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Crystal growth and anisotropy of ionic conductivity of trifluoride DyF_3

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Crystallographically oriented single crystals of DyF_3, a representative of the third structural group of rare-earth trifluorides (structure β-YF_3, sp. gr. *Pnma*, unit cell parameters $a = 6.4603(2)$, $b = 6.9104(1)$, $c = 4.3808(2)$ Å), were grown for the first time by the directional crystallization technique. Temperature (386−783 K) measurements of the ionic conductivity of this crystal were carried out along and perpendicular to the crystallographic b axis. It was found that DyF_3 crystals have weak anisotropy of electrical conductivity, the coefficient $\sigma_{\|b}/\sigma_{\perp b} = 2.2 \pm 0.1$ and $\sigma_{\|b} = 2.5 \cdot 10^{-6}$ S/cm (at 500 K). The relationship between the characteristics of ion transport and the crystal structure is discussed for the general family of rare earth trifluorides with the β-YF_3 structure, including RF_3 compounds (R = Dy, Tb, Ho), low-temperature modifications of β-RF_3 (R = Er, Y) and solid solutions $Gd_{0.3}Er_{0.7}F_3$, $Gd_{0.5}Y_{0.5}F_3$. It is shown that for this family of orthorhombic trifluorides, with an increase in the radius of rare earth cations, the activation enthalpy of ion transfer (vacancy mechanism) decreases, which leads to an increase in ionic conductivity.

Keywords: electrical conductivity, ion transport, point defects, dysprosium trifluoride, crystal growth.

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1. Introduction

The phenomenon of anisotropy in ionic conductivity in fluoride crystals is of great interest from the fundamental point of view for understanding the mechanisms of ion transfer in fluorine-conducting solid electrolytes. Experimental data for study of anisotropy of fluoride electroconductivity makes it possible to identify structural paths of ion transport and to study the relation of ion transport to the features of crystal structure [1]. However, such studies of fluorides are rare and complicated with certain circumstances. Orientation-dependent experiments require usage of large single crystals of the needed quality, and the growth of fluoride crystals from the melt is complicated by pyrohydrolysis [2]. Electrophysical measurements of fluorides should be carried out using impedance spectroscopy in a wide frequency range to determine the ionic conductivity at direct current (DC) (σ_{dc}) [3,4], with special attention paid to separating the bulk impedance of the crystal and the impedance of the crystal/electrode interface

The large homologous series of trifluorides of rare earth elements (REE) RF_3, comprising 17 compounds (R = Sc, Y, La and lanthanides Ce−Lu), is divided into five structural groups [5,6]. Group I includes compounds LaF_3, CeF_3, PrF_3 and NdF_3 with the tysonite-type structure (LaF_3), group II includes dimorphic compounds PmF_3, SmF_3, EuF_3 and GdF_3 with the structures LaF_3 (at high temperatures) and β-YF_3 (at low temperatures), group III includes compounds TbF_3, DyF_3 and HoF_3 with the structure β-YF_3, to group IV — dimorphic compounds ErF_3, TmF_3, YbF_3, LuF_3 and YF_3 with the structures α-YF_3 and β-YF_3 (at high and low temperatures respectivly) and group V — compound ScF_3 with the ReO_3-type structure. Crystals 16 of REE trifluorides (except for ScF_3 with cubic symmetry) must have anisotropic behavior of physical properties.

Chemical bonds in trifluorides RF_3 have practically the ion nature [7]. To date, studies of the anisotropy of ionic conductivity (by anions F^-) have been carried out only for a small number of REE trifluorides: LaF_3 [8–11], CeF_3 [12] (for two out of four compounds of group I), TbF_3 [13,14], HoF_3 [15] (for two out of three compounds of group III), ErF_3 [14], YF_3 [16,17] (for two out of five compounds of group IV), and also isovalent solid solution $Gd_{0.5}Y_{0.5}F_3$ [14,17].

