OPTICAL PROPERTIES OF LANTHANIDE-STRONTIUM FLUORIDE SOLID SOLUTIONS

E.A. Krivandina[(1)], Z.I. Zhmurova[(1)], T.M. Glushkova[(2)], S.A. Ivanov[(2)], D.F. Kiselev[(2)], M.M. Firsova[(2)], A.P. Shtyrkova[(2)]

[(1)]Institute of Crystallography, Russian Academy of Sciences
Leninsky pr. 59, 117333 Moscow, Russia
[(2)]Department of Physics, Lomonosov Moscow State University,
Leninsky Hills, 119889 Moscow, Russia, Fax: (095) 939 1489;
e-mail: isa@genphys.phys.msu.ru

Abstract

The results of the refraction study of two-component solid solution single crystals grown on the basis of rare-earth element (REE) fluorides with different content of strontium fluoride ($R_{1-x}Sr_xF_{3-x}$, where $R = La, Ce, Pr, Nd$; $0 \le x \le 0{,}15$) are presented. Experimentally obtained values of refractive indices and density have given the possibility to calculate some refraction characteristics of the crystals investigated: molar (Lorenz–Lorentz) refraction, polarizability, molar volume, and to analyze all the data obtained in two directions: with the increase of SrF_2 content x for each binary system and according to the REE atomic number for one and the same x.

1. Introduction

The wide use of fluoride materials in scientific experiments and modern technologies set up the problem of searching for the possibility of the fluoride-crystal characteristic variation. It was found that this problem can be successfully solved by using the multi-component fluoride systems instead of single-component ones.

2. Experiments and data processing

Our work is just devoted to the investigation of the physical properties (optical characteristics and density) of such complex crystals. The objects of our study were the solid solutions of the RF_3-SrF_2 (R – rare-earth elements (REE)) binary systems. The $R_{1-x}Sr_xF_{3-x}$ ($R = La, Ce, Pr, Nd$; $0 \le x \le 0.15$) single crystals with tysonit structure were grown from the melt by the Stockbarger method in the Institute of Crystallography of the Russian Academy of Sciences [1].

The samples for investigations had the form of a cylinder with the diameter of 10 mm and the height of 2-5 mm. The axis of the cylinder practically coincided with the optical axis of the crystal. The crystal density ρ was measured by hydrostatic weighting method with an accuracy of $\pm 10^{-3}$ g/cm^3; the refractive indices n_o, n_e were measured with the help of the Pulfrich refractometer to the nearest $\pm 10^{-3}$.

From the experimental data obtained some crystal characteristics were calculated. These ones were the molar volume — $V_{mol} = M/\rho$ (M is the molecular weight of the compound); the number of molecules in the unit volume $N = N_{Av}/V_{mol}$ (N_{Av} is the Avogadro number); the Lorenz-Lorentz molecular refraction R_{mol} and molecular polarizability $\alpha_{o,e}$; the last two

parameters were obtained with the help of the formula

$R_{mol\ o,e} = \frac{n_{o,e}^2 - 1}{n^2 + 2} \cdot \frac{M}{\rho} = \frac{4\pi}{3} \cdot N_{Av} \cdot \alpha_{o,e}$. Here $n = (2n_o + n_e)/3$ is the average refractive index of the medium and $\alpha_{o,e}$ are the polarizability components of the anisotropic molecule.

The experimental data obtained and the refraction parameters calculated were analyzed in two directions: in dependence on the SrF_2 content x for each binary system (composition range) and versus the REE atomic number Z for the crystals with one and the same x (lanthanide series).

3. Results and discussion

3.1. Composition range

Earlier [2,3] we have already obtained the n_o, n_e and ρ values for the $La_xSr_{1-x}F_{3-x}$ single crystals as functions of x. All three parameters are linearly decreasing with the x increase. It was revealed that for the CeF_3-SrF_2, PrF_3-SrF_2, NdF_3-SrF_2 binary systems the regularities of the measured characteristic alterations were maintained.

