INFLUENCE OF CONCENTRATION OF TRIFLUORIDES OF SOME RARE EARTHS (R = La, Ce, Pr, Nd) ON DEFECT STRUCTURE OF $Ba_{1-x}R_xF_{2+x}$ NONSTOICHIOMETRIC FLUORITE PHASES

B. P. SOBOLEV
Corresponding Member of the Section of Sciences and Technology
Institut d'Estudis Catalans (Barcelona)

and *V. B. ALEXANDROV, L. P. OTROSHCHENCO* and *L. E. FYKIN*
Institute of Crystallography, Russian Academy of Sciences, Moscow

SUMMARY

A comparative analysis of changes in the defect structure of the anionic motif of nonstoichiometric $Ba_{1-x}R_xF_{2+x}$ crystals (R = La, Ce, Pr, Nd; $0.22 \leq x \leq 0.5$) was made. With an increase in RF_3 content in the studied crystals, a tendency to a simultaneous occupation of the two sites (i, f) becomes evident, the i-site prevails. These findings correlate with nonmonotonous changes in some physical characteristics of $Ba_{1-x}R_xF_{2+x}$ crystals with variations in the RF_3 concentration. The concentration factor and its relation to the defect structure of nonstoichiometric fluorite $M_{1-x}R_xF_{2+x}$ phases has not been studied systematically so far. The establishment of the role of the concentration factor is important for interpretation of numerous dependences (composition-property) of nonstoichiometric crystals, because it suggests a correlation between these changes and the defect structure of crystals.

INTRODUCTION

The structure of fluorite nonstoichiometric phases with the general formula $M_{1-x}R_xF_{2+x}$ has been discussed since 1911 when Vogt discovered a new mineral, yttrofluorite (or fluocerite), that is, a fluorite with a high rare earths (RE) content [1].

These heterovalent solid solutions became most popular after V. M. Goldschmidt (1926) [2] had chosen them to illustrate the type of isomorphous substitutions with the filling of space. They were referred to in all textbooks on crystallography. The first X-ray diffraction study of $Ca_{0.6}Ce_{0.4}F_{2.4}$ crystals, however, was performed in 1969 [3] only. Specific features of isomorphous replacements of M^{2+} by R^{3+} (RE) in fluorite structure were revealed. Substitutions in the cationic motif were accompanied by a formation of new anionic (interstitial) sites as well as by a simultaneous formation of vacancies in the main anionic motif. These structural defects account for many specific features of the thermal behaviour and physical properties of $M_{1-x}R_xF_{2+x}$ crystals [4-6]

Further structural studies of grossly nonstoichiometric phases $M_{1-x}R_xF_{2+x}$, a brief review of which is made in [7] showed that there are two types of F^- ion incorporation into interstitials, which vary in the direction of their displacement relative to the center of a large cubic void (1/2, 1/2, 1/2). To avoid ambiguity in denoting additional anionic sites, we suggested using complexes with sp. gr. $Fm3m$ which are partially populated by fluorine ions: a 48-fold i-complex and a 32-fold f-complex [8].

Using the experimental data available at that time, the authors of [7] came to a conclusion that in $Ba_{0.73}Pr_{0.27}F_{2.27}$, $Sr_{0.84}Lu_{0.16}F_{2.16}$, $Ca_{0.607}Ce_{0.393}F_{2.393}$, $Sr_{0.69}La_{0.31}F_{2.31}$ crystals i- or f-sites are populated in accordance with the ratio of sizes of the replaced pair of cations, M^{2+} and R^{3+}. Moreover, refinement of the structure of the $Ca_{0.9}Y_{0.1}F_{2.1}$ crystals for which simultaneous occupation of the two sites had been reported earlier [9] showed that the single-site model [10] was preferable.