Dysprosium trifluoride belongs to structural group III RF_3 (R = Tb, Dy and Ho), showing identical geochemical behavior, not undergoing polymorphous transformations up to melting and directly crystallized from the melt in structural type β-YF_3 [18–20]. The same type of structure has low-temperature modifications β-RF_3 for R = Er, Tm, Yb, Lu, Y [21]. Small single crystals DyF_3 (several millimeters) were obtained from the melt using Bridgman-Stockbarger method in [22]. Crystals based on DyF_3 and TbF_3 are seen as promising materials for magnetooptical applications [22–25] and dosimetry of γ-radiation [26].

The objective of the study is to grow oriented single crystals DyF_3, to analyze their temperature dependences of ionic conductivity in different crystallographic directions and discussion of the interrelation between characteristics of ion transport and crystallochemical structure for the

Table 1. Parameters of ion transfer in crystals DyF_3 in different crystallographic directions in accordance with equation (2)

Direction	Low-temperature area	High-temperature area
$\parallel b$ [010]	$A_1 = 7.8 \cdot 10^3$ SK/cm $\Delta H_{\sigma,1} = 0.674 \pm 0.005$ eV $\sigma_{\parallel b} = 9.9 \cdot 10^{-7}$ S/cm (470 K)	$A_2 = 29.7$ SK/cm $\Delta H_{\sigma,2} = 0.38 \pm 0.02$ eV $\sigma_{\parallel b} = 1.8 \cdot 10^{-4}$ S/cm (829 K)
$\perp b$ [010]	$A_1 = 1.6 \cdot 10^3$ SK/cm $\Delta H_{\sigma,1} = 0.64 \pm 0.01$ eV $\sigma_{\perp b} = 4.8 \cdot 10^{-7}$ S/cm (471 K)	$A_2 = 9$ SK/cm $\Delta H_{\sigma,2} = 0.35 \pm 0.03$ eV $\sigma_{\perp b} = 8.0 \cdot 10^{-5}$ S/cm (826 K)

family of crystals RF_3 with structure β-YF_3, which belong to groups III and IV of homologous series of REE trifluorides

2. Experiment

Crystals of dysprosium trifluoride were grown from melt ($T_{fus} = 1439 \pm 10$ K [18]) in a two-zone setup of resistive type in a graphite crucible by technique of vertical directional solidification (Bridgman method) [27]. To suppress the reaction of pyrohydrolysis, the experiments to grow crystals DyF_3 were conducted in the fluorinating atmosphere $He + CF_4$. The initial reagent was dysprosium trifluoride synthesized from Dy_2O_3 (purity 99.998 %) by hydrofluoride method. The melt was maintained at 1500 K for homogenization for 3 h. The crystallization process was conducted using seeds oriented along the crystallographic direction [010], which were previously obtained from spontaneous crystallization of melt DyF_3. The crucible pulling rate was 3 mm/h at temperature gradient in the growth zone at 60 K/cm. The graphite crucible of special design was used, which makes it possible to decrease the weight losses of the reagent for evaporation, which did not exceed 0.5 wet.% of the initial charge mass. After crystallization, growth boules were obtained with diameter 10–15 mm and length of up to 30 mm (Figure 1). The content of oxygen impurities in the crystals did not exceed 150 ppm (measured by method of melting in the medium of inert gas on analyzer LECO ONH836). Orientation of specimens for electrophysical studies was conducted with account of their ideal cleavage in the crystallographic plane(010) [20,28].

Crystals DyF_3 are related to orthorhombic crystal system, space group $Pnma$, with the number of formula units per lattice cell equal to 4. The refined lattice parameters $a = 6.4603(2)$, $b = 6.9104(1)$, $c = 4.3808(2)$ Å (powder X-ray diffractometer Rigaku MiniFlex 600, radiation CuK_α) agree well with the structural data [25,29,30].

