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High-Pressure Phase Transitions of LaF_3 and CeF_3

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Abstract—The effect of high pressure on the structure of LaF_3 (tysonite), CeF_3, and nonstoichiometric LaF_3-based solid solutions (rhombohedral system, $P\bar{3}c1$, $Z = 6$) is discussed. In the systems MF_2–LaF_3 with M = Pb and Sr, fluorite-like $M_{1-x}La_xF_{2+x}$ solid solutions ($Fm3m$, $Z = 4$) are obtained in the composition range $0.5 \le x \le 0.75$ by quenching from 1500–1700 K at $p = 10$ GPa. By extrapolating the composition dependences of the lattice parameter for these cubic solid solutions, the lattice parameter of cubic LaF_3 is estimated at $a = 5.86 \pm 0.02$ Å. High-pressure x-ray diffraction studies indicate that CeF_3 undergoes a first-order phase transition similar to that revealed recently in LaF_3. At $p = 20.6$ GPa, the lattice parameters of orthorhombic CeF_3 ($Cmma$, $Z = 8$) are $a = 8.062 \pm 0.006$ Å, $b = 8.457 \pm 0.009$ Å, and $c = 5.091 \pm 0.006$ Å. The transition is accompanied by a 7.3% decrease in volume. The high-pressures structure of LaF_3 and CeF_3 can be thought of as a distorted modification of the structure of a hypothetical fluorite-like trifluoride. The lattice parameters of the orthorhombic and cubic cells are related by $a_{\text{ortho}} \sim b_{\text{ortho}} \sim \sqrt{2}\, a_{\text{cubic}}$ and $c_{\text{ortho}} \sim a_{\text{cubic}}$.

INTRODUCTION

LaF_3 (tysonite) and CeF_3 have a rhombohedral structure ($P\bar{3}c1$, $Z = 6$ [1]) which is the most densely packed among the known structures of the trifluorides of elements stable at normal pressure. This structure can be described on the basis of the hexagonal close-packed lanthanum sublattice, with the fluorine atoms residing in interstices: two-thirds of the anions occupy tetrahedral sites, and the rest sit in the center position of the shared faces of the octahedra. The M_3X compounds with M = alkali metal and X = Bi or Sb, isostructural with tysonite, demonstrate that a more densely packed configuration can be achieved if the M atoms occupy interstices in the cubic close-packed X sublattice: two-thirds of the M atoms occupy tetrahedral sites, as in the tysonite structure, while the rest sit in octahedra. In the case of trifluorides, it is convenient to represent such a hypothetical configuration in terms of the fluorite structure type (CaF_2, $Fm3m$, $Z = 4$), with additional fluoride ions sitting in all of the octahedra (or, in other words, in empty cubes of the anion sublattice) and compensating the larger charge on the cation.[1]

The difference in density between tysonite- and fluorite-like phases is 9.6%, judging from the data on Rb_3Sb, which exists in both forms [2]. This led a number of researchers to examine the possibility of a similar polymorphism in LaF_3 at high pressures. In this context, it was also of interest to synthesize fluorite-like solid solutions close in composition to LaF_3 in fluoride and oxyfluoride binary systems. In this paper, we review the main results in this area of research, which provide a general picture of the behavior of trifluorides under strong compression. We also report new experimental data on fluorite-like solid solutions in the PbF_2–LaF_3 and SrF_2–LaF_3 systems and on the phase transition of CeF_3. Data on the structure and properties of rare-earth fluorides, in particular YF_3 and LaF_3, are of immense importance in both science and technology [3].

EXPERIMENTAL

The starting reagents for this investigation were prepared at the Shubnikov Institute of Crystallography, Russian Academy of Sciences. Optical-quality SrF_2 and PbF_2 single crystals were grown in a fluorine atmosphere. LaF_3 and CeF_3 containing ≤0.07 wt % oxygen were also prepared in a fluorine atmosphere, by melting La_2O_3 and Ce_2O_3, respectively. Fluorite-like solid solutions were obtained by quenching at a rate of ~1000 K/s under a pressure of 10 GPa after 30-min holding at 1500–1700 K in hermetically sealed platinum capsules. The oxygen content of the synthesis products was no higher than 0.4 wt %. The phase purity of the samples was checked by powder x-ray diffraction (XRD).