Thus, the single-site model was confirmed several times at the first stage of structural investigations of fluorite phases with gross stoichiometry perturbations. At the same time, we found that upon replacement of R^{3+} in the series of rare earth elements, on passing over from large to smaller ones (at fixed MF_2 with calcium and strontium), there occurs a transition from phases with f-defects to phases with i-defects. We accumulated examples showing that calculated data were in a better agreement with the experimental data on assumption that both sites are populated. In the third series of $Ba_{1-x}R_xF_{2+x}$ fluorite phases, in which, apparently, until recently only one type of interstitial fluorine atoms was observed experimentally in the entire RE series, at high contents of trifluorides both of the sites turn out to be populated, one site being prevalent.

Further studies of the structure of $M_{1-x}R_xF_{2+x}$ phases and their physical properties demonstrated that changes in their defect structure are possible inside the homogeneity area of the phase (i.e., with arise in x - mole fraction of RF_3 in the solid solution).

This work was aimed at finding tendencies in the changes of the type of defects in nonstoichiometric $Ba_{1-x}R_xF_{2+x}$ crystals upon growth of RF_3 concentratioin in the solid solution. Cations of the cerium series of RE, La, Ce, Pr and Nd were chosen as R. Concentration of RF_3 in obtained $Ba_{0.5}Ce_{0.5}F_{2.5}$ crystals attained the saturation limit (under normal pressure and eutectic temperature) of the solubility of cerium fluoride [11] in BaF_2. Data on $Ba_{0.5}Ce_{0.5}F_{2.5}$ and $Ba_{0.73}Pr_{0.27}F_{2.27}$ crystals, obtained by us earlier [11] are used to analyze the general tendencies [8, 11].

EXPERIMENTAL

$Ba_{0.69}La_{0.31}F_{2.31}$, $Ba_{0.74}Ce_{0.26}F_{2.26}$, $Ba_{0.5}Ce_{0.5}F_{2.5}$, $Ba_{0.73}Pr_{0.27}F_{2.27}$, $Ba_{0.76}Nd_{0.24}F_{2.24}$ single crystals were grown by E. A. Krivandina and Z. I. Zhmurova using the

Bridgeman-Stockbarger technique. Usage of fluorinated-in-advance raw materi-als and an active fluorinating atmosphere during the growth process ensured the lowest possible oxygen content.

Defect structure of the nonstoichiometric phases $Ba_{1-x}R_xF_{2+x}$ can be most effectively studied by neutron diffraction techniques, because anions which statistically occupy a small part (10% and less) of the sites can be located with a relatively high multiplicity (48 and 32 per unit cell).

The experimental measurements were made on a SYNTHEX diffractometer (reactor at the Karpov Institute of Physical Chemistry, λ = 1.167, Cu-mono-chromator). It was not possible to make short wave measurements on this neutron diffractometer, the number of observed reflections was 36-40 for $\sin \Theta$ / $\lambda \leq 0.78$A. In order to obtain more independent experimental data and to raise their accuracy we measured 1/2 Ewald sphere and then averaged the equivalent intensities. No superstructural reflections, disturbances of systematic absences for sp.gr. *Fm3m*, no systematic deviations in the intensities of equivalent reflections were found.

The main technique used to reveal the defect character of the anionic motif of the fluorite nonstoichiometric phases $M_{1-x}R_xF_{2+x}$ is construction of the (110) cross-sections of three-dimensional difference nuclear density Fourier syntheses, alternating with LSM refinements.

The Fourier syntheses, full-matrix LSM refinements, using the Gramm-Charlier formalism and allowance for anharmonism of the thermal motion, correction for extinction according to the Becker-Coppens technique (type 1, Gaussian distribution of block mosaic misorientations) were made according to the "Prometheus" program system [12] adapted for a NORD-500 computer [13].

The structure of the solid solution was refined on the assumption of fully occupied cationic sites. At the first stage:

- isotropic thermal parameters at the sites of the fluorite model (4a, 8c), and site occupancy coefficients q of F_c atoms were refined by LSM;
- zero nuclear density Fourier syntheses were constructed to reveal atoms at other sites;
- their coordinates were determined and site occupancy coefficients were estimated.

At the second stage we performed LSM refinement of the whole model in isotropic approximation and constructed zero Fourier syntheses.

At the third stage we performed LSM refinement of all of the parameters in anharmonic approximation. We took into account only those parameters of atomic thermal motion which exceeded standard deviations by a factor of 2 and led to remarkably clear zero nuclear density Fourier syntheses near relevant atoms.

