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Short-Range Order in the $Ca_{1-x}La_xF_{2+x}$ Solid Solution: 1 : 0 : 3 or 1 : 0 : 4 Clusters?

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The defect structure of the $Ca_{1-x}La_xF_{2+x}$ solid solution ($0 \le x \le 0.38$) has been examined at room temperature by powder neutron diffraction. Two kinds of $\langle xxx \rangle$ interstitial anions, whose respective numbers increase linearly with increasing dopant cation concentration, have been found: one labeled F″ ($x \simeq 0.41$) is a true interstitial; the other labeled F‴ ($x \simeq 0.31$) can be considered a relaxed normal anion. Two 1 : 0 : *n* defect clusters are compatible, within the experimental errors, with these results: the 1 : 0 : 3 ($1V_F$, 0F′, 3F″, $2La^{3+}$) and the 1 : 0 : 4 ($1V_F$, 0F′, 4F″, $3La^{3+}$) clusters. Charge balance considerations and comparisons with the homologous $Ca_{1-x}M^{IV}_xF_{2+2x}$ solid solutions (M^{IV} = Th, U) allow us to think that the less dense 1 : 0 : 3 cluster is present for the whole domain of both kinds of solid solutions. © 1989 Academic Press, Inc.

I. Introduction

The understanding of short-range order in anion-excess fluorite-related solid solutions (*Fm*3*m* symmetry) has increased greatly in the last few years, thanks mainly to numerous structural studies of both low-temperature ordered superstructures, such as $Na_7Zr_6F_{31}$ (*1*), KY_3F_{10} (*2*), Pb_3ZrF_{10} (*3*), tveitite (*4*), β-U_4O_9 (*5*), and high-temperature disordered solid solutions or compounds, such as UO_{2+x} (*6, 7*), $Ca_{1-x}Y_xF_{2+x}$ (*8, 9*), $Pb_{1-x}Bi_xF_{2+x}$ (*10*), $Pb_{1-x}Th_xF_{2+2x}$ (*11*), $Na_{0.5-x}Y_{0.5+x}F_{2+2x}$ (*12*), $Pb_{1-x}Zr_xF_{2+2x}$ (*13*), $Ba_{0.73}Pr_{0.27}F_{2.27}$ (*14*), $Ba_{0.625}Er_{0.375}F_{2.375}$ (*15*), $Sr_{0.84}Lu_{0.16}F_{2.16}$ (*16*), $Ca_{1-x}Th_xF_{2+2x}$ (*17*), $Ca_{1-x}U_xF_{2+2x}$ (*18, 19*), $Ca_{1-x}Zr_xF_{2+2x}$ (*16, 19*), $Sr_{0.69}La_{0.31}F_{2.31}$ (*20*), and $Ca_{0.68}Ln_{0.32}F_{2.32}$ (*21*). There is now a general agreement about the presence of clusters associating one or several dopant cations, anionic vacancies, and interstitial anions. Two kinds of true interstitial anions have been found:

— The *X*′ interstitials ($\frac{1}{2}$, *x*, *x*; $x \simeq 0.37$) correspond to MX_8 square antiprisms associated in large size clusters such as the cuboctahedral 8 : 12 : 0 or 8 : 12 : 1 clusters (8 vacancies, 12 *X*′ and 0 or 1 *X*″ interstitials) present in $Na_7Zr_6F_{31}$, KY_3F_{10}, tveitite, β-U_4O_9, $Na_{0.5-x}Y_{0.5+x}F_{2+2x}$, $Ba_{0.73}Pr_{0.27}F_{2.27}$, $Sr_{0.84}Lu_{0.16}F_{2.16}$, and $Ba_{0.625}Er_{0.375}F_{2.375}$, or such as the columnar $2n + 2 : 4n : 2$ clusters (($2n + 2$) vacancies, $4n$ *X*′ and 2 *X*″ interstitials; $n = 1 \rightarrow \infty$) present in Pb_3ZrF_{10} and probably in the $Pb_{1-x}Zr_xF_{2+2x}$ solid solution.

—The *X*″ interstitials (*x*, *x*, *x*; $x \simeq 0.41$) correspond to MX_9 and MX_{10} polyhedra associated in small size clusters. These clusters, which associate around a single anionic vacancy 0 *X*′ and *n* *X*″ interstitials, are labeled 1 : 0 : *n*.

