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NEW DATA ON THE STRUCTURE OF SOLID SOLUTIONS

CaF_2 –TRF_3

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Solid solutions of calcium and yttrium fluorides, having the fluorite structure, occur in nature in the form of the mineral yttrofluorite and have repeatedly attracted the attention of mineralogists and crystal chemists.

It is obvious that, in heterovalent substitution of Ca^{2+} by TR^{3+}, the excess positive valences must be compensated in one way or another. Goldschmidt (^{1}) proposed that, simultaneously with yttrium ions, additional fluorine ions enter the fluorite structure, statistically occupying part of the positions 1/2 1/2 1/2 (the centers of the empty cubes of the initial CaF_2 structure). However, N. V. Belov (^{2,3}) showed that such an assumption is completely inadmissible from the standpoint of modern concepts. A hypothesis was advanced and experimentally confirmed (^{4,5}) that valences are compensated by replacement of part of the fluorine ions by oxygen ions. These studies cast doubt on the very possibility of the existence of solid solutions of TRF_3 in CaF_2.

Earlier, one of the authors of the present work established the existence of a wide range of isomorphous substitutions in the systems MeF_2 –TRF_3, where Me –Ca, Sr, Ba, and TR –lanthanides and Y, under conditions that completely exclude the presence of any appreciable amount of oxygen (^{6}). A study of the character of the change in the lattice parameters of homogeneous solid solutions with the fluorite structure (^{7}) showed that replacement of Ca^{2+} ($R_i = 0.99$ Å) by smaller lanthanide ions from Gd^{3+} ($R_i = 0.97$ Å) to Lu^{3+} ($R_i = 0.85$ Å) is accompanied by a substantial increase in the parameter of the cubic fluorite cell. These experimental data supported Goldschmidt' s hypothesis. It was established that the density values of the solid solutions obtained also agree well with the hypothesis of incorporation of fluorine ions. To clarify the question of the mechanism of isomorphous substitutions of Ca^{2+} by TR^{3+}, we undertook an X-ray study of the fine structure of solid solutions CaF_3 –TRF_3.

The object of study was a single crystal of composition $Ca_{0.607}Ce_{0.393}F_{2.393}$ (the composition was checked by chemical analysis), grown in an HF atmosphere by the Stockbarger method. The intensities of reflections were measured on a nonautomatic diffractometer with a scintillation counter and a monitor in the primary X-ray beam. In all, 66 reflections of type hhl were measured up to $\sin\theta/\lambda = 1.39$ Å^{-1} (MoK_α radiation). To calculate the quantities F^2_{hhl}, the mean intensity values from three series of measurements were taken; a correction for absorption was introduced into these values. The intensities of the same reflections in different series of measurements differed by no more than 3%.

The symmetry of the crystal under investigation was checked on the diffractometer. It was found that the lattice parameters along all three fourfold axes are equal within the accuracy of measurement ($a = 5.672 \pm 0.001$ Å), and no deviations from fluorite symmetry were detected (space group $Fm3m$).

As is known, in the fluorite structure all atoms are located in special positions: 4Ca at $0\,0\,0$ and 8F at $\frac{1}{4}\,\frac{1}{4}\,\frac{1}{4}$. Therefore all X-ray reflections for fluorite can be divided into three types:

1. $h + k + l = 4n$; $F_{hkl} = 4f_{\mathrm{Ca}} + 8f_{\mathrm{F}}$.
2. $h + k + l = 4n + 2$; $F_{hkl} = 4f_{\mathrm{Ca}} - 8f_{\mathrm{F}}$.
3. $h + k + l = 2n + 1$; $F_{hkl} = 4f_{\mathrm{Ca}}$.

