Single Crystals of the Fluorite Nonstoichiometric Phase \( \text{Eu}^{2+}_{0.916} \text{Eu}^{3+}_{0.084} \text{F}_{2.084} \) (Conductivity, Transmission, and Hardness)

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Abstract—The nonstoichiometric phase \( \text{EuF}_2+x \) has been obtained via the partial reduction of \( \text{EuF}_3 \) by elementary Si at 900–1100°C. \( \text{Eu}^{2+}_{0.916} \text{Eu}^{3+}_{0.084} \text{F}_{2.084} \) (EuF\(_{2.084}\)) single crystals have been grown from melt by the Bridgman method in a fluorinating atmosphere. These crystals belong to the CaF\(_2\) structure type (sp. gr. \( \text{Fm} \overline{3}m \)) with the cubic lattice parameter \( a = 5.8287(2) \) Å, are transparent in the spectral range of 0.5–11.3 µm, and have microhardness \( H = 3.12 \pm 0.13 \text{ GPa} \) and ionic conductivity \( \sigma = 1.4 \times 10^{-3} \text{ S/cm} \) at 400°C with the ion transport activation energy \( E_a = 1.10 \pm 0.05 \text{ eV} \). The physicochemical characteristics of the fluorite phases in the EuF\(_3\) – EuF\(_2\) systems are similar to those of the phases in the SrF\(_2\) – EuF\(_2\) and SrF\(_2\) – GdF\(_3\) systems due to the similar lattice parameters of the EuF\(_2\) and SrF\(_2\) components. Europium difluoride supplements the list of fluorite components \( M \text{F}_2 \) (\( M = \text{Ca, Sr, Ba, Cd, Pb} \)), which are crystal matrices for nonstoichiometric (nanostructured) fluoride materials \( M_{1-x}R_x \text{F}_{2+x} \) (\( R \) are rare earth elements).

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INTRODUCTION

\( M \text{F}_2 \) (\( M = \text{Ca, Sr, Ba, Cd, Pb} \)) crystals with fluorite structure (CaF\(_2\), sp. gr. \( \text{Fm} \overline{3}m \)) are stable refractory compounds (\( T_m = 1464°C \) for SrF\(_2\)). The methods for growing \( M \text{F}_2 \) (\( M = \text{Ca, Ba} \)) single crystals and their properties have been studied well, because they are widely used as optical materials transparent in the UV and IR ranges. The crystals with \( M = \text{Sr, Cd, and Pb} \) have been investigated less.

The phase diagrams of 80 systems of the \( M \text{F}_2 - RF_2 \) type (\( R = \text{La–Lu, Y} \)) [1] revealed the formation of nonstoichiometric phases \( M_{1-x}R_x \text{F}_{2+x} \) (solid solutions with a variable number of atoms per unit cell) with wide homogeneity ranges (to 50 mol % \( RF_2 \)) in each. Some properties of the single crystals of these phases give grounds to consider them promising polyfunctional multicomponent fluoride materials. Their advantages over conventional one-component fluorides \( M \text{F}_2 \) are (i) the possibility of controlling the operating characteristics in a wide range and (ii) some properties that are not inherent in \( M \text{F}_2 \) [2].

Difluorides of rare earth elements (REEs) \( RF_2 \) (\( R \) is REE), where heterovalent isomorphic substitutions (\( R^{2+} \) with \( R^{3+} \)) lead to the formation of nonstoichiometric phases, can also be considered crystal matrices with fluorite structure \( R^{2-}_{1-x}R^{3+}_{x} \text{F}_{2+x} \).

\( RF_2 \) single crystals have barely been studied due to the necessity of reducing commercial reagents \( RF_3 \) to \( RF_2 \) before crystal growth. The possibility of obtaining new fluorite matrices \( RF_2 \) is determined by the stability of these compounds. They are formed for only a few of the 15 REEs, and their stability is different for different elements.

There are several ways for estimating the tendency of \( RF_3 \) to reduction. We chose to estimate from the values of dissociation enthalpies (\( \Delta H_{\text{dis}}^0 \)), a technique proposed in [3, 4]:

\[ 3RF_2 \rightarrow R^0 + 2RF_3. \]

With respect to the \( \Delta H_{\text{dis}}^0 \) value, hypothetical \( RF_2 \) can be divided into three groups: (i) \( \text{EuF}_2, \text{YbF}_2, \) and SmF\(_2\) with positive \( \Delta H_{\text{dis}}^0 \) (in ascending order), which are expected to be stable; (ii) \( \text{Pr, Nd, Pm, Dy, Ho, Er,} \) and \( \text{Tm} \) difluorides with negative or near-zero \( \Delta H_{\text{dis}}^0 \), which allows for partial reduction under special conditions; and (iii) fluorides of \( \text{La, Ce, Gd, Tb, Y, and Lu} \) with large (in magnitude) negative values of \( \Delta H_{\text{dis}}^0 \), where the formation of \( RF_2 \) and \( R^{2+} \) ions in other crystal matrices is unlikely.

