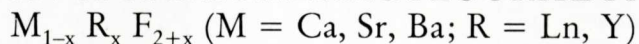


X-RAY AND NEUTRON DIFFRACTION STUDIES OF NON-STOICHIOMETRIC FLUORITE PHASES



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Non-stoichiometric cubic phases of the fluorite type are an object of intense interest because of a peculiar mechanism of heterovalent isomorphism in them, as well as because of their optical and electric properties that can be varied over a wide range by changing the composition of the phases.

One of the main specific features of the considered isomorphism is a large extension of homogeneity regions in binary systems formed by compounds having different cationic and anionic coordination numbers and differing in the type of both anionic and cationic packings. The radii of cations substituting one another vary also over a wide range, from 0.98 to 1.47 Å. Such a wide range of isomorphous cations in inorganic crystals that are simple in composition and structure is, apparently, unique.

There are three possibilities for the compensation for excessive positive valences when R^{3+} are implanted in the MF_2 structure:

1. Formation of cationic vacancies;
2. Replacement of some F^{1-} by O^{2-} ;
3. Appearance of new anionic sites in the structure.

The first one of these schemes looked a priori probable because it is common in oxide compounds relating to the pyrochlorine structural type derived from the fluorite type. However, measurements of specific weight of rare earth fluorites carried out by Zintl and Udgard,¹ and later by Short and Roy² showed that this type of compensation does not play a major role in fluorites (Fig. 1). Another contradiction was an increase of lattice parameters even upon the implantation of R^{3+} ion that is sufficiently smaller than the M^{2+} cation, eg Lu^{3+} in CaF_2 (Fig. 2).

Studies of phase diagrams under the conditions excluding the implantation of noticeable amounts of O^{2-} into the fluorite have shown that

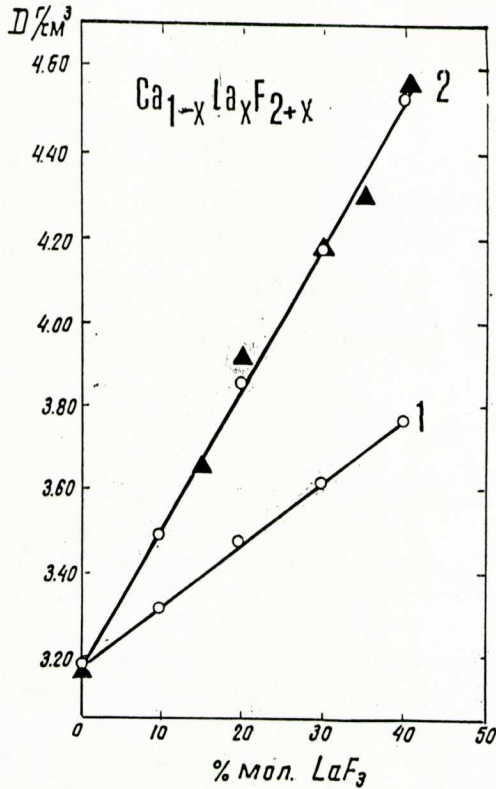


Fig. 1. Density dependences for different types of isomorphic substitutions in the $\text{Ca}_{1-x}\text{Y}_x\text{F}_{2+x}$ solid solutions. Circles—calculated values, dark triangles—experimental data [1].

purely fluoride phases can contain up to $50 \pm 2\%$ LnF_3 under normal pressures. Thus, the second compensation scheme is not manifested either, although it is highly probable that such a scheme can be encountered in natural rare earth fluoites.

The third variant was first considered by V.M. Goldschmidt⁴ in the course of the first X-ray structural study of natural ytthro-fluorite. He supposed that simultaneously with a replacement of Ca^{2+} by Y^{3+} additional fluorine ions are implanted into the fluorite, occupying **4b** sites in the centres of "void" anionic cubes of the structure. N. V. Belov was an opponent of this hypothesis.⁵ He pointed out that the fluorine ion would have had its ionic radius 30% reduced, in this case the closest coordination sphere of the anion would contain eight such anions, and only the second coordination sphere would contain cations, that would have resulted in a far less stability of the structure.