The compressibility and phase transition of CeF_3 were investigated by XRD (MoK_α radiation) at room

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[1] In what follows, phases with such structures will be called, for convenience, fluorite-like.

temperature, using a high-pressure diamond anvil cell. The pressure was calibrated using the R_1 ruby fluorescence line. As the pressure-transmitting medium, we used a 1 : 1 mixture of ethanol and methanol.

RESULTS AND DISCUSSION

The formation of fluorite solid solutions in CaF_2–RF_3 (R - rare earth) systems was first analyzed by Goldschmidt *et al.* [4]. In their model, random substitution of trivalent cations on the Ca site is accompanied, in conformity with the electroneutrality condition, by the incorporation of additional fluoride ions into some of the 1/2 1/2 1/2 sites (the center position of the empty cubes in the anion sublattice of the fluorite structure). The stability of this configuration was questioned by Belov [5], who supposed that the difference in ionic radius between Ca^{2+} and F^- is too large for an additional fluoride ion to be accommodated in an empty cube. Belov's assumption that fluorides may be oxidized to ROF, without changes in the total number of anions in the parent fluorite structure, proved valid in the case of BiF_3. The data cited in many reports as evidence for the existence of cubic BiF_3 were shown to be invalid [6]. Nevertheless, nonstoichiometric solid solutions containing additional fluoride ions in the fluorite structure are easily formed without oxidation, by a more complicated mechanism. Structural analysis of $Ca_{0.607}Ce_{0.393}F_{2.393}$ single crystals [7] shows that, instead of the conventional incorporation of an additional fluoride ion, one anion in position 1/4 1/4 1/4 (cube corner) is replaced by two anions in general positions on body diagonals. The two fluoride ions are displaced by ≃1/6 from the center position to the common unoccupied cube corner. Owing to the disordered distribution of the solute cations, additional anions, and vacancies, the space group of fluorite (*Fm*3*m*) remains unchanged. Simple calculations demonstrate that the filling of all the empty cubes in the fluorite structure leads to the saturation of solid solutions with the general formula $M^{2+}_{1-x}R_xF_{2+x}$ at $x = 0.75$.

Under normal pressure, the highest trifluoride content of such phases is $x \simeq 0.5$ [8]. Since the formation of solid solutions with $0.5 < x < 1$ is accompanied by a decrease in volume, the solid-solution range must become broader with increasing pressure. Indeed, the MF_2–LaF_3 (M = Ca [9], Sr, Pb) systems were shown to contain high-pressure fluorite-like solid solutions with x as large as 0.85, 0.75, and 0.75, respectively. Detailed single-crystal structural analysis of $Pb_{0.3}La_{0.7}F_{2.7}$ [10] demonstrates that the cubic (*Fm*3*m*) structure of this phase is formed by the mechanism described by Otroshchenko *et al.* [7], with the generation of anion vacancies. The structure of CaF_2-based solid solutions, in spite of the change in the mechanism of the incorporation of additional fluoride ions for $x > 0.75$, belongs to space group *Fm*3*m* up to $x = 0.85$. For lack of single crystals, we can do no more than assume that, in this composition range, further increase in x is accompanied by a decrease in the amount of anion vacancies and changes in the anion position in the cube. A similar pattern was reported for the LaOF–LaF_3 system [11], which was found to contain cubic $LaO_{1-x}F_{1+2x}$ solid solutions with a large anion excess ($x = 0.80$) relative to the fluorite-like compound LaOF, which belong to space group *Fm*3*m*. The lattice parameter of hypothetical cubic LaF_3 can be estimated by extrapolating the composition dependences of the lattice parameter for existing cubic solid solutions ($a = 5.867$ Å) (Fig. 1). It is of interest to note that, at normal pressure, all of the solid solutions in question have the tysonite (LaF_3) structure in the range $0.67 < x < 1$. Thus, the high-pressure phase transitions of tysonite-structure LaF_3, CeF_3, and other fluorides are closely related to the observed polymorphism of nonstoichiometric solid solutions.