For all four types of single crystals the tendency of the calculated parameter changes with the x increase are identical (see [2,3]). Firstly, this is the $\alpha_{o,e}$ decrease in the range of binary system compositions. As to molar volume V_{mol} and the value of N, these parameters are practically independent of SrF_2 content in the $R_{1-x}Sr_xF_{3-x}$ single crystals, or change very slightly. Thus, for NdF_3-SrF_2-system crystals the increase of V_{mol} is no more than 1-2 % when x varies from 0 to 0.15. For the PrF_3-SrF_2 solid solutions the change of V_{mol} is yet smaller. The N values of this crystal systems are changed in the same manner. From the above reported it can be concluded that the decrease of refractive indices with x in the composition range is caused only by the decrease of the polarizability.

3.2. Lanthanide series

Having studied the set of the solid-solution crystals with the systematic lanthanide substitution we obtain the possibility to follow the refraction parameter variations versus the rare-earth element (REE) atomic number. Unfortunately we have the fluoride single crystals only with four first elements of lanthanide series, namely *La*, *Ce*, *Pr*, *Nd*. The second component of solid solution in all cases was SrF_2 as it was already mentioned.

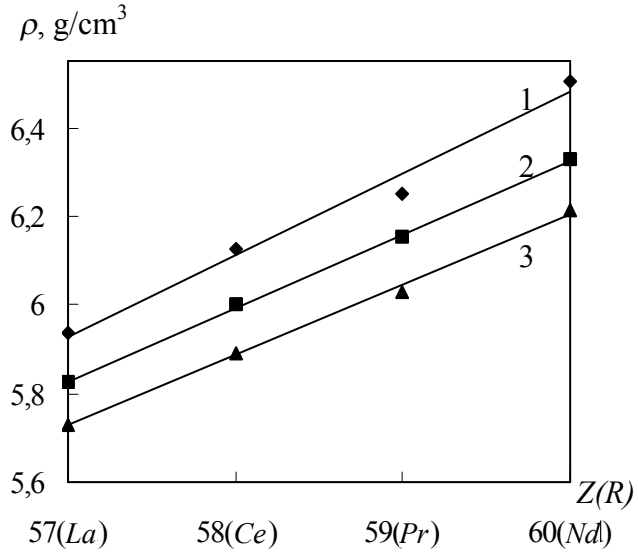

Fig. 1.
Density ρ of the $R_{1-x}Sr_xF_{3-x}$ single crystals as functions of the REE atomic number $Z(R)$ at x = 0 (1); 0.05 (2) and 0.10 (3)

The experimental values of density ρ and of refractive index n_o of the crystals under study with SrF_2 contents equal to 0, 5 and 10 mol.% are presented in fig. 1 (ρ) and fig. 2 (n_o). As it can be seen the density of all compounds is practically linearly increasing according to

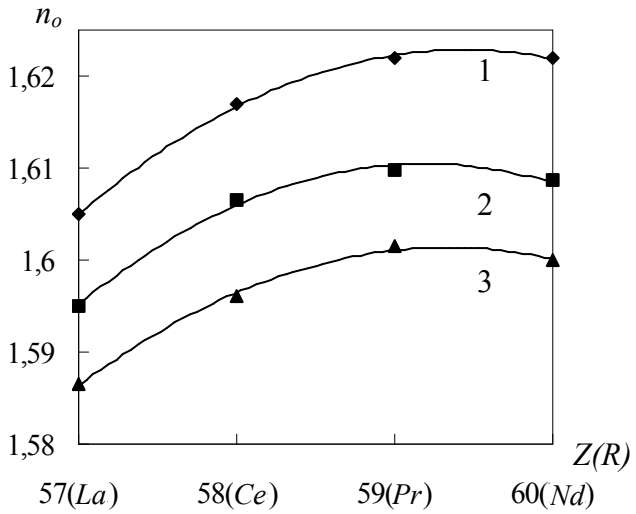

Fig. 2.
Refractive index n_o of the $R_{1-x}Sr_xF_{3-x}$ single crystals as functions of the REE atomic number $Z(R)$ at x = 0 (1); 0.05 (2) and 0.10 (3)

REE atomic number Z. This increase is caused evidently by the REE molecular weight rise.

