NEUTRON DIFFRACTION STUDY OF THE FEATURES OF FLUORINE IONS INCORPORATION INTO $Ba_{1-x} R_x F_{2+x}$ SOLID SOLUTIONS

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Disordered solid solutions of $M_{1-x} R_x F_{2+x}$ (M = Ca, Sr, Ba; R = La, Ce, Pr, Nd) with the fluorite-type structure attract the attention of investigators from the standpoint of practical application (laser and optical materials, solid electrolytes, etc.). Besides, their atomic structure is peculiar.

In solid solutions with the fluorite-type structure the compensation for excessive positive valences is made in the following way: fluorine ions occupy the sites of the space group Fm3m that remain vacant in the fluorite structure, namely, 32f on the three-fold axis and 48i on the two-fold axis.[1,2]. Basing on the analysis of four structures of fluorite solid solutions with contents x = 0.10–0.30 in a conclusion was made in[3] about a dependence of the particular site of the incorporated anions on the ratio of ionic radii of di-and trivalent cations. According to,[3] all Ba-solid solutions were supposed to contain additional anions only in i-site.

Our goal was to consider the mechanism of F ions incorporation into fluorite Ba-solid solutions when the concentrations x changed over a wide range for an almost constant ratio of ionic radii M^{2+}, R^{3+} (Fig. 1-4).

We studied single crystals grown by the Stockbarger method under the conditions when oxygen content in the obtained crystals was minimum. The experimental measurements were made on a Syntex automatic diffractometer installed in the VVRTs reactor of the Karpov Branch Institute of Physical Chemistry, $\lambda = 1.167$ Å, Cu monochromator sin $\theta/\lambda \leqslant 0.78$ Å^{-1}.

Fourier syntheses were constructed and least-squares refinement with the use of Gram Charlier formalism was perfomed with an account of anharmonicity of thermal vibrations up to the fourth order, as well as corrections for extinction were made according to the Becker–Coppens method used in PROMETHEUS program system[4] adapted for a NORD-500 computer.[5] The refinement of the structures of solid solutions with supposedly full occupation of the cationic site was performed during several stages. At the first stage we carried out a least-squares refinement of occupancy coefficients q and isotropic thermal atomic parameters at the sites of the fluorite model (4a and 8c); we constructed zero Fourier nuclear density synthesis with subtraction of the known atoms in order to find atoms at other siters, their coordinates were determined and an estimation of site occupancy coefficients was made. At the second stage we refined in isotropic approximation the atomic parameters of the fluorite model and the parameters of additional to stoichiometry F atoms, as well as those of F_c atoms in anharmonic approximation. Zero nuclear density synthesis were constructed. At the third stage we carried out the final least-square refinement of all the parameters in anharmonic approximation not only for F_c, but also for additional to stoichiometry fluorine atoms, if needed. We took into account only such thermal parameters that exceeded the standard deviatons by a factor of 2 and led to the clearing of zero Fourier synthesis in the vicinity of the appropriate atoms.

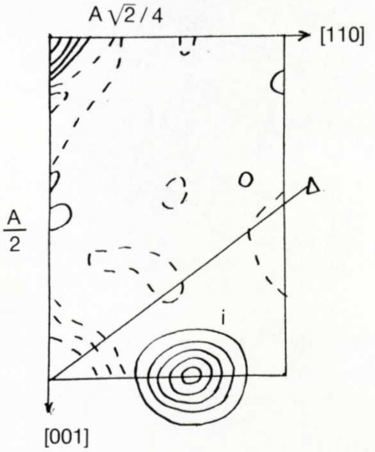
The ionic radii in the investigated solid solutions of $Ba_{1-x} R_x F_{2+x}$ are approximately the same, ranging from 1.11 to 1.16, while the R concentration in these solutions changes significantly from x = 0.22 to x = 0.50 mole %.

Thermal parameters in all the approximations (isotropic, anisotropic, anharmonic) for F atoms at i-site increase with an increase in concentration (for instance, B_{eqv} ranging from 3 to 7 10^{-2} Å). In $Ba_{0.69} La_{0.31} F_{2.31}$ (Fig. 3) the form of the maximum for the i-site implies the appearance of some F atoms at the f–site. To check this assumption we carried out a structure refinement with x = 0.22 and with x = 0.31 mole %R according to two identical schemes with one (i) or two (i and f) sites occupied. After the refinement of a double-site model of the solid solution $Ba_{0.78} Nd_{0.22} F_{2.22}$ (where the peak on the two-fold axis is more isometric) the occupancy of f-site by F ions was zero and the zero synthesis became worse. After the refinement of a double-site model of $Ba_{0.69} La_{0.31} F_{2.31}$ the f-site occupancy by F ions differed from zero (g = 0.06), the R-factor was slightly (R_w = 1.8%) lower as compared to the single-site model (R_w = 1.9%), but this difference was too insignificant to choose the single site model.

