JOURNAL OF SOLID STATE CHEMISTRY **28**, 51–58 (1979)

Phase Diagrams of the SrF_2–(Y, Ln)F_3 Systems Part I.—X-ray Characteristics of Phases

B. P. SOBOLEV,* K. B. SEIRANIAN, L. S. GARASHINA,
AND P. P. FEDOROV

*Institute of Crystallography, Academy of Sciences of the U.S.S.R., Moscow, U.S.S.R. and Erevan State University, Erevan, U.S.S.R.**

Received June 7, 1978

The phase equilibria in the subsolidus part of 14 binary systems of SrF_2–(Y, Ln)F_3 type (Ln—all lanthanides except Pm and Eu) were studied at temperatures over 850°C in equilibrated and quenched specimens by the X-ray analysis method. The oxygen concentration in the specimens before and after the thermal treatment was checked. The crystallographic characteristics of phases formed in the systems i.e. nonstoichiometric phases $Sr_{1-x}Ln_xF_{2+x}$ with fluorite type structure, phases with fluorite derived type structure, nonstochiometric phases $Ln_{1-y}Sr_yF_{3-y}$ with tysonite (LaF_3) type structure are given in this paper.

Introduction

The present paper extends the cycle of our investigations of phase diagrams of the MF_2–(Y, Ln)F_3 type systems, where M = Ca, Sr, Ba. In a preceding paper (*1*) the CaF_2–(Y, Ln)F_3 type systems are described. The phase composition and the fusibility of the SrF_2–(Y, Ln)F_3 systems were not nearly so studied as similar systems with CaF_2 and BaF_2.

The papers (*2, 3*) are dedicated to X-ray studies of the solid solutions LaF_3 in SrF_2 with fluorite type structure. The authors of these papers have shown that the solubility of LaF_3 is very high, but its limiting value was not determined. Later on, solid solutions based on SrF_2 were studied (*4*) for YF_3, and for fluorides of La, Ce, Nd, Sm, Gd, Ho, Lu (*5, 6*). In these studies the solubility limit was determined for quenched-from-the-melt specimens. The authors of Ref. (*7*) studied the density and parameter variations of elemental cells of solid fluorite solutions $Sr_{1-x}La_xF_{2+x}$ depending upon temperature and the annealing time. The phase equilibria in the subsolidus part of the SrF_2–EuF_3 system was studied (*8*). We described the results of studies of phase equilibria in the SrF_2–Y, Ln)F_3 system with Ln=Gd–Lu (*9*). In these systems phases with fluorite-derived structure were noticed for the first time.

The first indication on the formation of a solid solution with tysonite (LaF_3) type structure in the SrF_2–YF_3 system was made (*4*). Later on phases with tysonite type structure were noticed (*8, 10–12*). We systematically studied the formation and behavior of solid solutions $Ln_{1-y}Sr_yF_{3-y}$ with LaF_3 type structure for Ln=La–Yb (*13*).

Complete phase diagrams for the SrF_2–LaF_3 and SrF_2–YF_3 systems were

0022-4596/79/040051-08$02.00/0

constructed (*10, 11*), but the phase equilibria in the subsolidus part were not studied. We published preliminary results of phase diagram studies of the SrF_2-(Y, Ln)F_3 systems for the whole series of trifluoride lanthanides (*14*). The present paper contains detailed information about these results. It is divided into two parts. In the first part are given the data on phase equilibria in the subsolidus part and X-ray characteristics of phases. The second part contains information about the thermal behavior of phases.

The crystalline materials formed in the SrF_2–(Y, Ln)F_3 systems find use as active elements in optical quantum generators (their characteristics are shown in Ref. *15*), fluxes for electroslag fusion (*10, 11*), high fluorine conductivity solid electrolytes (*16*), and others. We obtained single crystals $Sr_{0.69}La_{0.31}F_{2.31}$ which are the most refractive materials among all known fluorides. But is might be well to point out that the study of possible practical application of materials in the SrF_2–(Y, Ln)F_3 systems has just started and we hope that the information about the phase diagrams of such systems will prove useful in selecting compositions to obtain single crystal materials.