The introduction of additional fluorine ions into the positions $\frac{1}{2}\,\frac{1}{2}\,\frac{1}{2}$ (in accordance with Goldschmidt' s hypothesis) should have increased the values of F_{hkl} for reflections of the first two types and decreased F_{hkl} in the case of the third type. At the same time, within each type the intensity ratio should not change in comparison with pure fluorite. In particular, reflections with different h, k, and l, but with the same sums of squares of the indices and, consequently, the same values of $\sin\theta/\lambda$, should have equal intensity (for example, the reflections 060 and 442). However, repeated measurements of such reflections in four quadrants indicated substantial differences in their intensities, reaching 15%. This could be due to two causes: 1) small displacements of atoms from the ideal “fluorite” positions and 2) the presence of a small number of atoms located at a considerable distance from the points $\frac{1}{2}\,\frac{1}{2}\,\frac{1}{2}$, $0\,0\,0$, and $\frac{1}{4}\,\frac{1}{4}\,\frac{1}{4}$ (in more “general” positions). The second possibility seemed more probable, since the differences in intensities were equally noticeable for reflections with low and high values of the indices h and k. A two-dimensional synthesis of the electron density, constructed from 66 values of F_{hkl} taken with positive sign (since a heavy atom is located at the origin), revealed, in comparison with pure fluorite, an additional peak with coordinates in projection along [110]: $x = 0.25$, $y = 0.079$. In addition to it, this projection contained one more weakly expressed maximum (comparable in magnitude with “ghosts”) with coordinates $x \approx 0.17$, $y \approx 0.08$. Identifying these maxima with excess fluorine ions made it possible to explain the inequalities noted above in the values of F_{hkl} for pairs of reflections with identical $h^2 + k^2 + l^2$.

Fig. 1. Difference projection of electron density $\rho_{(\mathrm{exp.})} - \rho((\mathrm{Ca},\mathrm{Ce}),\mathrm{F_I})$ along

Figure 1

Figure 1: Figure 1

[110]. Contours are drawn at intervals of 0.5 el/$\mathring{A}^2$. In the region of negative electron-density values, contours are shown by dashed lines.

The positions of two maxima on the projection along [110], corresponding to one complex in the cubic crystal occupied by additional fluorine atoms, are shown in Fig. 1.

In the process of converting the experimental values F_{hkl}^{exp} to an absolute scale it turned out that, on the plot of the dependence of $\ln(F^{\mathrm{exp}}/F^{\mathrm{calc}})$ on $(\sin\theta/\lambda)^2$, the reflections of the three types indicated above lie near three different, almost parallel straight lines, the upper straight line corresponding to reflections of the first type and the lower one to those of the second type. Hence the conclusion suggested itself that the position 1/4 1/4 1/4 in the structure under study is occupied incompletely by fluorine atoms. It was calculated that removal from this position of 1/5 of the fluorine atoms brings all three straight lines into coincidence. Thus it turned out that the number of vacancies in the main position of the fluorine atoms is almost exactly equal to the number of excess fluorine atoms in the formula of the solid solution under study. Further refinement of the structural model found was carried out by the method of difference (Fig. 1) and zero syntheses of the electron density. The occupancies of the atoms in the main and additional positions, as well as individual corrections to the thermal factor, were refined by the least-squares method. The values of the discrepancy factors at various stages of structure determination are given in Table 1. As a result, the presence in the solid solution under study of additional fluorine ions ($\sim$ 3.2 ions per full cubic cell), statistically distributed over the points of the 32-fold complex (xxx) with coordinate $x = 0.421$, was confirmed, as well as the presence of vacancies ($\sim$ 1.6 per cell) in the main positions of the fluorine ions 1/4 1/4 1/4.