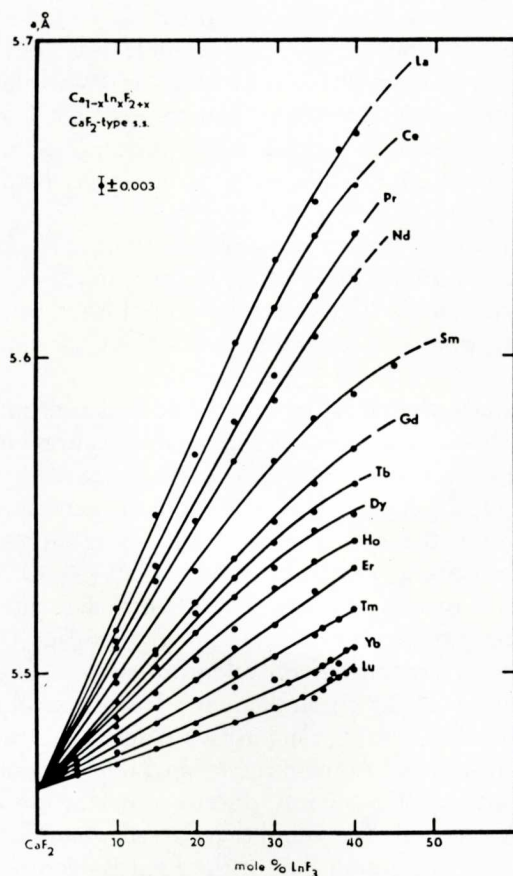


Fig. 2. Lattice parameter dependence on composition of phases $\text{Ca}_{1-x}\text{Ln}_x\text{F}_{2+2x}$.

We checked experimentally the Goldschmidt's hypothesis⁶ using a single crystals of $\text{Ca}_{0.6}\text{Ce}_{0.4}\text{F}_{2.4}$. Our X-ray diffraction studies showed that there are vacancies at 8c sites of the structure, while additional fluorine ions are statistically implanted into 32f sites. The number of these ions remarkably exceeds the number of vacancies. A similar situation was reported by Willis⁷ who carried out a neutron diffraction study of uranium oxides with the fluorite structure. He found two sites of implanted oxygen ions – 32f and 48i. A partial occupancy of one of these sites was later found in $\text{Ca}_{1-x}\text{Y}_x\text{F}_{2+2x}$ phases.⁸ Thus, in R^{3+} – containing fluorite phases the compensation for excessive positive valences is made at the expense of replacement of some anions of the main fluorite motif (at 8c-sites) by a larger number of anions implanted into void anionic cubes

in the structure. However, they are positioned not in the centres of these cubes, as had been proposed by Goldschmidt (4b site) but they are considerably displaced from these centres along two-fold- (48i site) or three-fold (32f site) symmetry axes. Apparently, such a displacement should be directed towards vacant cube vertices (8c complex). Ion implantation would be impossible without vacancies formation because the F-F distances are too short (less than 1.9 Å).

The next stage of the studies was aimed at finding the laws of additional ion distribution and laws of a change in the ratio of occupancy coefficients of anionic sites, as well as determination of interatomic distance for phases of different compositions and with different concentration of a trivalent cation.

In order to study the structures of the considered phases it is better to use neutron diffraction techniques that enable accurate location of ions statistically occupying some (10% and less) sites with a relatively high multiplicity (48 and 32 per cell). Unfortunately the neutron diffractometer that we used did not provide for measurements using short-wave radiation and the number of observed reflections was small (36-40 reflections). To increase the amount of independent experimental data and increase their accuracy we applied a single-crystal technique, measuring 1/2 Ewald sphere and a subsequent averaging of equivalent intensities. The samples were machined into sphere 0.4-0.8 cm in diameter. It was found that satisfactory results can be obtained using data arrays where the scatter of separate values of equivalent intensities from the mean value did not exceed 4-5%, arrays with a greater scatter (mainly due to imperfection of sample macrostructure) were rejected. We found that correct quantitative data can be obtained by neutron diffraction data if the final R-factors do not exceed 1.5-2%. At higher R (up to 3.5%) one can only quantitatively judge about site occupancy. It is also true for the case when powder diffraction data with the same $\sin \Theta/\lambda$ region are used.

The merits of X-ray diffraction technique consist in a possibility of studying small crystals and a large intensity array of observed reflection intensities. The main drawback is a high contrast in the scattering amplitude of atoms that makes it very difficult to reveal anions statistically implanted into sites with a high multiplicity. Besides, the high contrast lowers the accuracy of the determination of occupancy coefficients. Therefore, in all the cases when we have large and perfect single crystals neutron diffraction technique should be given preference.