The MF_2–(Y, Ln)F_3 systems can serve as suitable models to investigate phenomena of formation of nonstoichiometric phases with high concentrations of structural defects and ordering processes of such phases.

The technique of our experiment does not differ from the earlier described procedures (*1*). The oxygen concentration in the starting SrF_2 was equal to 0.02 wt% and the concentration in the samples after annealing was 0.07–0.15 wt%. The earlier mentioned (*1*) necessity of combining dynamic (thermal analysis–TA) and static (annealing and quenching) methods of investigating phase equilibria totally applies to the series of SrF_2–(Y, Ln)F_3 systems.

Results and Discussion

As a result of the X-ray study of phase equilibria in the subsolidus part of the SrF_2–(Y, Ln)F_3 systems it was found that the generating phases crystallize in three main structure types i.e. the fluorite, tysonite and α-YF_3(α-UO_3). The fourth rhombic β-YF_3 type structure was observed only for the pure components of LnF_3. With the decrease in temperature the nonstoichiometric phases with CaF_2 type structure undergo ordering with different types of distortions in the cubic lattice.

Structural Types and Crystallographic Characteristics of Phases in the SrF_2-(Y, Ln)F_3 Systems

1. *Nonstoichiometric phases $Sr_{1-x}Ln_xF_{2+x}$ with fluorite type structure (phase A)* are formed in all systems. As far as the X-ray studies of powders and single crystals permit to judge, the distribution of Sr^{2+} and Ln^{3+} in A phases is statistical in nature. Thanks to this the space group *Fm*3*m* and the magnitude of elemental cells parameters are retained, although the microsymmetry (coordination polyhedrons) of cations varies with composition. In Fig. 1 are shown graphs of the parameters of cubic elemental cells of the $Sr_{1-x}Ln_xF_{2+x}$ phases as a function of composition. It may be seen that they satisfactorily obey Vegard's rule throughout the homogeneity area.

In Table I are given the homogeneity areas (compositionwise) of $Sr_{1-x}Ln_xF_{2+x}$ phases and parameters of elemental cells of saturated disordered solid solutions with fluorite type structure for temperatures close to eutectic temperatures. These data significantly supplement the earlier given (*5*) crystallographic characteristics of the $Sr_{1-x}Ln_xF_{2+x}$ phases for seven systems. As may be seen from Table I the limiting concentrations of LnF_3 in the $Sr_{1-x}Ln_xF_{2+x}$ nonstoichiometric phases are very high and