Ionic conductivity σ_{dc} was defined from the spectra of complex impedance $Z^*(\omega)$ in the frequency range $5-5 \cdot 10^5$ Hz (Tesla BM-507 device). The description of the experimental setup (own design and manufacture by the Special Design Bureau of the Institute of Crystallography, Moscow) and the method of electrophysical measurements are given in [31,32]. For conductometric measurements, flat parallel specimens were cut from a boule with thickness

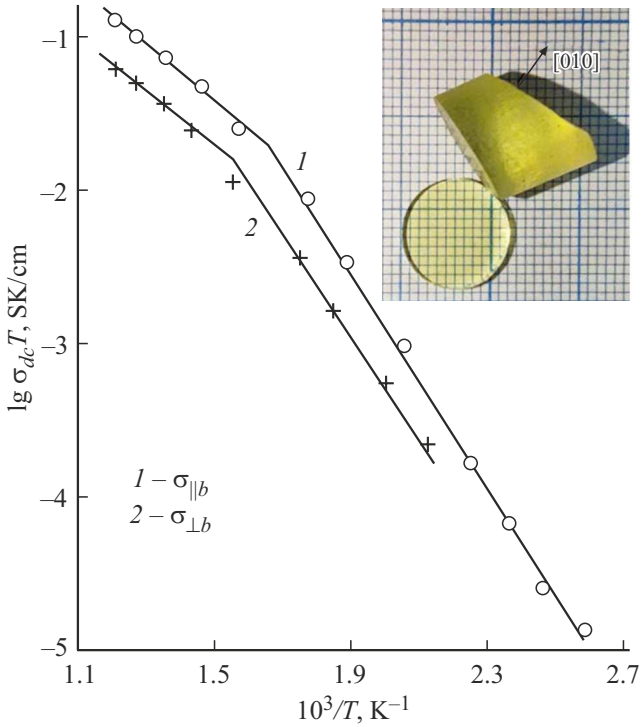

Figure 1. Orientation temperature dependences of ionic conductivity $\sigma_{dc}(T)$ and appearance of single crystals DyF_3.

of 2–3 mm, oriented along and perpendicularly to the crystallographic axis b. The ion-blocking electrodes were graphite paste DAG-580, the surface area of electrodes was 25–55 mm^2.

Measurements of impedance $Z^*(\omega) = \mathrm{Re}\,[Z^*] + j\,\mathrm{Im}\,[Z^*]$ (j — imaginary unit) of electrochemical system $C|DyF_3|C$ were conducted in vacuum ~ 0.1 Pa in the temperature range 428–783 K in the cooling mode. The presence of the blocking effect from inert (graphite) electrodes in the spectra of impedance $Z^*(\omega)$ of the electrochemical cell $C|DyF_3|C$ indicates the ion nature of electroconductivity of DyF_3 crystals. In [33,34] it is shown that the electron conductivity of REE trifluorides is insignificant. In virtue of significant difference in charges Dy^{3+} and F^- the mobility of triple-charged cations Dy^{3+} is unlikely, therefore ion transport is caused by mobile defects in the anionic (fluorine) sublattice. The results of the study ^{19}F NMR [8,11,35,36]

method indicate directly that the ion transfer in REE trifluorides occurs in the fluorine sublattice.

Bulk resistance R_b of specimens was determined using the crossing of the complex impedance hodograph $Z^*(\omega)$ with the axis of active resistances $\mathrm{Re}[Z^*(\omega)]$. The specific ion electroconductivity of specimens was calculated with account of their geometric dimensions:

$$\sigma_{dc} = (h/S)R_b^{-1}, \quad (1)$$

where h — thickness, S — electrode surface area. Relative measurement error σ_{dc} did not exceed 5%. Temperature dependence of ion conductivity $\sigma_{dc}(T)$ was described by Arrhenius-Frenkel equation:

$$\sigma_{dc}T = A\exp(-\Delta H_\sigma/kT), \quad (2)$$

where A — pre-exponential factor of ionic conductivity, ΔH_σ — enthalpy of ion transfer process activation, k — Boltzmann constant and T — temperature.