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In fact, around one anionic vacancy, four X'' interstitial positions are available; when only three of these positions are occupied, a 1 : 0 : 3 cluster is formed (Fig. 1a) as proposed for the $Ca_{1-x}M_x^{IV}F_{2+2x}$ (M^{IV} = Th, U), $Sr_{1-x}Th_xF_{2+2x}$ (*23*), $LaF_{1+2x}O_{1-x}$ (*24*), $ThF_{4x}O_{2-2x}$ (*25*) solid solutions; when four of these positions are occupied, a 1 : 0 : 4 cluster is formed (Fig. 1b) as proposed for the $Sr_{0.69}La_{0.31}F_{2.31}$ phase (*20*).

So, X'-based clusters seem to be essentially adapted to fluorites containing dopant cations of medium size adopting eightfold coordination (Zr^{4+}, Y^{3+}, Lu^{3+}, . . .) whereas X''-based clusters are suitable for fluorites with dopant cations of larger size, such as Th^{4+}, U^{4+}, and La^{3+}, usually found in nine- or tenfold coordination.

Actually, the structural study of the $Ca_{0.68}Ln_{0.32}F_{2.32}$ series (*Ln* = La, Nd, Tb, Ho, Er, Yb, Lu) (*21*) has shown that, with decreasing dopant cation size, F″ interstitials and F‴ relaxed normal fluorine atoms (x, x, x; $x \simeq 0.31$) are progressively replaced by F′ interstitials, which probably indicates the progressive substitution of large cuboctahedral 8 : 12 : 1 clusters for small 1 : 0 : 3 or 1 : 0 : 4 clusters. These results were confirmed by an EXAFS study of the same series (*23*).

In order, on the one hand, to check whether the small F″-based clusters are present for the whole compositional range of the $Ca_{1-x}La_xF_{2+x}$ solid solution (a previous study of the single $Ca_{0.95}La_{0.05}F_{2.05}$ composition had shown that near the prominent F″ site, a F′ site ($\frac{1}{2}$, x, x; $x \simeq 0.39$) was weakly occupied (*26*)), and on the other hand, to choose between the two possible 1 : 0 : 3 or 1 : 0 : 4 clusters, we have undertaken a powder neutron diffraction study of three other compositions (x = 0.10, 0.20, 0.38) of this $Ca_{1-x}La_xF_{2+x}$ solid solution.

II. Experimental

As for the $Ca_{0.68}Ln_{0.32}F_{2.32}$ series (*21*) the samples were prepared by heating at 1000°C intimate mixtures of high-purity CaF_2 and LaF_3 for 2 days in sealed nickel

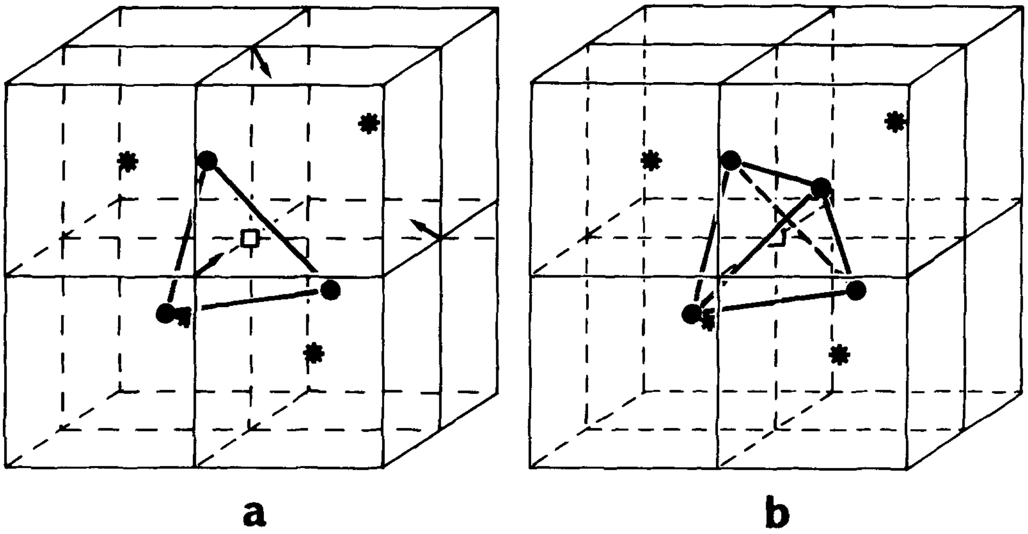

FIG. 1. Schematic views of two 1 : 0 : n clusters: (a) the 1 : 0 : 3 cluster; (b) the 1 : 0 : 4 cluster (cubic basis vectors are parallel to edges of the cubes and origin is at a cation site). *, Cations; ●, F″ interstitials; □, anion vacancy. Small arrows show the F → F‴ relaxation in the 1 : 0 : 3 cluster.

tubes, grinding and heating again for 2 days at the same temperature, and then quenching in cold water. XRD patterns indicated the presence, for all the samples, of a pure fluorite phase.