According to the data of [3, 4], \( \text{EuF}_2 \) is the most stable of the \( RF_2 \) compounds. In practice, the reduction of \( R^{3+} \) to \( R^{2+} \) in fluorides must be taken into account in the presence of such reducers as carbon and
some metals (materials of crucibles where solid-phase reactions, melting, or crystal growth (case under consideration) are performed). The partial reduction of europium was reported in [5] for the crystal growth from SrF₂ and EuF₃ melts in a graphite crucible.

The purpose of this study was to grow EuF₂⁺⁺ single crystals; analyze their optical transmission, hardness, and ionic conductivity; and compare some of the physicochemical characteristics of fluorite heterovalent solid solutions (nonstoichiometric phases): Eu₂⁺⁺Eu₂⁺⁺F₂⁺⁺⁺⁺, Sr₁−xGdₓF₂⁺⁺⁺⁺, and Sr₁−xGdₓF₂⁺⁺⁺⁺ based on EuF₂ and SrF₂, which have similar lattice parameters.

EXPERIMENTAL

The preparation of EuF₂ crystals includes two separate stages: (i) the reduction of commercial agent EuF₃ to EuF₂ and (ii) crystal growth.

Choice of the EuF₂ reduction technique. The methods for synthesizing stable RF₂ imply the use of three reducers: hydrogen, metallic REEs, and elementary silicon. Historically the first method of RF₂ reduction by metallic calcium to RF₂ [6] did not become widespread due to the high calcium content in the reaction products [4]. The use of metallic REEs as solid reducers requires the removal of excess metal from the reaction products. The reduction of RF₂ by REE vapor in vacuum in a two-chamber reactor with separate evaporation and reduction zones was proposed in [7]. The reduction by H₂ should be performed at high temperatures.

In the method proposed in [8], the reducer is elementary Si, whose excess can easily be removed due to the high Si volatility. We specifically chose this technique to reduce EuF₃. However, this method does not always provide complete EuF₃ reduction (a situation we came across).

The charge for the crystal growth was synthesized by sintering a mixture of EuF₃ and Si powders at 900–1100°C according to the technique [8]:

$$4\text{EuF}_3 + \text{Si} \rightarrow 4\text{EuF}_2 + \text{SiF}_4.$$  

The growth of EuF₂⁺⁺ crystals was performed from melt by the Bridgman method. The reduction product was molten in a graphite crucible and crystallized in a fluorinating atmosphere formed by the polytetrafluoroethylene pyrolysis products. We obtained dark-purple homogeneous crystals (Fig. 1).

X-ray powder diffraction analysis was performed on an XPERT PRO MPD diffractometer (PANalytical, the Netherlands) in the Bragg–Brentano geometry. The affiliation of the crystals grown to the fluorite structure type was confirmed.

The crystal composition interpretation from the concentration dependence of the lattice parameter is hindered by the scatter of data obtained by different researchers [7, 9] and by the same research team at different times [7, 10]. This problem was discussed in [11], where a generalized dependence of the lattice parameters of fluorite phases $M_{1−x}R_xF_{2+x}$ was derived from the cation ionic radii and experimental data. Recent data [12] differ from those of all previous studies.

An analysis of the existing dataset of measured unit-cell parameters $a$ of the EuF₂⁺⁺ phase shows that the equations $a(x) = a_0 − kx$, which were obtained by different researchers, differ according to the choice of $a_0$, and the straight lines reported by three (from four) teams [7, 11, 12] are simbatic. The scatter in the parameter $a$ for EuF₂ is 0.007 Å, which corresponds to a difference in compositions of 4.4 mol %. The average value is similar to the previously accepted one: $a_0 = 5.840 \text{ Å}$. Therefore, to estimate the composition of EuF₂⁺⁺ crystals, we used the equation $a(x) = 5.8400 − 0.1345x$ [11].

The cubic lattice parameter determined by the powder method (external Si standard) is $a = 5.8287(2) \text{ Å}$. The single-crystal composition, which was found from the concentration dependence of the lattice parameter for EuF₂⁺⁺ solid solutions [11], corresponds to $x = 0.084$. In an earlier study [13], $x$ was taken to be about 0.06 (the lattice parameter was determined with a lower accuracy). With allowance for the uncertainty in choosing the parameter $a_0$ for EuF₂, the error in determining the crystal composition is $\Delta x = ±0.002$.

The physical properties were investigated on unoriented plane-parallel 3-mm-thick plates with polished surfaces cut from a single-crystal boule.

The optical transmission spectra were recorded in the ranges of 0.2–0.9 μm (on a Specord M40 spectrophotometer) and 1.5–15 μm (on an AF-1 Fourier spectrophotometer).