RESULTS AND DISCUSSION

Figure 1 shows zero nuclear density Fourier syntheses for five nonstoichiometric crystals, arranged in ascending order of RE atomic numbers. The compositions of these crystals are close (or equal) to compositions of maxima on the melting curves of fluorite solid solutions in the relevant systems $BaF_2 - RF_3$ [14]. These are special points which are characterized by the highest thermal stability for each combination of Ba^{2+} and R^{3+} in the fluorite structure. One can see that for $Ba_{1-x}R_xF_{2+x}$ compositions with the maximum stabilization of the fluorite structure the view of the (110) cross-section is changed successively. For $Ba_{0.78}Nd_{0.22}F_{2.22}$ (Fig. 1) the maximum of the nuclear density of interstitial fluorine atoms at the i-site has a symmetric shape without any evidence of the nuclear density at the f-site on the three-fold axis.

For $Ba_{0.69}La_{0.31}F_{2.31}$ crystals (figure 1) isolines of nuclear density of the f-site are involved. An attempt to calculate observed intensity arrays for the two above crystals according to the two-site model (with simultaneously occupied i- and f-sites) led to the following results: for $Ba_{0.78}Nd_{0.22}F_{2.22}$ the occupancy (q) of a 32-fold f-site became zero, and the final zero synthesis became worse; while for $Ba_{0.69}La_{0.31}F_{2.31}$ for the occupancy $q = 0.06$. of the f-site the $\mathfrak{R}$ factor was slightly worse (1.8%) than in the single-site model (1.9%).

These results, taken separately, do not suggest a simultaneous occupation of i- and f- sites. However, data on $Ba_{0.74}Ce_{0.26}F_{2.26}$ and $Ba_{0.73}Pr_{0.27}F_{2.27}$ crystals (figure 1) reveal an intermediate form of the residual nuclear density with a centre of gravity at the i-site. It is not isotropic, as in $Ba_{0.78}Nd_{0.22}F_{2.22}$ crystal, but it is not so vividly deformed in the direction of the f-site, as in $Ba_{0.69}La_{0.31}F_{2.31}$.

In the series of crystals, shown in figure 1, at least two factors influence the defect structure: the ratio of Ba^{2+} and R^{3+} sizes, which, according to the data reported in [7], require and unambiguous occupation of i-sites and and increase in RF_3 content in $Ba_{1-x}R_xF_{2+x}$ solid solutions.

To check the role of the latter factor one can compare the data shown in figure 1, which provides a (110) section of the residual nuclear density for a $Ba_{0.5}Ce_{0.5}F_{2.5}$ crystal, according to [11]. The two sites are evident even after the first stage of refinement. A maximum of the nuclear density at the f-site cannot be due to the superposition of the peaks which are close to fluorine at the i-site, as it was shown in [15] for $Ba_{0.73}Pr_{0.27}F_{2.27}$ crystals at a high temperature. For such a supposition a maximum at the f-site, observed for $Ba_{0.5}Ce_{0.5}F_{2.5}$, is too large. As shown in [11], for the latter crystal the single-site model yields unsatisfactory results.