Both i and f sites are evident on the zero Fourier synthesis of the first stage, in the case of saturated $Ba_{0.5} Ce_{0.5} F_{2.5}$ solid solution (Fig. 4). Nevertherless, the refinement was made for three theoretical models: only

$Ba_{0.78}\,Nd_{0.22}\,F_{2.22}$

A = 6.094 (2), $\Sigma\,|F_{HKl}|$ = 415, 39 independent structure amplitudes,
R discrepancy = 3,8%, 11 refined parameters.



INITIAL DATA OF ZERO SYNTHESIS

Atoms	Coordinates	Occupancy	B
Ba, Nd	(0, 0, 0)	1	1.20
F_c	$\left(\frac{1}{4}, \frac{1}{4}, \frac{1}{4}\right)$	1.572	1.65

R_w = 8.7%, R = 7.7%

Fig. 1. Residual nuclear density of zero Fourier synthesis constructed after least-sguare refinement of atomic parameters of (Ba, R), F_c atoms in isotropic approximation. (110) section (interval isolines 0.02 10^{-12} cm A^{-3}).

FINAL RESULTS OF REFINEMENT

Atoms	Coordinates	Occupancy	Thermal parameters	
Ba, Nd	(0, 0, 0)	1	B = 1.22 (2)	
F_c	$\left(\frac{1}{4}, \frac{1}{4}, \frac{1}{4}\right)$	1.604 (6)	B = 1.79 (2)	
F_i	$\left(\frac{1}{4}, U, U\right)$	0.616 (6)		
	U = 0.136 (1)		B_{11} = 0.030 (1) $B_{22} = B_{33}$ = 0.020 (1) B_{23} = 0.002 (1) $D_{2223} = D_{2333}$ = – 0.020 (2) D_{2233} = 0.018 (4)	$B_{EQV.}$ = 3.0

R_W = 1.9% R = 1.7%

$Ba_{0.73}\ Pr_{0.27}\ F_{2.27}$

$A = 6.076\ (2)$, $F_{HKL} = 239$, 40 independent structure amplitudes, 13 refined parameters.

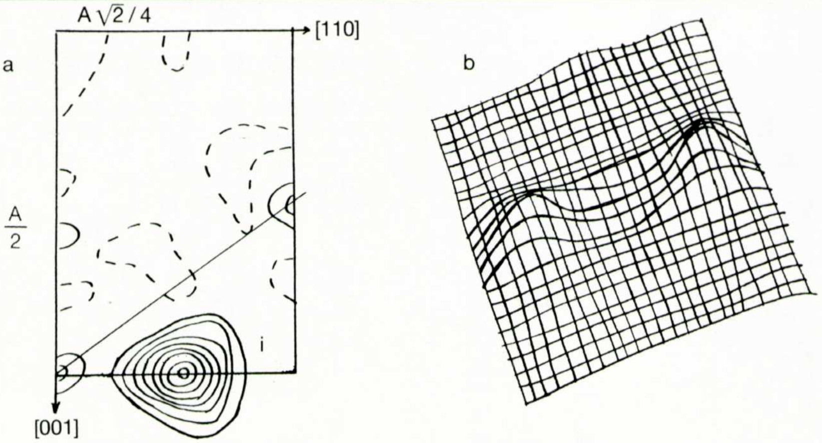


Fig. 2. Residual nuclear density of zero Fourier synthesis after least-sguare refinement of atomic parameters of (Ba, R), F_c atoms in isotropic approximation. a: (110) section (interval isolines 0.02 10^{-12} cm A^{-3}). b: axonometric projections of the same near 1/21/21/21.