We observe that the refractive index in lanthanide series behaves in a different way: at first the value of n_o (and n_e also) increases and then (at R=Pr) stops its increase. The refractive index is a complex function of several physical parameters, but the main ones are the number N of polarizing particles, that is the number of $R_{1-x}Sr_xF_{3-x}$-molecules in the unit volume, and their polarizability α.

The value of N, as it was already mentioned, was calculated from the molar volume magnitude. Within each binary system the value of V_{mol} remains approximately constant, i.e. it does not noticeably depend on the SrF_2 content x in the compound. But in REE series V_{mol} is decreasing, namely for the single crystals with $R = La$, Ce, Pr, Nd the molar volume V_{mol} = 33.00, 32.20, 31.65, 31.10 cm^3, consequently. The N value change with REE atomic number is demonstrated in fig. 3.

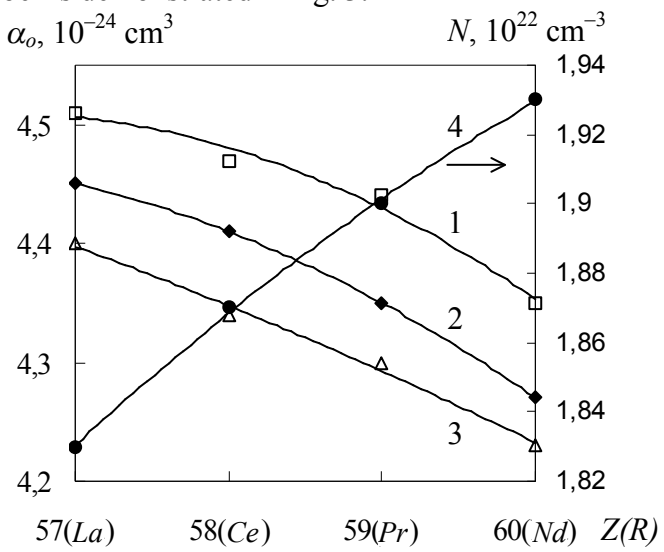

Fig. 3.
Polarizability α_o of the $R_{1-x}Sr_xF_{3-x}$ single crystals at x = 0 (1), 0.05 (2), and 0.10 (3) and parameter N (4) – at all x, as functions of the REE atomic number $Z(R)$.

It is necessary to note that the invariability of the molar volume V_{mol} with x takes place

exactly only for the crystals of two systems: with $R = La$ and Ce. For crystals with $R = Pr$ and Nd such independence of SrF_2 content x is disturbed. However, these deviations are so slight that they cannot distort the common image of V_{mol} and N variations in the lanthanide series for the binary systems, studied in this work.

The polarizability α of the $R_{1-x}Sr_xF_{3-x}$ molecule is monotonically decreasing with REE atomic number increase for all values of x (fig. 3). Such a change of α is caused by the decrease of the polarizability of trivalent ion R^{3+} [4] with the REE atomic number. This behavior, in turn, is conditioned by the well known effect of the lanthanide contraction.

Thus, two parameters — N and α, which, finally, determine the variation of refractive index in the REE series are changing in two contrary directions: N is increasing and α is decreasing with Z increase. Namely these competing tendencies define the nonmonotonic variation of the $R_{1-x}Sr_xF_{3-x}$ single-crystal refractive indices with the REE atomic number. Formerly in [5] it was reported about the change of optical parameters of *R*-*Na*-fluoride crystals with hexagonal structure. The results of the present work do not contradict the character of the $n_{o,e}$ change for the $Na_{0.4}R_{0.6}F_{2.2}$ single crystals, where R in given case [5] is a REE-ion of the second part of the lanthanide series from Dy^{3+} to Lu^{3+}.

4. Conclusion

Thus, the analysis of the refractive index behavior in the $R_{1-x}Sr_xF_{3-x}$ single crystals carried out both for x-dependence (with the invariable R) and depending on R (when $x = const.$), reveals some refraction peculiarities for these complex compounds.

The effect of lanthanide contraction (inherent only to the members of the REE series) results finally in a complex character of the refractive index variation of the two-component systems under study. This effect is responsible also for the rarely found antibateness in the change of the density ρ and refractive index n of the solid solution single crystals with respect to the REE atomic number. In practice, the set of data presented extends the possibility of the searching of the materials with the performance characteristics required.

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