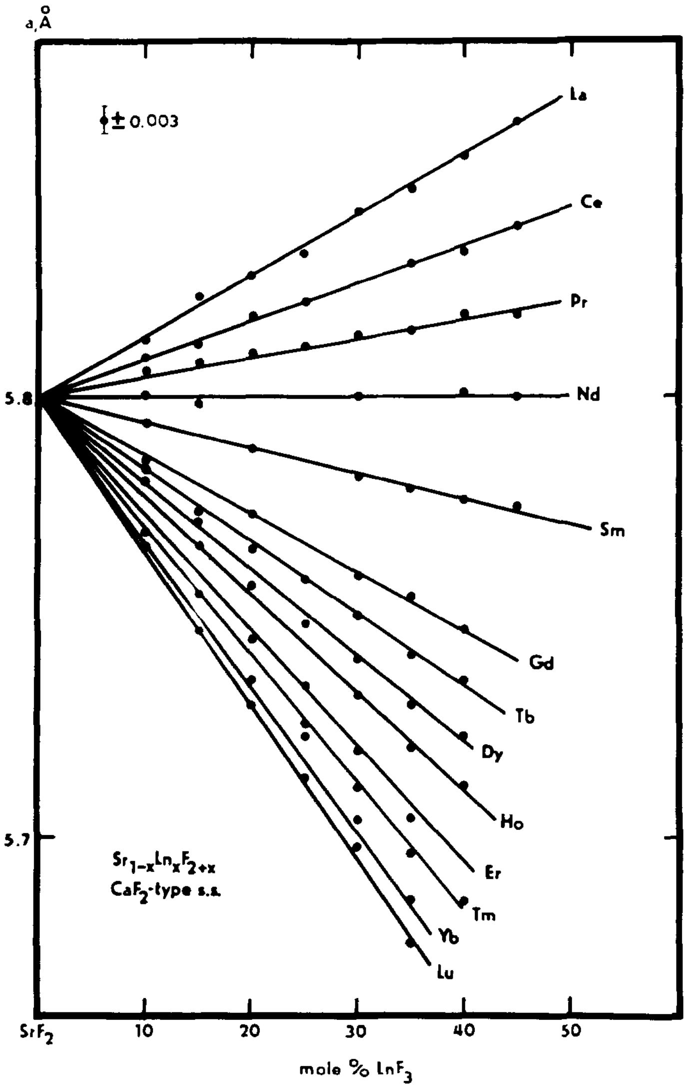

FIG. 1. Graph of the parameters of elemental cells of $Sr_{1-x}Ln_xF_{2+x}$ type phases with fluorite type structure as a function of the composition.

each 52 mole%. The direct study of the atomic structure of $Sr_{1-x}Ln_xF_{2+x}$ was not made. But this study is of much interest because of the abnormalities in the fusibility curves of these phases. In all systems we succeeded in retaining *A* phases in the disordered metastable state by the quenching method because their decomposition processes were strongly slowed down. For this reason annealing is necessary to establish equilibrium state in these regions of diagrams.

The limiting solubilities of LnF_3 in SrF_2 do not vary monotonically for series of lanthanides. They are arranged in different groups. For the systems with Ln = La–Sm it is about 50 ± 2 mole% LnF_3, for the systems with Ln = Eu–Tm about 42 ± 2 mole% LnF_3 and for systems with YbF_3 and LuF_3 amounts to 38 mole%. Such a division of the LnF_3

TABLE I

COEFFICIENTS OF EQUATIONS DESCRIBING CONCENTRATION DEPENDENCE OF LATTICE CONSTANTS OF FLUORITE TYPE PHASES $Sr_{1-x}(Y, Ln)_xF_{2+x}$ ($a = a_0^a + kx$)

R	Homogeneity area (x)	Experimental lattice constants of LnF_3 saturated phases, Å $a \pm 0.003$	k	Dispersion $s^2 \times 10^6$
La	0–0.49	5.868	0.1357	3.2
Ce	0–0.50	5.843	0.0858	5.7
Pr	0–0.49	5.821	0.0446	2.3
Nd	0–0.50	5.800	0.0000	0.5
Sm	0–0.52	5.770	−0.0570	1.6
Gd	0–0.45	5.740	−0.1318	3.1
Tb	0–0.43	5.728	−0.1669	4.2
Dy	0–0.41	5.720	−0.1991	5.1
Ho	0–0.43	5.704	−0.2248	2.1
Er	0–0.41	5.692	−0.2704	2.3
Tm	0–0.40	5.684	−0.2954	2.8
Yb	0–0.37	5.677	−0.3199	3.1
Lu	0–0.37	5.670	−0.3442	6.1
Y	0–0.41	5.704	−0.2602	5.0

[a] $a_0 = 5{,}800$ Å.