INITIAL DATA OF ZERO SYNTHESIS

Atoms	Coordinates	Occupancy	B
Ba, Pr	(0, 0, 0)	1	1.57
F_c	$\left(\frac{1}{4}, \frac{1}{4}, \frac{1}{4}\right)$	1.59	2.15

$R_w = 12.0\%$, $R = 11.0\%$

FINAL RESULTS OF REFINEMENT

Atoms	Coordinates	Occupancy	Thermal parameters	
Ba, Pr	(0, 0, 0)	1	$B = 1.54\ (2)$	
F_c	$\left(\frac{1}{4}, \frac{1}{4}, \frac{1}{4}\right)$	1.585 (7)	$B = 2.10\ (1)$	
F_i	$\left(\frac{1}{2}, U, U\right)$	0.675 (7)	$B_{11} = 0.027\ (2)$	
	$U = 0.135\ (1)$		$B_{22} = B_{33} = 0.027\ (1)$ $B_{23} = 0.018\ (1)$ $C_{222} = C_{333} = -0.008\ (5)$ $D_{2222} = D_{333} = 0.007\ (3)$ $D_{1123} = 0.008\ (3)$ $D_{2223} = D_{2333} = 0.006\ (4)$	$B_{EQV} = 4.0$

$R_W = 1.5\%$ $R = 1.5\%$

$Ba_{0.69}\ La_{0.31}\ F_{2.31}$

$A = 6.105\ (2)$, $\Sigma\ |F_{HKL}| = 481$, 33 independent structure amplitudes,
R discrepancy = 3,7%, 9 refined parameters.

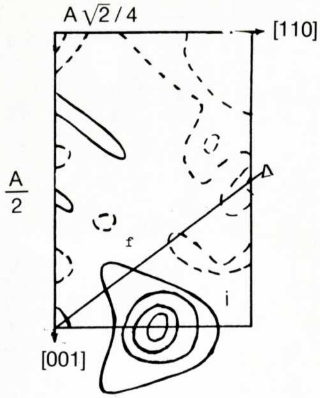


Fig. 3. Residual nuclear density of zero Fourier synthesis for constructed after least-sguare refinement of atomic parameters of (Ba, R), F_c atoms in isotropic approximation. (110) section (interval isolines 0.02 10^{-12} cm A^{-3}).

INITIAL DATA OF ZERO SYNTHESIS

Atoms	Coordinates	Occupancy	B
Ba, La	(0, 0, 0)	1	1.46
F_2	$\left(\frac{1}{4}, \frac{1}{4}, \frac{1}{4}\right)$	1.53	1.93

$R_w = 8.7\%$, $R = 7.2\%$

FINAL RESULTS OF REFINEMENT

Atoms	Coordinates	Occupancy	Thermal parameters	
Ba, La	(0, 0, 0)	1	B = 1.49 (3)	
F_c	$\left(\frac{1}{4}, \frac{1}{4}, \frac{1}{4}\right)$	1.53 (1)	B = 1.94 (3) $C_{123} = 0.002$ (1)	
F_i	$\left(\frac{1}{2}, U, U\right)$	0.78 (1)	$B_{11} = 0.042$ (4)	
	U = 0.132 (2)		$B_{22} = B_{33} = 0.028$ (2) $B_{23} = 0.017$ (2)	$B_{EQV.} = 5.0$

$R_W = 1.9\%$, $R = 1.5\%$

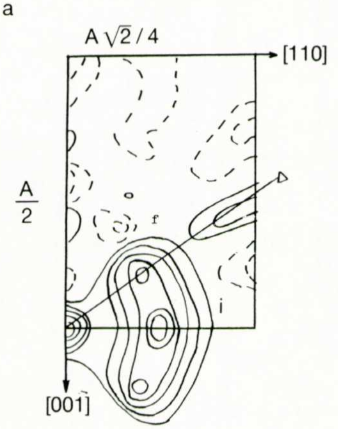
$Ba_{0.5}\,Ce_{0.5}\,F_{2.5}$

$A = 6.033\ (2)$, A, $\Sigma\ |F_{HKL}| = 445$, 37 independent structure amplitudes, 21 refined parameters.