For the crystal studied, high values of the individual isotropic thermal factors B are characteristic: 1.3 for the cations, 2.8 for the fluorine atoms in the main positions, and

Table 1

Values of discrepancy factors R of the calculated and experimental quantities F_{hhl} at various stages of structure determination

Occupancies of fluorine atoms in the theoretical model	Occupancies of fluorine atoms in the theoretical model	Values of R-factors, %	Values of R-factors, %
main positions	additional positions	for all reflections	without the three strongest reflections
8	0	8.70	5.95
6.4	0	6.10	3.98
3	1.6	4.95	3.09
6.4	3.2	4.72	2.59

2.6 for the atoms in the additional positions. The corresponding values for CaF_2 are 0.63 for calcium and 0.74 for fluorine (8), and for natural fluorite, according to our data, 0.45 for calcium and 0.73 for fluorine. It may therefore be assumed that the high values of the B-factors in crystals of the solid solution CaF_2—TRF_3 are due to a considerable extent to statistical displacements of the atoms from ideal positions. If it is assumed that the thermal component of the B-factor is 0.8 $Å^2$, then the amplitude of the probable statistical displacements of the F ions from the positions found is about 0.2 Å. The shape of the maxima on the projection of the electron density $\rho_{(110)}$, and also the presence in the zero synthesis of three characteristic minima around the point $x = 0$, $y = 1/4$, indicate the anisotropic character of these displacements, directed predominantly along the threefold axes of the crystal. An attempt at simultaneous refinement of the magnitudes of the displacements and of the number of displaced atoms did not give unambiguous results.

Thus, as a result of the X-ray diffraction study it has been established that the excess positive valences in solid solutions CaF_2—TRF_3 (not containing oxygen), as Goldschmidt assumed, are compensated by an increase in the number of fluorine ions. However, what occurs here is not the simple introduction of additional fluorine ions, but the replacement of one ion of the initial structure (a vertex of the filled cube) by two ions for each TR^{3+}; moreover, these ions are located not at the centers of the empty cubes of the fluorite structure, but are displaced from them by $\sim 1/6$ along the body diagonal of such cubes. The displacement is evidently directed toward the vacant common vertex of the cubes, since otherwise the distances between the main and additional fluorine ions would prove to be inadmissibly small.

(1.68 Å). The F—F distance for a pair of additional ions is 2.75 Å, and the (Ca, Ce)—F distance is 2.47 Å. The average distance between fluorine ions in the basic and additional positions is 2.65 Å. The considerable nonuniformity of these distances, 2.31-3.12 Å, is evidently compensated by the above-mentioned statistical displacements of the fluorine ions. All four cubes adjacent to a common vacant vertex can be filled by additional ions. In this case a new empty

Fig. 2

Figure 2: Fig. 2

polyhedron is formed—a regular tetrahedron of fluorine ions with an edge of 2.75 Å. Since an additional ion is displaced along a threefold axis from the center of a cubic void, it can belong to only three polyhedra filled with cations.

In the solid solution studied, about 4/5 of all empty cubes are filled by additional F^- ions. The average coordination number for cations

Fig. 2. Examples of probable coordination polyhedra in the structure of the solid solution CaF_2—CeF_3. Circles denote (Ca, Ce) ions. The initial cubes of the structure of pure fluorite are shown by dashed lines.

is found to be $8^4/_5$. However, the coordination numbers of individual cations may vary from 6 (two vacant vertices in one polyhedron without additional atoms) to 12 (two vacant vertices and 6 additional atoms). The kinds and quantitative ratios of the polyhedra cannot be estimated precisely; however, the smallest local spatial difficulties arise if the structure consists mainly of 8-, 9-, and 10-vertex polyhedra. Examples of some probable polyhedra are given in Fig. 2. The distribution and mutual orientation of these low-symmetry polyhedra are apparently statistically disordered, and the structure as a whole retains the cubic symmetry of fluorite and, probably, also its space group $Fm3m$.

Thus, in CaF_2—TRF_3 solid solutions an unusual scheme of heterovalent substitution is realized, in which one of the anions of the initial structure is replaced by two analogous anions. The spatial difficulties arising in this case can apparently be resolved only in relatively open structures with large cations. An increase in the cation radius (for example, replacement of Ca^{2+} by Ba^{2+}, and also of heavy lanthanide ions by large ions of elements of the cerium group) should lead to an expansion of the stability range of the solid solutions. This was confirmed in studies of the MeF_2—TRF_3 systems (7).

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