series as per their solubility in SrF_2 takes into account the structure of phase diagrams and the imposition of ordered phases on them. The equilibrium existence areas of nonstoichiometric phases $Sr_{1-x}Ln_xF_{2-x}$ in binary systems are much wider than in similar structure phases in the UO_2–UO_3 and other oxide systems. The concentration of structural defects attains record values for strongly ionic substances. The types of defects in the disordered phases $M_{1-x}Ln_xF_{2+x}$ are discussed in detail (*1, 18–20*). The comparison of our data (*18*), about the atomic structure $Ca_{0.607}Ce_{0.393}F_{2.393}$ with the data given (*21*) for UO_{2+x} structure and for $Ca_{0.9}Y_{0.1}F_{2.1}$ (*19*), reveals extraordinary structural similarity of nonstoichiometric phases in binary fluorite and oxide systems of type MX_2–MeX_3 where one of the components crystallizes in the CaF_2 type structure. But it must be mentioned that the study of nonstoichiometric phases in fluorite systems is less than the study of oxide systems. This to a known extent is due to the lack of data about phase diagrams for a large number of MF_2–MeF_3 systems which, as we hope to prove in our studies, will furnish numerous different examples of nonstoichiometric phases of some structural types and different examples of ordering them.

2. *Phases with CaF_2-derived structure.* For the first time we reported the formation of new phases with a structure derivative from the fluorite type structure in the SrF_2-$(Y, Ln)F_3$ system (*9*), but detailed characteristics of such phases were not given. The ordered phases are formed as the disordered fluorite-type solid solutions $Sr_{1-x}Ln_xF_{2+x}$ with contents of LnF_3 close to the solubility limit decompose. In the studied temperature interval (above 850°C) the ordered phases were noticed by us for systems with LnF_3 from GdF_3 to LuF_3. As per Ref. *8* ordering of fluorite type structures is not observed in the SrF_2–EuF_3 systems upon slow cooling of the specimens. But it is not excluded that at temperatures less than 850°C the ordering processes cover the systems with cerium subgroup trifluoride lanthanides.

We did not succeed in isolating single crystals of ordered phases suitable for X-ray studies. For this reason the X-ray data given in this paper characterize subcells. Indexing was carried out without taking into account some weak superstructural reflections. In Fig. 2 are shown X-ray diagrams for all types of ordered phases. For the systems with LnF_3 ranging from GdF_3 to YbF_3 four types of distortions of the fluorite type structure were