The main technique of the analysis of the defect structure is the construction of (110) section of three-dimensional Fourier syntheses, alternating with least-squares refinement. First of all, a zero Fourier synthesis was constructed for each phase, the atoms of the main fluorite matrix were set

without account of defects. This synthesis is preceded by refinement of thermal isotropic parameters. The obtained (110) section indicates the presence of anionic vacancies at the 8c site and additional atoms at the remaining sites. Occupancies of all anionic sites are estimated roughly. At the next stage, after the refinement of the obtained model (coefficients of site occupancies, thermal isotropic parameters of all atoms) a difference synthesis with subtraction of cations and anions was constructed. Basing on the analysis of the obtained synthesis the question about the occupancy of 32f, 48i and 8c, 48i sites was solved. The appropriate peaks are positioned close to one another (about 0.65 Å) and thus there is a strong correlation between occupancy coefficients and thermal parameters for these peaks.⁹ An example of making a choice of models with one or two sites of implanted anions is given in a report by L.P. Otroshchenko at this seminar and in¹⁴. The final refinement was carried out in anharmonic approximation up to the fourth rank with account of only those anharmonism parameters that exceeded 2σ and lead to a significant cleaning of the zero Fourier synthesis near the occupied sites. As it was shown, if anharmonism of cationic and especially anionic oscillations at 8c site is not taken into account the question about 32f and 48i site occupancies will be solved incorrectly^{9,10}.

The results of determination of anionic site occupancies are demonstrated on Fig. 4. We see that the occupation of site 48i takes place at lower x values. For Ba-phases the range of existence of such phases is rather wide. Only one phase with $x = 0.5$ was found among them, in this phase both 48i and 32f sites are occupied simultaneously by approximately equal number of anions. In the case $M = Sr$ we clearly see that the site of an implanted anion is changed from 48i to 32f as x increases. Ion implantation into the 32f site is characteristic of Ca-phases, at present there is only one phase known with $R = Y$ and $x = 0.1$, that contains anions at the 48i site. Apparently, there can be other similar phases for lower x phases. Thus, we can assume that the position of an implanted anion is mainly affected by the cationic radii¹⁰, by the concentration x of a trivalent cation, as well as, apparently, by the unit cell volume. Perhaps, the ratio of occupancy coefficients of implanted ions in the transition region can depend on the growth conditions, too.

The data obtained using diffraction methods do not provide direct information on any laws of the local association of vacancies and R^{3+} cations. That is why any attempts of such interpretation of these data require the use of a priori crystal chemical considerations.

For anions at the 32f site the experimentally found distances between the site and the cube vertices of the anionic matrix (8c site) are from 1.6 to 1.7 Å in different structures, i.e. they are smaller than the sum of ionic radii by over 35%. That is why one can be definite enough that in case of

anion implantation at the 32f site the closest site of the anionic motif of the fluorite matrix should be vacant (Fig. 3). There can be four implanted fluorine ions near this vacancy the distances between them are 2.61-2.78 Å for the studied structures and the distances between these ions and the closest matrix anions are 2.32-2.47 Å. The latter are less than the sum of ionic radii only by 6-11% and can be compensated for by slight shifts of the nearest matrix anions. When all the four 32f sites around one vacancy are occupied there is a local increase of charge for 3 units.

A characteristics of the mean local concentration of the implanted ions is the relation of experimentally found values: occupancy coefficient of 32f site and the number of vacancies at the 8c site. In different structures this ratio varies from 2 to 4. Since the largest distance between the 32f sites

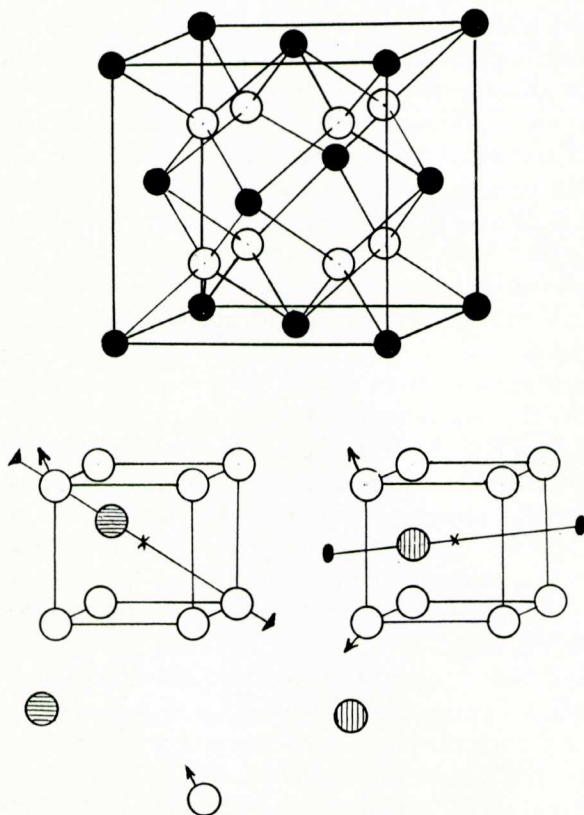


Fig. 3. a) Fluorite structure (note the small anionic cube around the central point of unit cell). b) Small anionic cube with excess anion in 32f-position. c) Small anionic cube with excess anion in 48i-position. Circles with arrows – vacancies.