Contrary to the previous neutron diffraction experiments which were performed on a time-of-flight diffractometer on the Melusine reactor at the CEN in Grenoble, the present ones were performed at room temperature on the D2B diffractometer at the ILL in Grenoble, up to the (800) reflection (exposure time: 3–4 hr, vanadium can; $\lambda \simeq 1.36$ Å). The diffraction pattern of the $Ca_{0.80}La_{0.20}F_{2.20}$ sample is shown in Fig. 2. The intensities listed in Table I were obtained by fitting the experimental profile to Gaussians and the background to a first-order polynomial. Standard deviations were determined from the counting statistics. Observed (I_o) and calculated (I_c) intensities were adjusted by least-squares refinements (*27*) to give structural parameters defining the contents of the average unit cell. All structure refinements were performed in space group *Fm*3*m* using neutron scattering lengths of 4.90, 8.27, and 5.65 fm for Ca, La, and F, respectively. Overlapping data (e.g., 333 and 511 reflections) were included in each of the refinements. In order to localize interstitial fluorine atoms, Fourier-difference sections based on initial refinements of the perfect fluorite lattice were calculated for every composition. One such section calculated in the (110) plane passing through the normal lattice anion, octahedral interstitial, and cation sites is shown in Fig. 3.

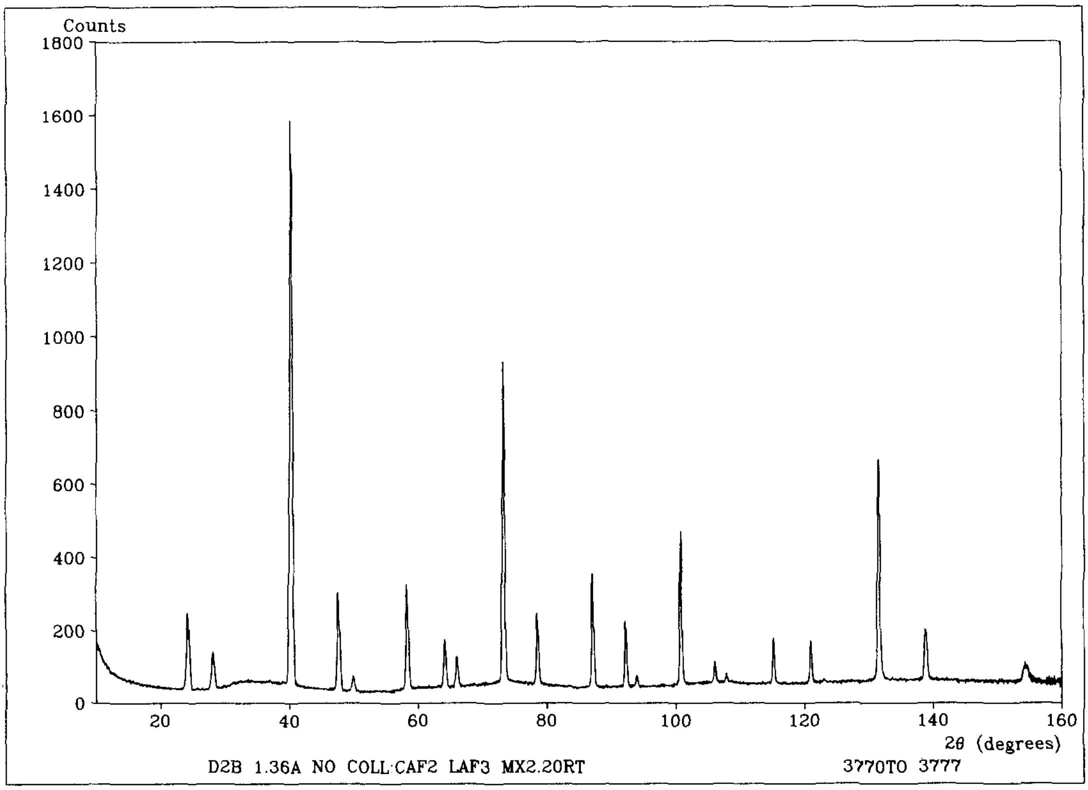

FIG. 2. Diffraction pattern at room temperature of the $Ca_{0.80}La_{0.20}F_{2.20}$ sample (D2B diffractometer).