3. Results and discussion

Temperature dependences of ionic conductivity of DyF_3 crystals along and perpendicularly to axis b of the lattice cell are shown in Figure 1. Further, when the conductivity is specified in crystallographic directions, we will omit dc index. Maximum values σ_{dc} are observed along axis b. Temperature dependences $\sigma_{\|b}(T)$ and $\sigma_{\perp b}(T)$ are broken into two sections at $T_0 \approx 550$ K. In each section the dependences $\sigma_{\|b}(T)$ and $\sigma_{\perp b}(T)$ are described by equation (2). Bends in dependences $\sigma_{\|b}(T)$ and $\sigma_{\perp b}(T)$ at $T = T_0$ indicate the change of the ion transfer mechanism in this temperature area.

Parameters of ion transfer in dysprosium trifluoride for two crystallographic directions are given in Table 1. Enthalpies of ion transport activation at high- and low-temperature sections for DyF_3 (Table 1) agree well with the values $\Delta H_{\sigma,1} = 0.65-0.75$ eV and $\Delta H_{\sigma,2} = 0.37-0.45$ eV for previously studied compounds RF_3 (R = Tb, Ho, Er, Y) with the structure of type β-YF_3 [13–16].

For the studied REE trifluorides with structures β-YF_3 and LaF_3 (space group $P\bar{3}c1$) the condition $\Delta H_{\sigma,1} > \Delta H_{\sigma,2}$ is met, which is due to the participation of fluorine vacancies of various crystallographic positions in the ion transfer mechanism for low- and high-temperature areas of electroconductivity [8–16,37].

As you can see in Figure 1, in the temperature interval of 386−829 K crystals DyF_3 have minor anisotropy of ion conductivity $\sigma_{\|b}/\sigma_{\perp b} = 2.2 \pm 0.1$. In isostructural solid solution $Gd_{0.5}Y_{0.5}F_3$ it practically disappears: $\sigma_{\|b}/\sigma_{\|a} = \sigma_{\|b}/\sigma_{\|c} = 1.1$ [14,17].

According to the results of the studies [13–16,35] in closely-packed orthorhombic structures RF_3 with β-YF_3 structure, point defects are formed according to Schottky mechanism (cation and fluorine vacancies). Besides, the mobile charge carriers are vacancies of fluorine that determine the ion electroconductivity mechanism. The vacancy mechanism of ion electroconductivity is related to the translational jumps of fluorine ions in the vacant structural positions in the crystalline lattice.

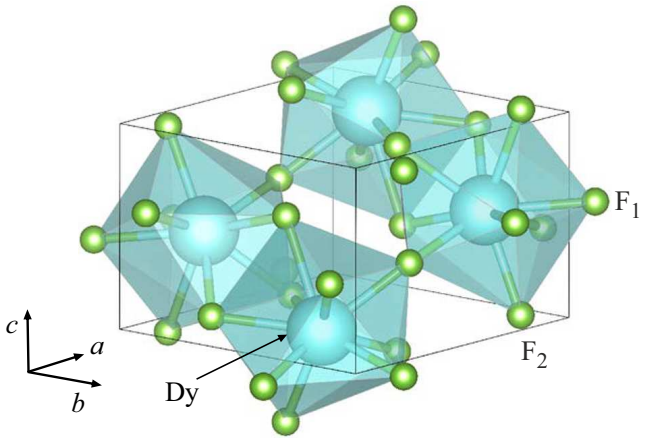

Figure 2. Unit cell of crystal DyF_3 (type β-YF_3, space group $Pnma$).

Table 2 provides experimental data [8–15,38] on anisotropy of ionic conductivity of crystals RF_3 with structures β-YF_3 and LaF_3. You can see that anisotropic effect of ion transfer for REE trifluorides DyF_3 (TbF_3, HoF_3) and LaF_3 (CeF_3), crystallizing in various structural types, is rather weak.

Besides, in REE trifluorides the path of highest ion conductivity has crystallographic directivity: axis b of orthorhombic lattice cell (type β-YF_3) and axis c of trigonal lattice cell (type LaF_3). Maximum values of ionic conductivity along axis b (space group $Pnma$) and axis c (space group $P\bar{3}c1$) were provided by highest value of fluorine ion mobility in these directions, since the lattice parameters b and c have maximum values for orthorhombic and trigonal unit cells, accordingly. A low value of anisotropy of ionic conductivity in all studied crystals RF_3 with structures β-YF_3 and LaF_3 indicates three-dimensional $3D$-nature of ion transport and absence of dedicated conductivity channels in these structures.