within one cube is 1.55-1.77 Å, such a cube can contain only one fluorine ion at this site. That is why the limiting number of the implanted anions cannot exceed unity per formula unit. In this case the required number of vacancies should not be smaller than 1/4, i.e. the limiting concentration x of R^{3+} ions should not be greater than 3/4. Thus, the limiting composition of the phase where the implanted anions occupy only 32f site, can be expressed by the formula $M_{0.20}R_{0.80}F_{2.80}$.

The $Pb_{0.3}La_{0.7}$ phase that we have recently studied by X-ray diffraction technique, where all the implanted anions occupy the 32f site (1.0 per formula unit), the number of vacancies at 8c site is 0.3. The values were obtained at an dependent refinement of parameters at fixed sum of occupancies. At an independent refinement of n (32f) and n (8a) with the final values of other parameters the number of vacancies is 0.31, while the number of implanted anions 0.98, that quite well agrees with the formula of the sample.

The situation is much more complex when the implanted fluorine atoms occupy the 48i site (Fig. 3). Two vacancies in the main anionic motif of the fluorite are required for the implantation of one anion at this site, otherwise, the distances between the two anions would be 1.64-1.85 Å. A pair of two adjacent vacancies belongs simultaneously to two "vacant" cubes of the initial fluorite matrix. However, it is difficult to locate additional anions near such a pair in both cubes, because the distance between the corresponding points of the 48i site is 1.71-2.03 Å. The ratio of the number of the implanted anions to the number of vacancies increases with polymerization: in the case of an infinite linear chain of vacancies this ratio tends to 1. The greatest gain in the number of excessive negative valences is in the case of three-dimensional association of vacancies that is realized, in particular, in the $(M, R)_6 F_{36}$ cluster suggested in¹², where the number of the implanted atoms exceeds the number of vacancies by a factor of 1.5. If we admit, following¹³ that such clusters cannot directly contact with each other, in such a replacement mechanism $x \geq 0.25$. In fact, as it follows from the communication of Dr. L. P. Otroshchenko, the phases on the basis of BaF_2 with $x > 0.25$, besides the occupation of the 48i complex, show partial occupancy of the 32f complex, too. In sample with $x = 0.5$ a simultaneous occupation of both complexes is proved reliably. As for a possibility of a simultaneous occupation of two 48i sites by additional anions within the same "void" cube of the fluorite matrix the situation is not quite clear. The largest distance between points of the 32f site within one cube is about 2.3 Å for some of the studied phases, i.e., it is smaller than the sum of ionic radii only by 12%. In such cases, apparently, it is possible. However, for two studied phases with the lowest concentration x (in this phases $R = Y$; $M = Ca$ and Sr) the appropriate

distances are much smaller and the implantation of two fluorine ions into one "void" cube is hardly probable.

The widest ranges of concentrations x , at which anions are implanted the 48i site, are observed for phases based on BaF_2 . In this case we have not found any phase where additional anion would be located at 32f site only, its occupancy has been reliably determined in one specimen – $\text{Ba}_{0.5}\text{Ce}_{0.5}\text{F}_{2.5}$, where additional anions are arranged over the two sites simultaneously, approximately in equal shares.

In phases based on BaF_2 the implanted anions were observed at both sites (and at the two sites simultaneously), the occupation of 48i complex being more characteristics of the largest rare earth ions at small (up to 25-30%) concentrations of R^{3+} .