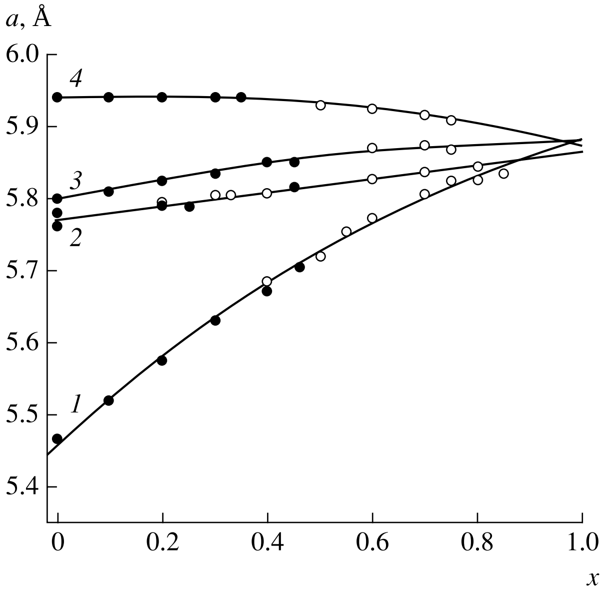

Fig. 1. Composition dependences of the lattice parameter for fluorite-like solid solutions: (*1*) $Ca_{1-x}La_xF_{2+x}$ (● [8], ○ [9]), (*2*) $LaO_{1-x}F_{1+2x}$ (● [12], ○ [11]), (*3*) $Sr_{1-x}La_xF_{2+x}$ (● [13], ○ this work), (*4*) $Pb_{1-x}La_xF_{2+x}$ (● [14], ○ this work); ● normal pressure, ○ high pressure.

It seems likely that the extent of solid solutions that can be quenched and stored under normal conditions depends on the concentration of anion vacancies and the relative amounts of solute ions in the cation and anion sublattices. A random distribution of such defects raises the entropy of the solid solution and favors the formation of a metastable phase. From this viewpoint, the existence of metastable fluorite-like LaF_3 or other trifluoride appears unlikely. For example, just like the trifluorides, the RH_3 compounds have no cubic polymorphs: the fluorite-like structures of LaH_3, CeH_3, and

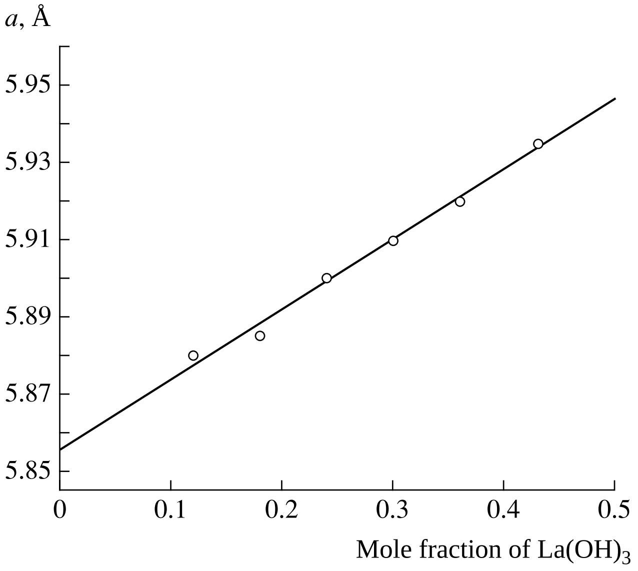

Fig. 2. Composition dependence of the lattice parameter for $La[(F_{1-y}(OH)_y]_3$ fluorite-like solid solutions [6].