The data about the structure of the reported crystals are summarized in Table 1. An increase in RF_3 content leads to a higher occupancy of the i-site by F atoms, as well as larger thermal factors (B_{eq}) of these atoms. This parameter reflects mostly statistical anionic displacements form i-sites, while in figure 1 we
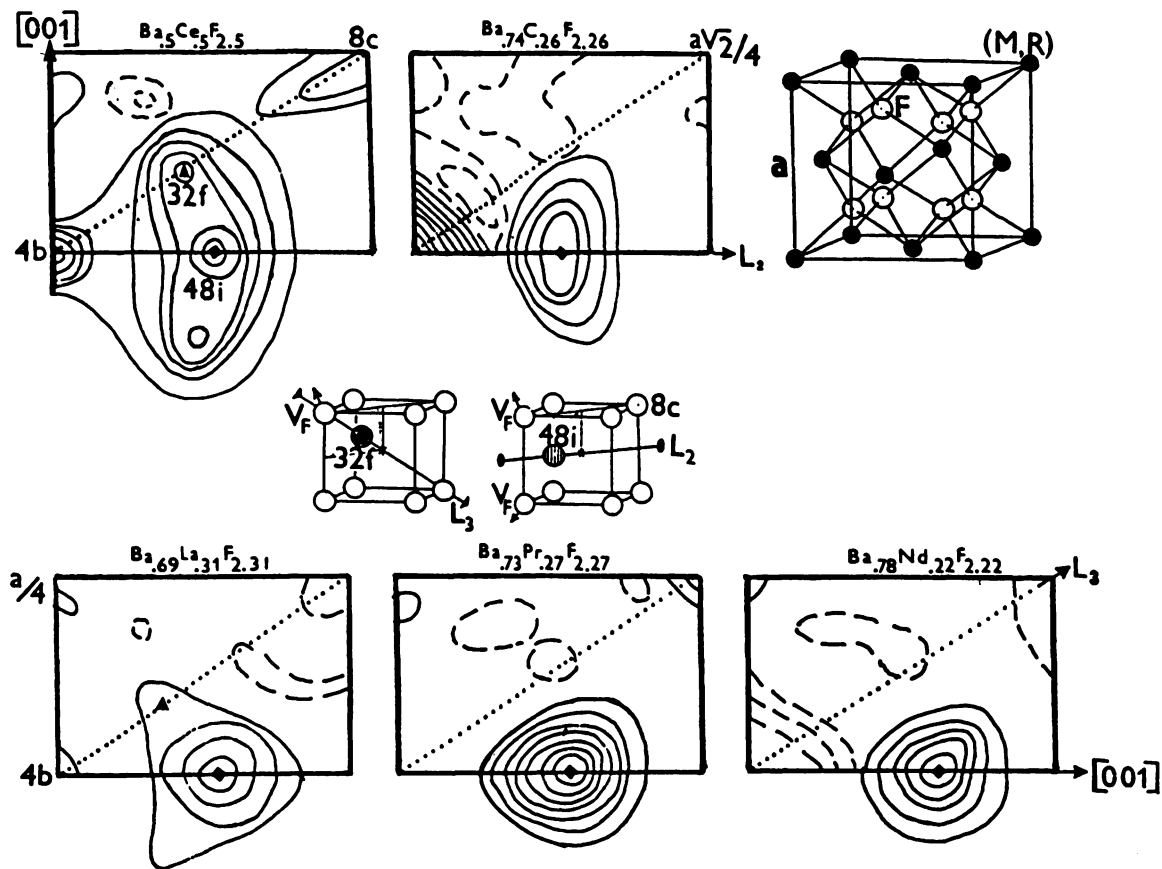
FIGURE 1. Residual nuclear density on zero Fourier syntheses for some $Ba_{1-x}R_xF_{2+x}$ crystals, constructed after LSM refinement of parameters of atoms in isotropic approximation in (110) cross sections.

TABLE 1. Final results of refinement of the structure of $Ba_{0.69}La_{0.31}F_{2.31}$, $Ba_{0.74}Ce_{0.26}F_{2.26}$ and $Ba_{0.78}Nd_{0.22}F_{2.22}$ crystals.