In the cases of phases based on CaF_2 anion implantation at a single 48i site was found only in one sample ($\text{Ca}_{0.9}\text{Y}_{0.1}\text{F}_{2.1}$). Although in /8/ the model with two sites of the implanted ions was suggested for this structure the authors of /10/ have carefully analysed the experimental data from /8/ and they showed that this model is doubtful. Thus, the concentration regions where there exist phases with implanted additional anions at 48i site are narrowed as the ionic radius M^{2+} decreases, that can be attributed to a decrease in the radii ratio of M^{2+} and R^{3+} ions, as well as to a total volume reduction of unit cells of the phases. In the case when additional anions occupy two sites simultaneously the ranges of the concentration are, apparently, also reduced to a large extent on the transition from phases based on BaF_2 to phases based on CaF_2 (Fig. 4). In the first case the transition region is limited by compositions with x from 0.25 to 0.5, as for phases with Sr, its size, apparently, is 0.1. For $\text{M} = \text{Ca}$ it is still smaller. Probably, the dimensions of the transition region depend also on growth conditions – cooling rate, annealing time etc.

There are interesting conclusions following from the analysis of interatomic distances between a cation and anions occupying different sites. Since all the cations in the structures of the phases studied fully occupy one regular point system (4a) with the basis atom at the origin, one can calculate cation-anion distances for any anion from experimentally obtained u and v , irrespective of the local defect associations. Unfortunately, it is impossible to distinguish between the distances for di- and tri-valent cations using the diffraction data. One can judge about the given bond length relative to some cation only by a correlation between bond length and type of cation and cation concentration.

The anionic site 8c has no variable parameters, and in this case the distance depends only on the mean cationic radius in the given phase. Naturally, in this case it is impossible to obtain any information on the relation of some bond to a particular cation.

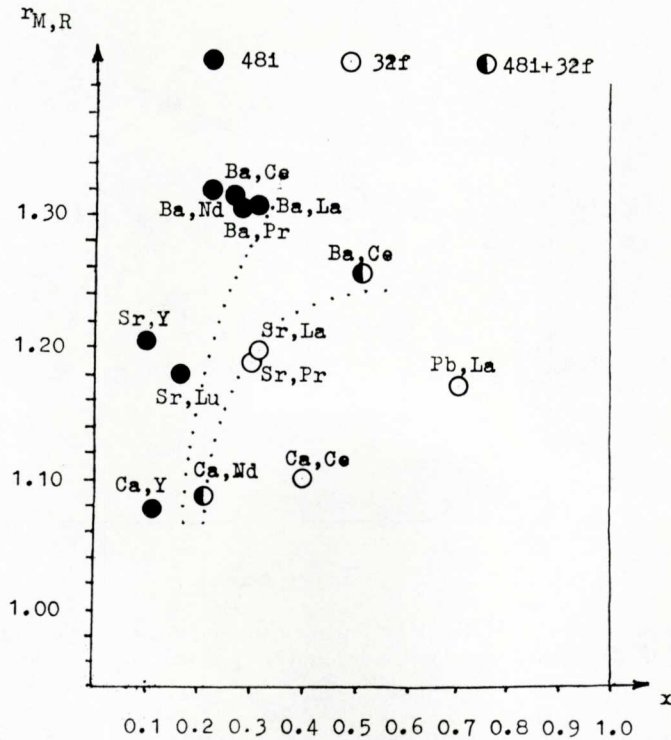


Fig. 4. Positions of implanted anions in $M_{1-x}R_xF_{2+x}$ solid solutions ($M = Ca, Sr, Ba, Pb$; $R = Ln, Y$) with different mean cationic radii $r_{(M,R)}$ and R -concentration (x). Probable transition area is shown by dotted lines.

For anions occupying single - parameter 32f and 48i sites changes in bond lengths at different a , u and v parameters can bear information on the preferred relation of these bonds to a certain cationic type. In the phases with additional anions occupying the 48i site, in the case of $R = Y$ and $x = 0.1$ for $M = Sr$ this distance is 2.27 Å, but for $M = Ca$ - 2.14 Å. For Lu^{3+} in the SrF_2 matrix this distance (2.19 Å) is larger than that for a larger Y^{3+} ion in CaF_2 matrix (2.14 Å). However, these distances do not exhibit any preferential dependence on any of three parameters either. Moreover, upon change of $r_{(M,R)m}$ (mean) these distances behave just like in the case of anions at the 8c site. The slopes of curves, describing approximately this change, in Fig. 5 are almost the same. We see in fig. 5 that for equal $r_{(M,R)}$, bond length for anions at 32f and 8c sites are practically identical. They differ by no more than 2% in each phases, while for anions in the 48i complex they are systematically shorter than