TABLE I

EXPERIMENTAL (I_o) AND CALCULATED (I_c) INTENSITIES FOR DIFFERENT COMPOSITIONS OF THE $Ca_{1-x}La_xF_{2+x}$ SOLID SOLUTION

	$MF_{2.10}$		$MF_{2.20}$		$MF_{2.32}$ (*21*)		$MF_{2.38}$	
h k l	I_o	I_c	I_o	I_c	I_o	I_c	I_o	I_c
1 1 1	5,374	5,094	4,628	4,403	4,555	4,386	4,501	4,399
2 0 0	3,034	2,924	2,141	2,109	813	963	588	690
2 2 0	29,022	28,974	28,816	28,682	32,241	32,142	32,630	32,449
3 1 1	4,560	4,706	5,030	5,093	7,305	7,288	7,145	7,309
2 2 2	1,190	1,242	733	820	286	373	179	279
4 0 0	6,071	6,127	4,989	5,146	4,783	4,788	4,416	4,596
3 3 1	2,317	2,356	2,243	2,320	2,998	2,931	2,979	3,055
4 2 0	2,147	2,164	1,381	1,332	545	528	500	484
4 2 2	16,075	15,920	13,350	13,269	12,981	12,998	12,438	12,329
5 1 1 3 3 3	2,698	2,554	2,961	2,905	4,147	4,223	4,613	4,578
4 4 0	5,913	5,934	4,782	4,888	4,838	4,851	4,612	4,689
5 3 1	2,539	2,586	2,652	2,644	3,592	3,669	3,591	3,579
6 0 0 4 4 2	1,195	1,208	442	518	60	54	63	76
6 2 0	8,430	8,391	6,039	5,943	4,973	5,025	4,574	4,499
5 3 3	778	771	793	785	874	863	881	868
6 2 2	748	771	320	292	1[a]	7	1[a]	10
4 4 4	2,508	2,533	1,801	1,818	1,547	1,542	1,346	1,444
7 1 1 5 5 5	1,666	1,734	1,673	1,680	1,920	1,978	2,100	2,110
6 4 0	575	522	100	108	1[a]	8	1[a]	57
6 4 2	15,636	15,660	10,898	10,898	8,407	8,324	8,730	8,723
7 3 1 5 5 3	3,258	3,205	2,784	2,753	3,132	3,049	3,317	3,268
8 0 0	3,046	2,885	1,445	1,446	—	—	797	780

[a] Values fixed arbitrarily to 1 for unobserved peaks.

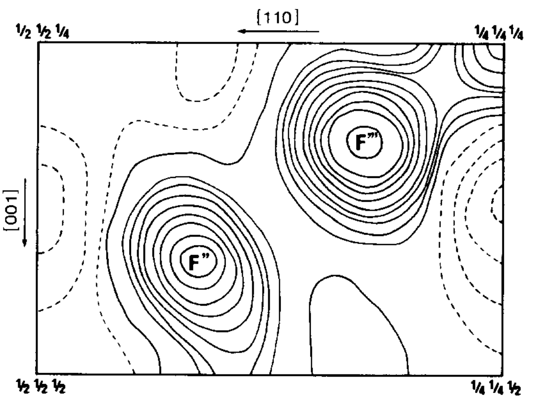

FIG. 3. Fourier-difference section in a ⟨110⟩ plane for the $Ca_{0.68}La_{0.32}F_{2.32}$ phase. Positive contours are shown as full lines and negative contours as broken lines.

III. Results and Discussion

For all of the samples examined, as for the previously studied $Ca_{0.68}Ln_{0.32}F_{2.32}$ (*Ln* = La, Nd, Tb) phases (*21*),

—no cation shift from ideal site (0, 0, 0) and no F′ interstitials are observed

—only F″ interstitials and some F‴ relaxed normal anions, whose number cannot be determined with great accuracy because of the high correlations occurring during the refinements between their parameters and those of the close normal anion F (in fact only the sum ($n_F + n_{F'''}$) and then the