Atoms and coordinates	Parameters	$Ba_{.69}La_{.31}F_{2.31}$	$Ba_{.74}Ce_{.26}F_{2.26}$	$Ba_{.78}Nd_{.22}F_{2.22}$
(**Ba, R**) 4a(000)	$B \times 10^2$	1.49(3)	1.14(3)	1.22(2)
F_c	q, occupanncy	1.530(10)	1.603(7)	1.604(6)
8c	$B \times 10^2$	1.94(3)	1.62(3)	1.79(2)
(1/4; 1/4; 1/4)	$C_{123} \times 10^3$	0.002(1)	–	–
F_i	q	0.780(10)	0.660(10)	0.616(6)
	$B_{11} \times 10^2$	0.042(4)	0.030(3)	0.030(1)
48i	$B_{22} = B_{33} \times 10^2$	0.28(2)	0,14(1)	0.020(9)
(1/2; u; u)	$B_{23} \times 10^2$	0.017(2)	– 0.013(2)	0.002(1)
	$C_{223} \times 10^3$	–	0.013(2)	–
	$D_{2223} = D_{2333} \times 10^3$	–	– 0.033(3)	– 0.020(2)
	$D_{2233} \times 10^4$	–	–	– 0.018(4)
	$B_{eqw} \times 10^2$	5.0	3.0	3.0
	u	0.132(2)	0.134(1)	0.136(1)
R_w %		1.9	2.4	1.9
R %		1.5	1.8	1.7
a, A		6.105(2)	6.102(2)	6.094(2)
F_{hlk}		481	430	415
Independent structure amplitudes		33	40	39
R % discrepancy		3.7	6.2	3.3
Crystals diameter, cm		0.50	0.62	0.66

B, C, D – thermal parameters

observed a tendency of some fluorine atoms to be shifted from i- to f-sites, with an increase in RF_3 content.

This effect follows from general considerations about crystal-chemical limits of RF_3 solubility in MF_2 for two different models, provided that they are single-site. This was reported in detail in [16], here we shall confine ourselves to giving conclusions of this work in brief.

A principal difference in the formation of f- and i-defects (incorporated fluorines) is the relation between occupancies of these sites and vacancies in the main anionic motif. Incorporation of fluorine atoms at the f-site gives rise to a vacancy in the closest anionic node of the main motif (8c site, see figure 1). Incorporation at the i-site is accompanied by the formation of vacancies in two close main nodes, because in the case of one vacancy the distance between F_c and F_i atoms would be very short (1.64 - 1.85 A). A pair of F_c vaancies belongs to two void cubes simultaneously. However, it is impossible to accommodate additional F_i anions in them, because the distance between appropriate points of the 48-i complex is 1.71 - 2.03 A. The necessity of a certain spatial configuration of these two types of defects follows from the condition of the maximum use of vacancies at the 8c site for accommodation of interstitial fluorine atoms at the 48 i-site. This problem can be solved with an assumption about defect clusters. If we take the cluster $(M, R)_6F_{36}$ as the main configuration, where the number of incorporated ions F_i exceeds the number of fluorine vacancies at the 8c site by a factor of 1.5 ($12F/8V_F$), and there is no contact between the clusters, the limiting value of x would be 0.25.

Higher concentrations of RF_3 in $Ba_{1-x}R_xF_{2+x}$ crystals (and others), apparently, require partial involvement of f-sites. In the latter case the $M_{0.25}R_{0.75}F_{2.75}$ composition will be a crystal-chemical limit, to which a recently studied $Pb_{0.3}La_{0.7}F_{2.7}$ crystal is quite close [17].

CONCLUSIONS

A comparative analysis of changes in the defect structure of the anionic motif of nonstoichiometric $Ba_{1-x}R_xF_{2+x}$ crystals (R = La, Ce, Pr, Nd, $0.22 \leq x \leq 0.5$) determined by neutron diffraction technique, shows that as the difference between the sizes of Ba^{2+} and R^{3+} becomes larger, the single-site model (partial occupatioin of i-sites only) is preferable.

With an increase in RF_3 content in the studied crystals, a tendency to a simultaneous occupation of the two sites (i, f) becomes evident, the i-site prevails.

These findings correlate with nonmonotonous changes in some physical characteristics of $Ba_{1-x}R_xF_{2+x}$ crystals with variations in the RF_3 concentration.

The concentration factor and its relation to the defect structure of nonstoichiometric fluorite $M_{1-x}R_xF_{2+x}$ phases has not been studied systematically so far. This study confirms an assumption made in [11] about the influence of concentration of a solid solution on their structure.

The establishment of the role of the concentration factor is important for interpretation of numerous dependences (composition-property) of nonstoichiometric crystals, because it suggests a correlation between these changes and the defect structure of crystals. Similar studies of fluorite phases based on other MF_2 with the same structural type, including the whole RE series, should be undertaken.

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