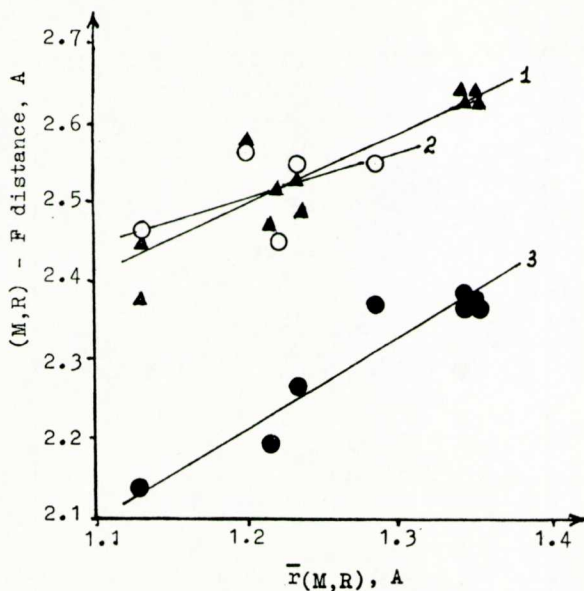


Fig. 5. Interatomic distances (M, R) - F for different positions of F. Triangles - for 8c, light circles - for 32f, dark circles - for 48i. Guide for eyes - 1, 2 and 3 respectively.

the previous ones by 12% and more. This is, apparently, due to a smaller degree of ionicity of bonds of anions at 48i sites as compared to anions at 8c site (in the fluorite matrix).

The studied non-stoichiometric phases have significantly higher thermal oscillation parameters, the highest values of B_{eq} and some anharmonicity coefficients are characteristic of fluorine atoms in the main fluorite motif in most phases (complex 8c). For instance, in most non-stoichiometric fluorite phases studied by us the values of B_{eq} for anions of this complex were about 2-3 \AA^2 , while for stoichiometric fluorite this value is 0.74 $\text{\AA}^2/15\%$. We assume that a substantial contribution to these values is made by not only thermal atomic oscillations proper but also by statistic displacements of atom from their mean sites due to local defects in the structure. We assume that the thermal oscillation proper account for approximately one half of the experimentally founded values of B_{eq} , and that the number of displaced atoms of 8c complex be greater than the number of anions at 48i and 32f sites (for which the number of closest anion-cation contacts is 2 and 3, respectively). In this case the mean value of displacements of 8c cations will be within the range 0.15 to 0.25 \AA for different structures, i.e. it is 12-20%. As is known, the anionic pacing in fluorite is not the closest one, and anionic shifts to such extents, not towards the

shortest bonds, will not result in the formation of bonds less than a doubled radius of F^{1-} ion.

In particular, this refers to "loose" phases containing large Ba^{2+} and Sr^{2+} ions, these phases have larger lattice parameters (about 6 Å). Thus, the presented preliminary estimations of possible values of displacements indicate that there can be local compensation of distances in the anionic motif due to anionic shifts in the $8c$ complex in non-stoichiometric phases. Besides, these shifts are remarkably anharmonic, they are directed preferably along the three-fold axes passing through the atoms of this complex, i.e. along cube space diagonal formed by adjacent anions of the same complex. Apparently, the absence of a closest anionic packing in the fluorite structure and related significant potentialities of a local adjustment of the anionic motif to implantation defects and the vacancies result in the broadening of homogeneity regions in the considered non-stoichiometric phases. This assumption is in a good agreement with the broadening of homogeneity regions due to an increase in lattice parameters of the phases.

The anions occupying different crystallographic sites in non-stoichiometric fluorite phases differ in their coordination number relative to cations. A four-membered coordination (regular tetrahedron) is characteristic of the $8c$ site. Anions of $32f$ complex have a three-membered coordination (they are positioned slightly shifted from the centre of an equal-sided triangle built of cations). And finally, anions in the $48i$ complex have a two-membered coordination, the angles between bonds being about $125-130^\circ$. Lowering of the coordination numbers is accounted for by a formation of stronger cation-anion bonds. In the case of anions at the $32f$ site there occurs a change in the coordination so that non-stoichiometric phases become closer to the extreme component in the MF_2-RF_3 system (where $R = La-Sm$)-tysonite (LaF_3 type) solid solutions, where one third of all the anions have three-membered (triangle) coordination, and two thirds have a four-membered (tetrahedral) one. Besides, the tendency of the structure of non-stoichiometric phases to become were like the tysonite structure is manifested as follows. The anions at $32f$ site almost precisely center the triangles of the anionic packing in the fluorite, transforming it locally to the closest one, that is characteristic of LaF_3 . However, such a process can continue until the aptitude to the implantation of additional ions at $32f$ without distorting the cationic motif is no longer preserved. A complete deformational transformation of the latter towards LaF_3 motif is impossible due to general differences in cationic packings in these two phases. Cations in fluorite are arranged according to the law of cubic packing (ABCABC), while the basis of the tysonite structure is the hexagonal packing (ABAB). That is why a hypothetical transition from one structural type to the other

one is of a strongly reconstructive character, that leads to a noticeable biphasic regions in the systems.