TABLE II

FINAL VALUES OF REFINED STRUCTURAL PARAMETERS FOR THE $Ca_{1-x}La_xF_{2+x}$ SOLID SOLUTION

$2 + x$	2.10	2.20	2.32 (*21*)	2.38
a_F (Å)	5.520(3)	5.575(3)	5.639(3)	5.670(3)
$B_{Ca/La}$ (Å^2)	1.13(2)	1.25(3)	1.18(2)	1.45(2)
n_F	1.88(1)	1.77(2)	1.57(2)	1.46(3)
B_F (Å^2)	1.15(2)	1.71(3)	2.09(3)	2.14(3)
$x_{F''}$	0.414(3)	0.414(1)	0.412(1)	0.413(1)
$n_{F''}$	0.11(2)	0.28(2)	0.48(3)	0.53(4)
$B_{F''}$ (Å^2)	0.6(4)	1.5(4)	2.9(2)	2.2(1)
$x_{F'''}$	0.300(4)	0.309(4)	0.313(2)	0.305(2)
$n_{F'''}$	0.11(2)	0.15(3)	0.27(3)	0.39(4)
$B_{F'''}$ (Å^2)	0.3(6)	1.7(8)	1.6(3)	2.8(3)
R (%)	1.0	0.9	1.1	1.0
R_w (%)	1.3	1.1	1.1	1.1

number of true vacancies ($n_{V_F} = 2 - n_F - n_{F'''}$) are accurately known), are present.

The results of the full-matrix least-squares refinements are given in Table II. The evolution with x of the occupation numbers for normal F, relaxed F‴, and interstitial F″ anionic sites is shown in Fig. 4. Each evolution is linear with slopes $n_{V_F}/x \simeq \frac{1}{2}$, $n_{F''}/x \simeq \frac{3}{2}$ indicating that for the whole solid solution, as for the $Ca_{1-x}M_x^{IV}F_{2+2x}$ (M^{IV} = Th, U) solid solutions (*17–19*), the same 1 : 0 : 3 clusters are probably present. Such clusters actually correspond to very reasonable cation–anion and anion–anion distances: (Ca, La)–F = 2.414 Å, (Ca, La)–F″ = 2.406 Å, F″–F″ = 2.59 Å, F–F″ = 2.26 Å, F″–F‴ = 2.34 Å.

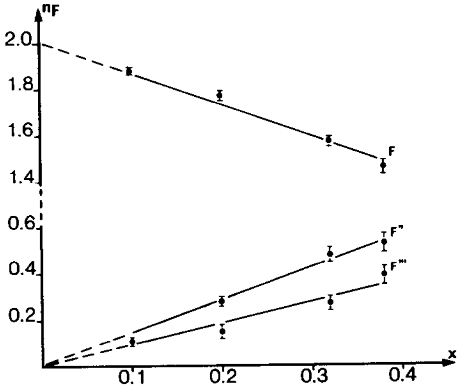

FIG. 4. Evolution with composition of the number of normal F, relaxed F‴, and interstitial F″ anions for the $Ca_{1-x}La_xF_{2+x}$ solid solution ($0.10 \le x \le 0.38$).

In fact, a careful examination of the values reported in Table III and of the curves shown in Fig. 5 indicates that if the 1 : 0 : 2 cluster can easily be eliminated, it is difficult to choose unambiguously between the 1 : 0 : 3 and 1 : 0 : 4 clusters, and this is true for all the phases characterized by F″-based 1 : 0 : n clusters. Fortunately, in the case of $Ca_{1-x}M_x^{IV}F_{2+2x}$ solid solutions, charge balance considerations can help us to remove the difficulty: actually, only the 1 : 0 : 3 cluster, with one M^{4+} dopant cation, one anionic vacancy, and three F″ interstitials, allows a perfect balance of charges. It is not the case with the $Ca_{1-x}La_xF_{2+x}$ solid solu-

TABLE III

COMPARISON OF EXPERIMENTAL n_{V_F}/x AND $n_{F''}/x$ RATES WITH THEORETICAL ONES FOR THE $Ca_{1-x}La_xF_{2+x}$ SOLID SOLUTION

	Experimental				Theoretical		
	$x = 0.10$	$x = 0.20$	$x = 0.32$ (*21*)	$x = 0.38$	Cluster 1 : 0 : 2 (n = 1 cation per cluster)	Cluster 1 : 0 : 3 (n = 2 cations per cluster)	Cluster 1 : 0 : 4 (n = 3 cations per cluster)
n_{V_F}	0.1	0.4	0.5	0.395	1	0.5	0.33
$n_{F''}$	1.1	1.4	1.5	1.395	2	1.5	1.33