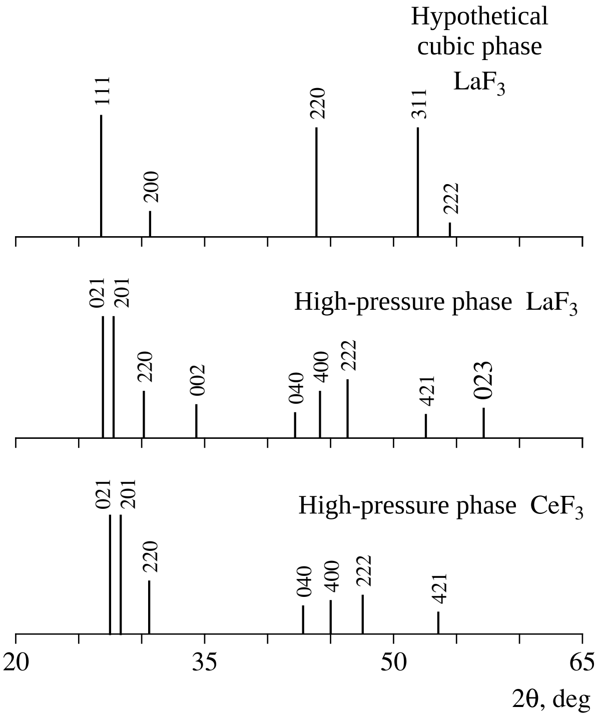

Fig. 3. Splitting of peaks in the XRD pattern of an orthorhombically distorted cubic phase.

PrH_3 are tetragonally distorted [5]. The above-mentioned intermetallic compounds form fluorite-like phases either as a result of mutual substitutions in the two sublattices (Sb and Rb) of Rb_3Sb (which is unlikely in predominantly ionic phases) or in the presence of two alkali metals (Na_2KSb), which is equivalent to the presence of two kinds of anions in fluoride phases. Indeed, it is via partial substitution of OH^- ions for fluoride ions (more than 12%) in LaF_3 that the stoichiometric phase can be stabilized. Cubic $La[F_y(OH)_{1-y}]_3$ solid solutions (sp. gr. $Fm3m$) were obtained in the composition range $0.45 < y < 0.88$. The lattice parameter of cubic LaF_3 evaluated by extrapolation in this system (Fig. 2) is $a = 5.855$ Å. The average over all the systems in question, $a = 5.86 \pm 0.02$ Å, provides an estimate of the relative difference in volume between tysonite and hypothetical fluorite-like LaF_3: $\Delta V/V_{tysonite} = -0.082$. Judging from the T–x phase diagram of the LaF_3–$La(OH)_3$ system, these phases are in equilibrium starting at $p = 10$ GPa and $T \sim 1900$ K [16]. From the displacement of certain points in this phase diagram upon an increase in pressure from 7.7 to 10 GPa, one can roughly estimate the slope of the line representing this equilibrium in the p–T phase diagram. In this way, we find that the equilibrium in question (real or hypothetical) occurs in the range 15–20 GPa.

As shown by in situ XRD, LaF_3 compressed in a high-pressure diamond anvil cell undergoes a first-order phase transition accompanied by a 7.7% decrease in volume [17]. At room temperature, the transition occurs at 19 GPa, in accordance with theoretical predictions, but the high-pressure phase has an orthorhombically distorted fluorite-like structure (Fig. 3). The lattice parameters of the orthorhombic phase ($Cmma$, $Z = 8$; $a = 8.221(6)$ Å, $b = 8.589(9)$ Å, and $c = 5.231(6)$ Å at 16.0 GPa) are related to the lattice parameter of the cubic unit cell by $a_{ortho} \sim b_{ortho} \sim \sqrt{2}\,a_{cubic}$ and $c_{ortho} \sim a_{cubic}$. The reverse transformation occurs at 14 GPa. The hysteresis of the transition, large as it is (5 GPa), is insufficient for the dense phase to persist down to normal pressure.