In both cases of additional ion implantation, naturally, the mean cationic coordination number increases. We suppose that first of all the coordination numbers of larger cations will increase. For instance, it is difficult to assume that the coordination number of Ba^{2+} will be smaller than that of Lu^{3+} . Therefore, more logical is the assumption that polyhedron of Ba^{2+} should include the implanted anions, increasing its coordination number and thus weakening the valence forces applied to anions of its coordination polyhedron. In their turn, these anions transmit most of the valence forces to relatively low-coordinated R-cation. Significant reduction of cation-anion bonds for the anions implanted at the 48i site well agrees with this assumption. The 48i site is more typical for combinations of large M^{2+} ions. If ions having different valences in the structure are similar in their radii and ions are implanted into 32f site, then the coordination numbers apparently, increases preferable of R^{3+} cation and no significant redistribution of bond forces occurs.

The formation of new bonds in the structure as non-stoichiometry becomes stronger results in changes of some physical properties of non-stoichiometric phases. A perfect fluorite fracture whose rupture planes pass through the centres of void anionic cubes in the structure, vanishes with ion implantation in these cubes. Changes in coordination numbers of cation and anions are the greatest in case of the latter being implanted at 48i sites. Besides, shortening of some cation-anion bonds in this case can account for melting maxima in the middle part of homogeneity field of this phases. This is typical only for non-stoichiometric phases. Indeed, in all the considered cases, the melting temperature of the phases increases in the region of changing of x , where there is an increased anionic occupancy of the 48i site. In this case the maxima positions, within the accuracy of our experimental data, correspond to the fact that the occupation number of 48i site is no longer increase. In contrast to this, anion implantation at 32f site, lowers the melting temperature of the phases.

In this paper we have considered only non-ordered non-stoichiometric phases retaining the cubic fluorite symmetry. We have not presented here any data on the structure of ordered low-temperature phases with similar compositions. We have used only the objective data provided by X-ray and neutron diffraction studies of non-ordered phases. The use of the data on the structure of ordered phases can assist in interpreting the data obtained in our studies.

Some information on this point is presented in a report by P. Fedorov at this seminar. The ordering process goes on gradually (Fig. 6)/16/ and its mechanism consists, apparently, in the formation of certain types of defect

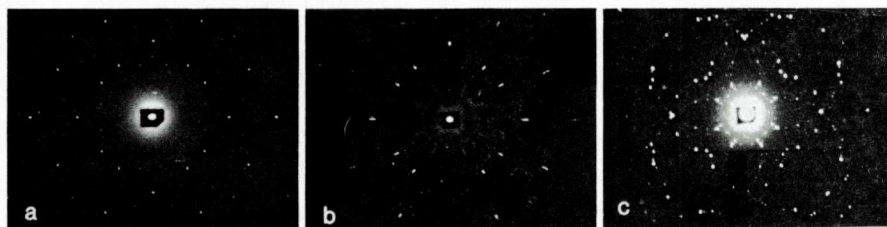


Fig. 6. Laue photographs (unfiltered Mo-radiation) of: a) disordered solid solution $\text{Ca}_{0.61}\text{Ce}_{0.39}\text{F}_{2.39}$, b) partially ordered and c) fully ordered solid solutions $\text{Ca}_{1-x}\text{Tm}_x\text{F}_{2+x}$, with $x = 0.39$ and 0.40 correspondently.

associations and a regular distribution of such associations within the structure.

CONCLUSIONS

1. A new type of heterovalent isomorphism is manifested in non-stoichiometric $\text{M}_{1-x}\text{R}_x\text{F}_{2+x}$ phases, when vacancies in the initial anionic matrix are formed simultaneously with anion implantation at certain crystallographic sites that were not occupied in the structure of a pure component.

2. The defects in the structure of non-stoichiometric fluorite-type phases are spatially related to certain regular point systems, therefore they can be called "crystallochemically localized" defects.

3. In non-stoichiometric phases the implanted ion site (32f or 48i) is defined by M^{2+} and R^{3+} cationic radii, the concentration of R^{3+} and unit cell volume. In each $\text{MF}_2\text{-RF}_3$ system the occupation of 32f site instead of 48i site takes place as a concentration x increases, and there is a transition concentration region, where both sites are occupied simultaneously.

