure [with Ca(1) occupied by Na, Ca(2) by Ca, Ca(3) by Lu, and Ca(4) by Ca] and inverse structure [with Ca(1) occupied by Ca, Ca(2) by Na, Ca(3) by Ca, and Ca(4) by Lu] may exist. This would readily account for the end-member composition of $NaCa_2LuSi_2O_7F_2$. Finally, La^{3+} and other trivalent *LREE* are actually too large for both Ca(3) and Ca(4); occupancy of Ca(3) by the large La^{3+} cation (Table 5) would not flex O(1) away from the charge field of the high-valence cation.

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