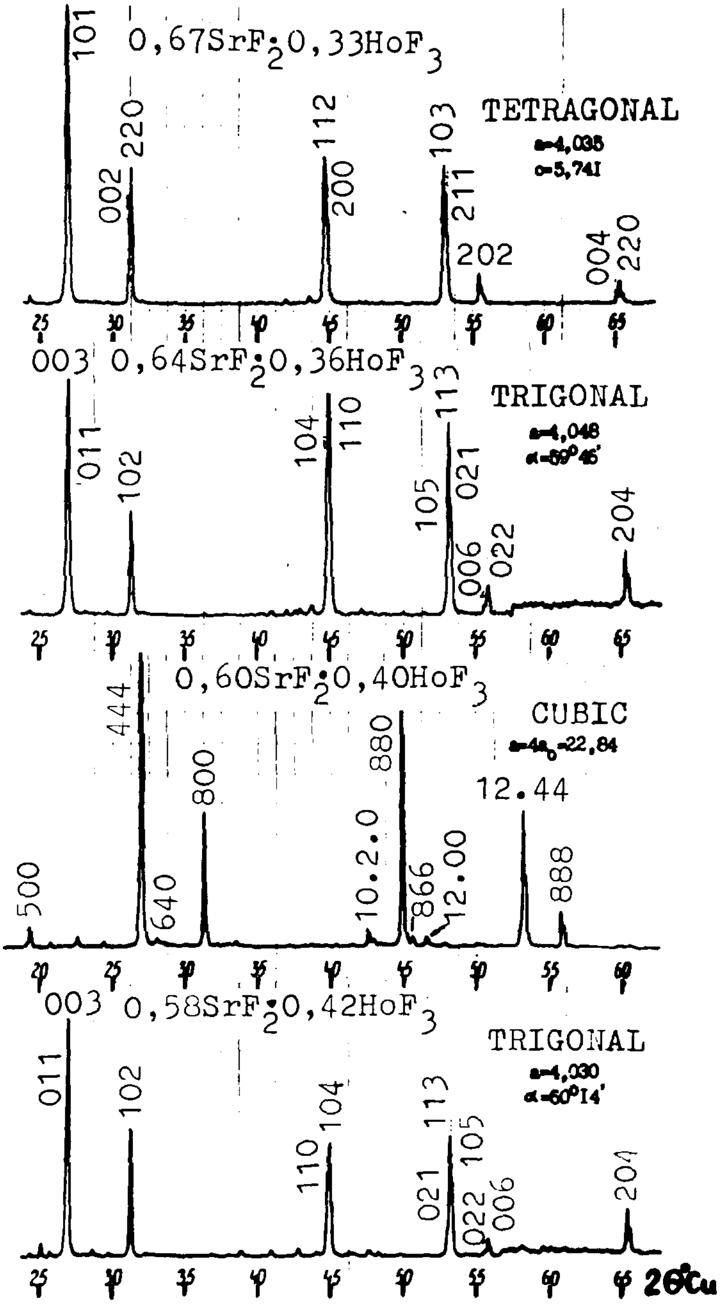

FIG. 2. X-ray powder diagrams of ordered phases with structure derivative from the CaF_2 for the SrF_2–HoF_3 system.

singled out: tetragonal type based on $2SrF_2 \cdot LnF_3$, trigonal type based on $0.64SrF_2 \cdot 0.36LnF_3$, cubic with increasing parameter of the elemental cell (main superstructural reflections are identified for $a = 4a_0$) based on $3SrF_2 \cdot 2LnF_3$ with a small homogeneity area, finally another trigonal type based on $0.58\ SrF_2 \cdot 0.42\ LnF_3$. Despite the similarity in X-ray powder diagrams we could isolate diphase areas between different compounds by profile variation analysis of some groups of diffraction lines. For the systems with GdF_3, HoF_3, LuF_3 the closeness of investigated compositions was 1 mole%.

In Fig. 3 is shown the variation of parameters of subcells for each type of ordered phases in the series of lanthanides trifluorides. It is obvious that the parameters decrease with increase in the atomic number of lanthanides. The phases in the systems with YF_3 are arranged between the systems with HoF_3 and ErF_3 according to X-ray characteristics.

In the SrF_2–LuF_3 systems the ordering scheme differs somewhat, i.e. continuous transition between two trigonal types of distortions of the fluorite structure is observed. In the process of transition the angle α (see Fig. 3B) varies. For contents of LuF_3 more than 44 moles%, transition to the distortion with lower symmetry is observed. Additional studies are required to establish its type.

In the SrF_2–LnF_3 systems, we succeeded in observing the decomposition of nonstoichiometric phases with disordered fluorite type structure in several discrete compounds. Unlike ordered phases in the oxide systems with fluorite derived structure the ordering in the majority of SrF_2–$(Y, Ln)F_3$ systems is recorded by the thermal analysis method. By X-ray analysis double phase areas both between different types of ordered phases and between them and the nonstoichiometric phase were found. Thus, the problem of phase transition of the nonstoichiometric phase to ordered compounds is decided in favor of first order phase transformation.