In the structural motif β-YF_3 (Figure 2) along axis b the anionic layers formed by atoms F_1, and cation-anion layers containing REE atoms and F_2 alternate. Ratio of anions of different types in a lattice cell β-YF_3 is equal to $F_1 : F_2 = 2 : 1$. According to [13,15] at $T < T_0$ in crystals with structure β-YF_3 the anion transfer occurs in the fluorine subsystem F_1, at $T \approx T_0$ there is exchange of fluorine vacancies between subsystems F_1 and F_2, at $T > T_0$ the anion transfer happens in all fluorine positions.

Figure 3 shows dependence of enthalpy of ion transfer activation in low-temperature area $\Delta H_{\sigma,1}$ on the value of ion radius of rare-earth cations r_{cat} for orthorhombic REE trifluorides that belong to groups III and IV of homologous series of REE trifluorides. The analysis of conductometric

Table 2. Comparison of anisotropy of ionic conductivity of REE trifluoride crystals with structure β-YF_3 and LaF_3

Crystal	Structure type	r^{**}_{cat}, Å	T, K	σ_{dc}, S/cm / $\Delta H_{\sigma,1}$, eV	Coefficient of anisotropy $\sigma_{\parallel b}/\sigma_{\perp b}$, $\sigma_{\parallel c}/\sigma_{\perp c}$	Reference
TbF_3	Type β-YF_3, space group Pnma	1.095	500	$8 \cdot 10^{-6}$ $(\sigma_{\parallel b})$/0.61	2	[13]
DyF_3		1.083	500	$2.5 \cdot 10^{-6}$ $(\sigma_{\parallel b})$/0.674	2.3	this study
HoF_3		1.072	500	$5 \cdot 10^{-6}$ $(\sigma_{\parallel b})$/0.765	1	[15]
$Gd_{0.5}Y_{0.5}F_3^*$		1.091	500	$1.6 \cdot 10^{-5}$ $(\sigma_{\parallel b})$/0.73	1.1	[14]
LaF_3	Type LaF_3, space group $P\bar{3}c1$	1.216	500	$1.5 \cdot 10^{-3}$ $(\sigma_{\parallel c})$	1.6	[8]
			500	$3 \cdot 10^{-4}$ $(\sigma_{\parallel c})$	4	[10]
			300	$1 \cdot 10^{-6}$ $(\sigma_{\parallel c})$	1.6	[9]
			300	$7 \cdot 10^{-7}$ $(\sigma_{\parallel c})$/0.3 – 0.4	2	[11]
CeF_3		1.196	500	$5.6 \cdot 10^{-4}$ $(\sigma_{\parallel c})$/0.44	2.4	[12]

Note: * solid solution, ** values r_{cat}, are given in the system of „effective ion radii“ for CN = 9 [38].

data shows the following trend. As the value of REE cation radius increases, enthalpy of ion transfer activation (vacancy mechanism) decreases, which causes increase of crystal ionic conductivity. Crystal TbF_3 has the maximum value of ion electroconductivity. Similar pattern of ionic conductivity value change depending on REE cation radius is found for crystals KR_3F_{10} (R = Tb, Dy, Ho, Y) [39].