INITIAL DATA OF ZERO SYNTHESIS

Atoms	Coordinates	Occupancy	B
Ba, Ce	(0, 0, 0)	1	1.41
F_c	$\left(\frac{1}{4}, \frac{1}{4}, \frac{1}{4}\right)$	1.51	2.84

$R_w = 15.0\%$, $R = 13.0\%$



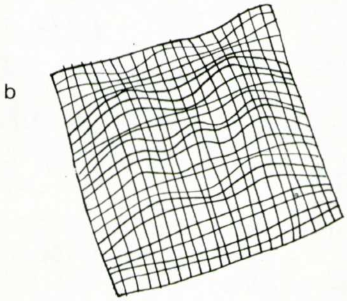


Fig. 4. Residual nuclear density of zero Fourier synthesis for constructed after least-sguare refinement of atomic parameters of (Ba, R), F_c atoms in isotropic approximation. a: (110) section (interval isolines $0.02\ 10^{-12}$ cm A^{-3}). b: axonometric projections of the same near 1/21/21/21.

FINAL RESULTS OF REFINEMENT

Atoms	Coordinates	Occupancy	Thermal parameters
Ba, Ce	(0, 0, 0)	1	$B = 1.412\ (6)$
F_c	$\left(\frac{1}{4}, \frac{1}{4}, \frac{1}{4}\right)$	1.53 (1)	$B = 2.836\ (12)$ $C_{123} = 0.005\ (1)$ $D_{1111} = D_{2222} = D_{3333} = -0.003\ (1)$ $D_{1122} = D_{1133} = D_{2233} = 0.002\ (1)$
F_i	$\left(\frac{1}{2}, U, U\right)$ $U = 0.128\ (1)$	0.514 (7)	$B_{11} = 0.020\ (1)$ $B_{22} = B_{33} = 0.021\ (1)$ $B_{23} = 0.018\ (1)$ $C_{223} = C_{233} = 0.007\ (3)$ $B_{EQV} = 3.0$ $D_{1111} = -0.019\ (3)$ $D_{1123} = 0.008\ (1)$
F_f	(V, V, V) $V = 0.396\ (1)$	0.463 (8)	$B_{11} = B_{22} = B_{33} = 0.038\ (1)$ $B_{EQV} = 5.6$ $B_{12} = B_{13} = B_{23} = 0.013\ (1)$

$R_W = 1.8\%$ $R = 1.8\%$

i –sites occupied (I), only f-sites occupied (II) or both these sites occupied (III). These models were compared in isotropic, anisotropic and anharmonic approximations.

In isotropic approximation, the zero synthesis and R –factor were the best in model III. In anisotropic and anharmonic approximation models I and III are approximately the same as far as these criteria are concerned, but in model I the thermal parameters of F ion at i-site are so large that the range of their vibrations overlaps f-sites. (Fig. 5). After the refinement of model II the R-factor was not lower than 8% (Table 1), that is why that model was no longer analyzed.

Comparison of the results of the refinement of the $Ba_{0.73}$ $Pr_{0.27}$ $F_{2.27}$ and $Ba_{0.78}$ $Nd_{0.22}$ $F_{2.22}$ structures with the final results of the refinement of $Ba_{0.5}$ $Ce_{0.5}$ $F_{2.5}$ structure shows that these structures are much closer in values of thermal parameters to model III than to model I, the latter exhibiting remarkably anomalous parameters of anisotropic and anharmonic vibrations.

Thus, the experimental data can be considered in the framework of models I and III, the latter yielding better R-factors at all refinement stages. The residual nuclear density with subtracted cations and F_c atoms can be interpreted either as occupation of one i-site with remarkable anisotropy and anharmonism of thermal vibrations (overlapping also the f-sites,

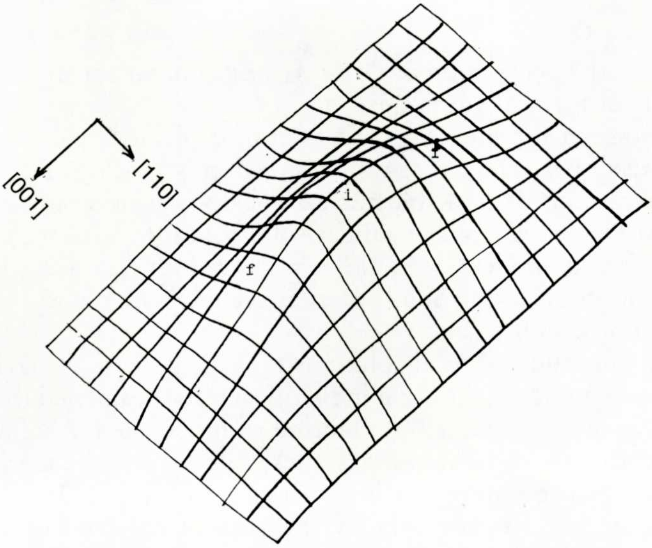


Fig. 5. Axonometric projection of (110) section of probability density near i and f sites of the structure of $Ba_{0.5}$ $Ce_{0.5}$ $F_{2.5}$ solid solution while refining model 1 in anharmonic approximation up to the 4th order.