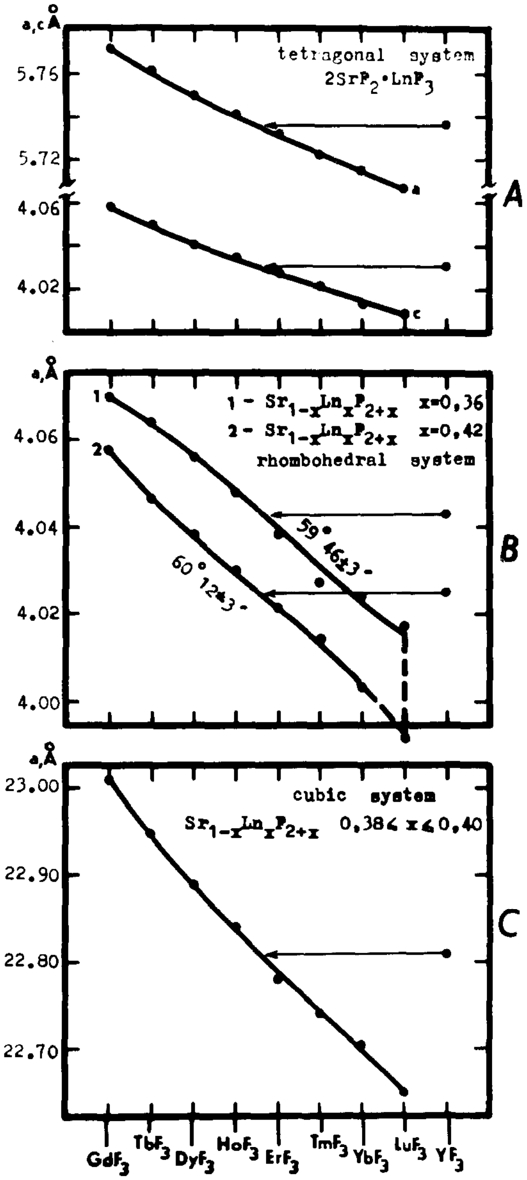

FIG. 3. Variation of parameters of subcells of ordered phases in the SrF_2–LnF_3(Ln=Gd–Lu) systems.

3. *Phases with tysonite* (LaF_3) *type structure* are formed in all the SrF_2–$(Y, Ln)F_3$ systems but their position on the phase diagrams is different. The phases with LaF_3 structure in all the systems have maxima on

the fusibility curves the coordinates of which vary along the lanthanides series. In the group of SrF_2–LnF_3 systems (Ln=La–Gd) the $Ln_{1-y}Sr_yF_{3-y}$ phases are solid solutions based on tysonite type modifications of LnF_3. Beginning with the SrF_2–TbF_3 systems, $Ln_{1-y}Sr_yF_{3-y}$ phases separate, acquiring all distinctive symptoms of compounds with variable composition, i.e., berthollides. The berthollide phases with LaF_3 structure have been discussed in detail (*13*) and the relationships between the parameters of elemental cells and the compositions are represented graphically (*22*). The parameters of $Ln_{1-y}Sr_yF_{3-y}$ phases change linearly in the whole range of homogeneity. The X-ray characteristics of compositions with maximum and minimum contents of SrF_2 in the solid solution at eutectic temperatures are given in Table II. These characteristics were obtained for specimens quenched down to room temperature.

TABLE II

THE LATTICE CONSTANTS OF TYSONITE TYPE PHASES (Y, Ln)$_{1-y}Sr_yF_{3-y}$

		Experimental lattice constants of saturated compositions	
R	Homogenity area (*y*)	*a* ±0.007 Å	*c* ±0.007 Å
La[a]	0–0.17	7.19–7.17	7.35–7.37
Ce[a]	0–0.18	7.12–7.13	7.29–7.32
Pr[a]	0–0.19	7.08–7.09	7.24–7.30
Nd[a]	0–0.19	7.03–7.06	7.20–7.25
Sm	0.0.23	6·96[b]–7.001	7.13[b]–7.196
Gd	0–0.27	6.89[b]–6.962	7.07[b]–7.159
Tb	0.09–0.29	6.887–6.940	7.054–7.118
Dy	0.12–0.30	6.864–6.921	7.400–7.085
Ho	0.16–0.31	6.845–6.919	7.014–7.075
Er	0.19–0.33	6.840–6.912	6.998–7.043
Tm	0.22–0.33	6.838–6.906	6.985–7.011
Yb	0.26–0.33	6.850–6.890	6.955–6.997
Lu	[c]	6.847	6.963
Y	0.16–0.31	6.840–6.912	7.010–7.054

[a] The lattice constants depend upon the conditions of preparations. The scattering of the values is about ±0.02 Å.