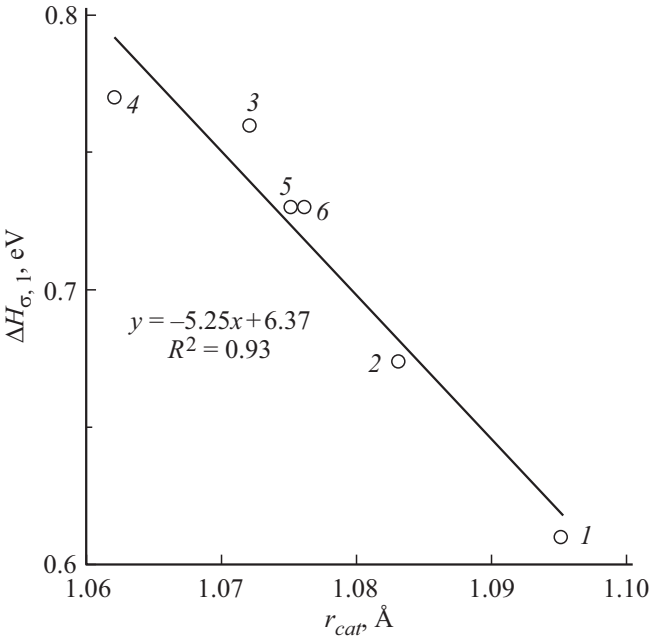

Figure 3. Dependence of enthalpy of ion transport activation $\Delta H_{\sigma,1}$ (low-temperature area) on the value of ion radius of rare-earth cations r_{cat} for compounds TbF_3 [13] (*1*), DyF_3 (*2*), HoF_3 [15] (*3*), modifications β-ErF_3 [14] (*4*), β-YF_3 [14] (*5*) and solid solution $Gd_{0.3}Er_{0.7}F_3$ [14] (*6*). Line — approximation of experimental data by linear equation ($x = \Delta H_{\sigma,1}$, $y = r_{cat}$, R — correlation coefficient).

Large REE cations (R = Tb) increase the volume of the lattice cell of crystals with structure β-YF_3, which causes reduction of enthalpy of anion transfer activation and, as a result, increase of fluorine-ion conductivity. The size effect is not very high. It causes the reduction in enthalpy of ion transfer activation by 0.16 eV and increase of conductivity at 500 K $\sim$ 5 times.

It is necessary to highlight the high difference in the absolute value of ion conductivity of orthorhombic and tysonite REE trifluorides RF_3 (Table 2). From the crystallochemical positions, it is explained by reduction of coordination number (CN) of REE cations R^{3+} for structural type β-YF_3 compared to tysonite type [40]. The typical anion polyhedron of cation R^{3+} is trigonal prism providing for minimum CN = 6. The method of spatial location of such prisms causes increase in CN = 9 for structure of type β-YF_3 and CN =11 for tysonite-type structures. In structure β-YF_3 (contrary to structure LaF_3) the formation of anion-deficient solid solutions $R_{1-y}M_yF_{3-y}$ [40], and, therefore, the appearance of mobile anion vacancies are complicated.

Since the area of solubility of heterovalent impurities in compounds with structure β-YF_3 is practically absent, this does not allow for increasing the value of ionic conductivity therein by heterovalent doping as it may be done in the case of tysonite-type solid solutions $Dy_{1-y}M_yF_{3-y}$ (M = Ca, Sr) [41,42].

4. Conclusion

The techique of directional crystallization was used to grow oriented single crystals DyF_3 — representative of structural group III from a large homologous series of REE trifluorides. Dysprosium trifluoride unit cell parameters are equal to $a = 6.4603(2)$, $b = 6.9104(1)$, $c = 4.3808(2)$ Å.

Temperature measurements of ionic conductivity $\sigma_{dc}(T)$ of crystallographically oriented specimens DyF_3 were carried out. Low anisotropy of anion conductivity DyF_3 with coefficient $\sigma_{\|b}/\sigma_{\perp b} = 2.2 \pm 0.1$ was found. Maximum ionic conductivity is observed along axis b: $\sigma_{\|b} = 2.5 \cdot 10^{-6}$ S/cm at 500 K. Orthorhombic REE trifluorides with structure β-YF_3 from group III, same as the trigonal REE trifluorides with structure LaF_3 from group I, have practically three-dimensional ion $3D$-conductivity: $\sigma_{\|b,c}/\sigma_{\perp b,c} = 2-4$ at 300−500 K.

It was shown that in the family of orthorhombic RF_3, including compounds of group III and low-temperature modifications of group IV, as the value of ion radius increased in REE cations, the enthalpy of fluorine-ion transport activation decreased, which caused increase in their ionic conductivity.

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Conflict of interest

The authors declare no conflict of interest.

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