4. The crystal chemical limit of the existence of phases when the 48i site is occupied, is the composition with $x = 0.25$, and with $x = 0.75$ for the case when the 32f complex is occupied. The upper limit of x at an atmospheric pressure is not achieved, the transition region becomes narrower and is shifted towards lower concentration with a decrease in unit cell volume.

5. Two types of implanted anions differ in their coordination relative to cations (2 for 48i complex and 3 for 32f), as well as in the length of cation-anion bond. Bond lengths for anions of 48i site are smaller, than those for anions at 32f and 89c complexes. Apparently, the degree of bond ionicity is smaller in the first case.

6. The appearance of new bonds, changes in the coordination numbers of both anions and cations leads to a greater stability of the structures that is manifested in the vanishing of their mechanical properties, and in case of anion implantation into the 48i complex due to a reduction of some cation-anion bonds, an increase in the melting temperature of non-stoichiometric phases as compared to the initial MF_2 fluorite.

ABSTRACT

By means of alternating least square and Fourier difference synthesis a number of disordered fluorite-type solid solutions were refined, using single crystal neutron and X-ray data. It was shown, that all anionic defects are localized in certain symmetry points of $\text{Fm}\bar{3}\text{m}$ space group: vacancies in 8c, implanted anions in 32f and 48i positions (statistically occupied up to 1/8 and 1/12 respectively). Anions in 32f has the same bond lengths as main fluorite anion position (8c), but for 48i they are shortened for 12%. The three anionic positions have different coordination numbers relative to cations (4, 3 and 2 respectively). Defect formation is of significant influence on some physical properties of the crystals.

REFERENCES

1. ZINTL E., UDGARD A. Z., *Z. anorg. Chem.*, 1939, Bd. 240, pp 150-156.
2. SHORT J., ROY R., *J. Phys. Chem.*, 1963, vol. 67, # 9, pp 101-103.
3. SOBOLEV B. P., FEDOROV P. P., *J. Less, Commun Metals*, 1978, vol. 60, # 1, pp 33-46.
4. GOLDSCHMIDT V. M., *SKRIFT NORSK. Vidensk. Akad. Oslo, mat.-nat. kl*, 1926, pp 88-94.
5. BELOV N. V., *Geochimiya*, 1960, # 6, pp 75-77 (in Russian).
6. ALEXANDROV V. B., GARASHINA L. S., *DOKLADY AN SSSR*, 1969, vol. 189, # 2, pp 307-309 (in Russian).
7. WILLIS B. T. M., *J. de Physique*, 1964, vol. 25, # 5, pp 435-439.
8. CHEETHAN A. K., FENDER B. E. F., STEELE D., TAYLOR R. J., WILLIS B. T. M., *Sol. Stat Comms*, 1970, vol. 8, pp 171-176.
9. MURADIAN L. A., MAKSIMOV B. A., ALEXANDROV V. B., OTROSHCHENKO L. P., BYDANOV N. N., SIROTA M. N., SIMONOV V. I., *Soviet Physics Crystallography* 31(4), July-August 1986, pp 390-392.
10. ALEXANDROV V. B., OTROSHCHENKO L. P., FYKIN L. E. BYDANOV N. N., SOBOLEV B. P., *Kristallografiya*, 1989, vol 34, # 6, pp 1497-1501 (in Russian).
11. MAKSIMOV B. A., MURADIAN L. A., SIMONOV V. I., 'Kristallografiya i Kristalochimiya', Moscow, NAUKA Publishers, 1986, pp 16-21 (in Russian).
12. BEVAN D. J., GREIS O., STRALE J., *Acta Cryst.*, 1980, vol A 36, pp 889-892.
13. GOLUBEV A. M., SIMONOV V.I., *Kristallografiya*, 1986, vol. 31, pp 478-485 (in Russian).
14. OTROSHCHENKO L. P., ALEXANDROV V. B., BYDANOV N. N., SIMONOV V. I., SOBOLEV B. P., *Soviet Physics Crystallography*, vol. 33(3), May-June 1988, pp 449-451.
15. TOGAVA S., *J. Phys. Soc. Japan*, 1964, vol. 19, # 9, pp 20-24.
16. FEDOROV P. P., IZOTOVA O. E., ALEXANDROV V. B., SOBOLEV B. P., *Solid State Chem.*, 1974, vol. 9, # 4, pp 368-374.