Table 1. Isotropic thermal factors B/A^2/ heights of residual maxima $\rho/10^{-12}$ cm A^{-3}/ on zero nuclear density maps and R-factors /%/ for various models of occupaneies of i-and f-sites.

Approximatioin	Characteristics	Models		
		1	11	111
Isotropic	B_f	–	9.5	5.1
	B_i	5.4	–	2.9
	ρ_b	1.2	1.2	1.4
	ρ_f	0.8	–	–
	ρ_i	–	1.0	–
	R_w	7.9	8.9	5.1
	R	7.2	8.7	5.0
Anisotropic	ρ_b	1.4	1.2	1.2
	ρ_f	–	–	–
	ρ_i	–	0.8	–
	R_w	3.4	8.8	2.9
	R	3.4	9.1	2.8
Anharmonic	ρ_b	1.2	1.2	1.2
	ρ_f	–	–	–
	ρ_i	–	0.8	–
	R_w	2.2	8.6	1.8
	R	2.3	8.6	1.8

Fig. 4), or as the occupation of i– and f-sites simultaneously, with smaller coefficients of thermal vibrations.

The maxima at f-sites (Fig. 4) cannot be explained by overlapping edges of adjacent peaks of the i-sites, observed in $Ba_{0.73}$ $Pr_{0.27}$ $F_{2.27}$ crystals at high temperature.[6] Remarkable nuclear density was never observed in the previous studies of crystals of similar solid solutions with the i-site occupied. That is why model III should be preferred for $Ba_{0.5}$ $Ce_{0.5}$ $F_{2.5}$. In any case fluorine atoms in this solid solution occupy both i- and f-sites with a rather high probability (Fig. 5).

Thus, our study of solid solutions of Ba_{1-x} R_x F_{2+x}, R having almost identical ionic radii but differing in R concentration, showed that at x 0.25 – 0.30 only i-site is occupied by fluorine atoms, while for higher x values F ions occupy not only i- but also f-sites. Apparently, the mechanisms of fluorine ion incorporation at additional sites in Ba_{1-x} R_x F_{2+x} solid solutions is accounted for not only by the ratio of the radii of isomorphic cations but also by the concentration x of rare-earth cations.

ABSTRACT

A neutron diffraction structural study of crystals of $Ba_{0.70}$ $Nd_{0.22}$ $F_{2.22}$. $Ba_{0.73}$ $Pr_{0.27}$ $F_{2.27}$ $Ba_{0.69}$ $La_{0.31}$ $F_{2.31}$, $Ba_{0.50}$ $Ce_{0.50}$ $F_{2.50}$ when R have approximately equal ionic radii has been carried out. The mechanism of F^{-1} ion incorporation into solid solutions with the fluorite structure, when the rare earth content x changes from $x = 0.22$ to $x = 0.5$ is considered. It was found that in compounds with $x < 0.30$ the i-site is occupied with fluorine ions on the two-fold axis, while in compounds with $x > 0.30$ the i– and f-sites are occupied simultaneously on the two and three-fold axes.

REFERENCES

1. V. B. Alexandrov, L. S. Garashina. Dokl. Akad. Nauk SSSR *189*, 307 (1969).
2. V. B. Alexandrov, L. P. Otroshchenko, L. E. Fykin, V. A. Sarin, V. I. Simonov, B. P. Sobolev. Kristallografiya *29*, 381 (March-April 1984).
3. B. A. Maksimow, L. A. Muradyan, and V. I. Simonov. Crystallogr. and Crystal Chemistry (in russian), Nauka, Moskow, 215 (1986).
4. U. H. Zucker, E. Perenthaler, W. F. Kuhs et al. J. Appl Crystallogr. *16*, 398 (1983).
5. L. A. Muradyan, M. I. Sirota, M. P. Makarova, and V. I. Simonov. Crystallogr. *30*, 258 (1985).
6. L. A. Muradyan, B. A. Maksimov, V. B. Alexandrov, et al. Crystallogr. *31*, 661 (1986).