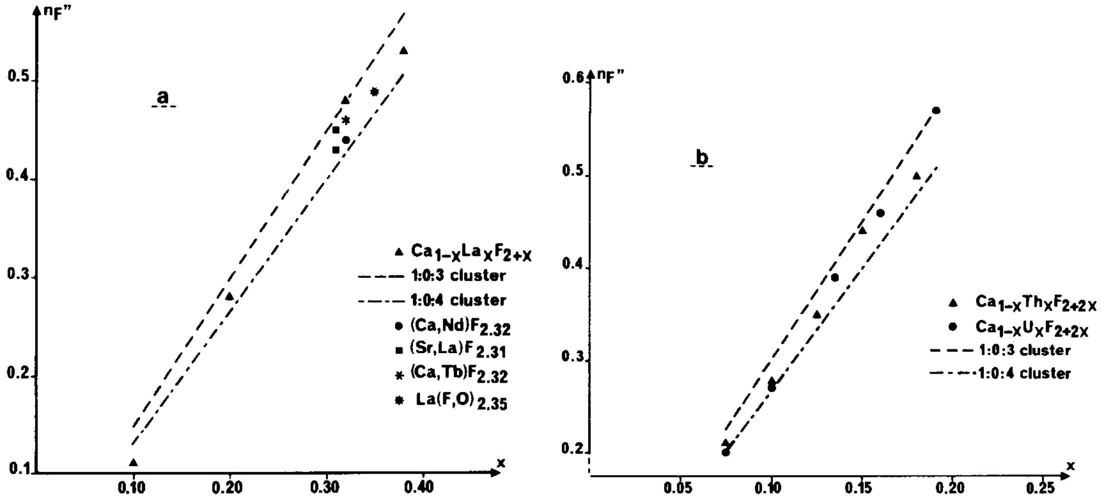

FIG. 5. Comparison of experimental $n_{F''}$ with theoretical ones (1 : 0 : 3 and 1 : 0 : 4 clusters) for (a) $M^{II}_{1-x}Ln_xF_{2+x}$ phases (M^{II} = Ca, Sr). The two values given for the (Sr, La)$F_{2.31}$ compound correspond to different refinement conditions (see Ref. (*20*)). (b) $Ca_{1-x}M^{IV}_xF_{2+2x}$ phases (M^{IV} = Th, U).

tion, for which neutral 1 : 0 : 3 (two La^{3+} dopant cations, one anionic vacancy, three F″ interstitials) and 1 : 0 : 4 (three La^{3+} dopant cations, one anionic vacancy, four F″ interstitials) clusters can be proposed. Nevertheless, if we consider that

(1) F‴ highly relaxed normal anion ($x \approx 0.31$ against $x = 0.25$ for normal anion F) only justifiable by the dissymetry of the 1 : 0 : 3 cluster (see Fig. 1a (arrows) and Ref. (*17*)) are observed, in the same quantity, for both types of solid solutions;

(2) the limits of the composition range of these phases, prepared under the same thermal conditions (quenching at 900–1000°C), correspond to nearly the same number of anions in excess ($MF_{2.38-2.40}$) and not to the same concentration of dopant cations (with nearly the same size), it is then very reasonable to think that the same 1 : 0 : 3 cluster is present in both $Ca_{1-x}La_xF_{2+x}$ and $Ca_{1-x}M^{IV}_xF_{2+2x}$ (M^{IV} = Th, U) solid solutions.

Conclusions

This study once more shows that the main factor determining the nature of short-range order in anion-excess fluorites is not the dopant cation charge but the dopant cation size with respect to the host cation size. So, with this kind of medium-size host and dopant cations (1–1.16 Å), despite the theoretical possibility of achieving a full occupation of the four F″ interstitial sites around a normal anionic vacancy, the most stable cluster seems to be the 1 : 0 : 3 cluster. However, it is not impossible that a more dense 1 : 0 : 4 cluster could be present in fluorite matrices of higher size (Ln^{3+}-doped SrF_2, PbF_2, and BaF_2, for instance) or in the $Ca_{1-x}La_xF_{2+x}$ solid solution at higher temperatures. That could explain why the compositional range of this solid solution increases progressively with increasing temperature above 1000°C, up to a limit $MF_{2.50}$ (*28*) (such a composition implies that the 1 : 0 : 3 clusters are adjacent, a situation highly improbable in a disordered solid solution), whereas the upper limit of the $Ca_{1-x}M_x^{IV}F_{2+2x}$ solid solutions (M^{IV} = Th, U) does not change with increasing temperature even above 1000°C (*17, 19*).

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