A similar transition in tysonite-structure CeF_3 was revealed in this work by the same method. The table shows the indexing scheme for the high-pressure phase (20.6 GPa). The orthorhombic ($Cmma$) cell parameters are $a = 8.062 + 0.006$ Å, $b = 8.457 + 0.009$ Å, and $c = 5.091 + 0.006$ Å. At $Z = 8$, the pressure dependences of the relative volumes for the tysonite and orthorhombic phases were identical, to within experimental accuracy, to those for LaF_3, which were determined more carefully (Fig. 4). This led us to conclude that the coefficients of the Murnagan–Birch equation of state [18] calculated for LaF_3 can be assigned, as a first approximation, to the two phases of CeF_3: $K_0 = 147(10)$ GPa, $K' = 3$ for tysonite and $K_0 = 207(6)$ GPa, $K' = 2.1$ for the orthorhombic phase.

The existence of cubic $La(F,OH)_3$, whose stoichiometry is identical to that of trifluorides, and some features of the behavior of nonstoichiometric solid solutions suggest that, by raising the temperature, the orthorhombically distorted phases can be converted into high-symmetry fluorite-like forms. Judging from

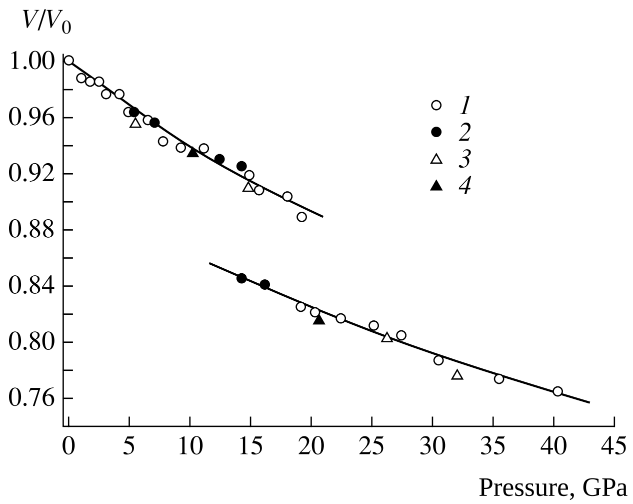

Fig. 4. Relative volumes of LaF_3 and CeF_3 as functions of pressure: (*1*) LaF_3, loading cycle [17]; (*2*) LaF_3, unloading cycle [17]; (*3*) CeF_3, loading cycle (this work); (*4*) CeF_3, unloading cycle (this work).

NMR data [19] and ionic conductivity measurements [20, 21], the fluoride ion in the cubic solid solutions under consideration has a high mobility at high temperatures, at a level of good solid electrolytes. The vacancy mechanism underlying the incorporation of additional anions into the fluorite structure under ordinary conditions reflects the situation at high temperatures, where the least stable fluoride ions can move along the body diagonals of the small cubes. Clearly, such anions do not occupy any particular crystallographic sites, and the symmetry of the high-temperature phase will be determined by that of the fcc cation sublattice (*Fm*3*m*). Thus, the stability of the fluorite-like structure of stoichiometric trifluorides depends on whether the temperature is high enough for the delocalization of some of the fluoride ions without changes in the symmetry of the cation sublattice. A search for such phases involves a number of technical problems since in situ XRD measurements must be performed not only at high pressures (≃20 GPa for LaF_3 and CeF_3) but also at high temperatures.

XRD data for high-pressure CeF_3 (20.6 GPa)

hkl	*I*, %	d_{obs}, Å	d_{calc}, Å
021	100	3.255	3.253
201	100	3.159	3.161
220	45	2.923	2.918
040	23	2.114	2.114
400	27	2.016	2.016
222	32	1.918	1.918
421	18	1.716	1.713

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