[b] Extrapolation.

[c] The homogeneity area was not determined. The lattice constants were measured for the composition with 28% SrF_2.

The $Ln_{1-y}Sr_yF_{3-y}$ phases are stabilized by heterovalent isomorphous substitutions of Ln^{3+} by Sr^{2+} in the tysonite type structure. Thanks to stabilization, the LaF_3 type solid solutions remain stable in the systems with LnF_3 (Ln=Tb–Lu) which in the clear form do not have modifications with tysonite type structure. The formation of vacancies in the anion sublattice, (*23*, *25*), stabilizes the tysonite type structure. We showed that the isomorphous substitution of Ln^{3+} by Sr^{2+} has a limit that corresponds to the composition $SrLn_2F_8$ (*22*). This is due to the distinctive characteristics of the atomic structure of LaF_3 (*24*) and this is the crystallo-chemical limit of berthollide phases $Ln_{1-y}Sr_yF_{3-y}$. In the studied temperature interval the distribution of different cations in the La^{3+} is statistical in nature in the tysonite type.

4. *Phases with α-YF_3(α-UO_3) structure* are formed in the SrF_2–(Y, Ln)F_3 systems with Ln=Er–Lu. There are solid solutions, based on high temperature modification α-LnF_3, which crystallize in α-UO_3 structural type (*26, 27*). We did not succeed in quenching α-($Ln_{1-y}Sr_y$)F_{3-y} phases but their existence is clearly supported by the thermal analysis method. In all the systems, these phases decompose as per the eutectoid type. The authors of Ref. *28* obtained by quenching an isostructural α-UO_3 phase of composition $Tl_{0.89}Sr_{0.11}F_{2.89}$ in the SrF_2–TlF_3 system.

5. *Phases with β-YF_3 structure.* The components of LnF_3 with Ln=Gd–Lu itself are the phases with orthorhombic β-YF_3 type structure in the SrF_2–(Y, Ln)F_3 systems. Within our experimental error, SrF_2 does not dissolve in LnF_3 orthorhombic forms. Among all the four basic structural type phases which are formed in the SrF_2–(Y, Ln)F_3 systems the orthorhombic β-YF_3 type structure is the only stucture which

practically does not permit heterovalent isomorphous substitution of Ln^{3+} by Sr^{2+} within a wide range. The cause of such a behavior of orthorhombic LnF_3 is still not fully known. The authors of Ref. *29*, who undertook precise determination of lattice constants, have reported a small solubility of SrF_2 in some orthorhombic β-LnF_3.

References

1. B. P. Sobolev and P. P. Fedorov, *J. Less-Common Metals*, **60**(1), 33 (1978).
2. J. A. A. Ketelaar and P. J. H. Williams, *Rec. Trav. Chem. Pays.-Bas.* **56**, 29 (1937).
3. E. Zintl and A. Udgard, *Z. Anorg. Chem.* **240**(2), 150 (1939).
4. B. P. Sobolev, E. G. Ippolitov, B. M. Zhigarnovskii, and L. S. Garashina, *Izv. Akad. Nauk SSSR, Neorg. Mater.* **1**(3), 362 (1965).
5. E. G. Ippolitov, L. S. Garashina, and B. M. Zhigarnovskii, *Dokl. Akad. Nauk. SSSR*, **173**(1), 101 (1967).
6. E. G. Ippolitov, L. S. Garashina, and B. M. Zhigarnovskii. *Izv. Sib. Otd. Akad. Nauk. SSSR*, ser. Khim. Nauk, **2**(4), 49 (1968).
7. H. Hahn, W. Seemann, and H. L. Kohn, *Z. Anorg. Chem.* **369**(1/2), 48 (1969).
8. B. Tanguy, J. Porter, M. Vlasse, and N. Pouchard, *Bull. Soc. Chim. Fr.* **3**, 946 (1972).
9. K. B. Seiranian, R. O. Sharkhatunian, L. S. Garashina, and B. P. Sobolev, IV Vsesouznoye soveshaniye po rostu kristallov, Trudy, Part I, p. 127, Izdatelstvo AN Armianskoi SSR, Erevan (1972), p. 127.
10. R. H. Nafziger and N. Riazance, *J. Amer. Ceram. Soc.* **55**(3), 130 (1972).
11. R. H. Nafziger, R. L. Lincoln, and N. Riazance, *J. Inorg. Nucl. Chem.* **35**(2), 421 (1973).
12. B. P. Sobolev, L. S. Garashina, P. P. Fedorov, N. L. Tkachenko, and K. B. Seiranian, *Kristallografiya* **18**(4) 751 (1973).
13. B. P. Sobolev and K. B. Seiranian, *Kristallografiya* **20**(4), 763 (1975).
14. K. B. Seiranian, L. S. Garashina, K. S. Gavrichev, and B. P. Sobolev, IV Vsesouzny simpozium po khimii neorganischeskikh ftoridov, 29 Sept. 1975, Dushanbe. Tezisy dokladov, p. 21, Izdatelstvo "Nauka" (1975).
15. A. A. Kaminskii, "Lazernye kristally," Izdatelstvo "Nauka", M. 1975.
16. L. E. Nagel and M. O'Keeffe *in* "Fast Ion Transp. Solids. Solid State Batteries and Devices. Proc. NATO Adv. Study Inst. Belgerate 1972" (W. van Gool, Ed.) North-Holland, Amsterdam (1973), p. 165.
17. B. P. Sobolev, P. P. Fedorov, N. L. Tkachenko, K. B. Seiranian, A. M. Kevorkov, Kh. S. Bagadasarov, V. S. Sidorov, and D. D. Ikrami, Trudy, VNII luminoforov, Stavropol, Vol. 15, 1977, p. 73.
18. V. B. Alexandrov and L. S. Garashina, *Dokl. Akad. Nauk. SSSR* **189**(2), 307 (1969).
19. A. K. Cheetham, B. E. F. Fender, D. Steele, R. I. Taylor, and B. T. M. Willis, *Solid State Commun.* **8**(3), 171 (1970).
20. B. E. F. Fender, in "Solid State Chemistry," Vol. 10, p. 244 (L. E. J. Roberts, Ed.), Butterworth, London (1972).
21. B. T. M. Willis, *J. Physique* **25**(5), 431 (1964).
22. B. P. Sobolev, V. B. Alexandrov, P. P. Fedorov, K. B. Seiranian, and N. L. Tkachenko, *Kristallografiya* **21**(1), 96 (1976).
23. B. Aurivillius and T. Lundqvist, *Acta Chem. Scand.* **9**(7), 1209 (1955).
24. M. Mansmann, *Z. Kristallogr.* **122**(5/6), 375 (1965).
25. L. S. Garashina and B. P. Sobolev, *Kristallografiya* **16**(2), 307 (1971).
26. R. E. Thoma and G. D. Brunton, *Inorg. Chem.* **5**(11), 1937 (1966).
27. B. P. Sobolev and P. P. Fedorov. *Kristallografiya* **18**(3), 624 (1973).
28. J. Ravez, J. Grannec, and J. Portier, *Rev. Chim. Mineral.* **8**, 131 (1971).
29. O. Greis and T. Petzel, *Z. Anorg. Chem.* **403**(1), 1 (1974).