Dielectric Spectra of Divalent Rare-Earth Metal Ions in LaF₃ Crystals

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Abstract. The dielectric spectra of LaF₃ crystals activated by rare-earth ions Eu^{2+} , Sm^{2+} , and Yb^{2+} , gradually cooled from 300 to 240 K, were investigated. Obtained experimental data were compared with experimental data obtained previously by other authors. The reorientation activation energies for RE^{2+} dipoles in LaF₃ are 0.49, 0.55, 0.56, and 0.58 eV for Ba²⁺, Sm^{2+} , Eu^{2+} , and Yb^{2+} , respectively. A reorientation of fluorine vacancy is observed, across the F1 positions.

INTRODUCTION

In the 1980s the optical spectra of trivalent rare earths RE^{3+} in the crystals of lanthanum fluoride were studied in depth, also a large number of papers were devoted to the analysis of the mechanisms of ionic conductivity, while very few studies addressed dielectric relaxation [1–4].

The aim of this study was to examine the reorientation of dipoles and to determine the nature of the charge compensator of Eu^{2+} , Sm^{2+} , and Yb^{2+} ions in LaF₃ crystals.

Previously, many structural analyses of samples of LaF₃ crystals produced various results of unit cell symmetry: P3c1 [5,6], P6₃/mcm [7], P6₃cm [8,9], P6₃/mcm [10]. There are three possible positions of fluorine ion in the unit cell of the LaF₃ crystal. Moreover, if we consider a cell with hexagonal symmetry, only two unique averaged positions of fluorine atom relative to the vacancy are possible (Fig. 1).



FIGURE 1. Positions of anionic vacancy in LaF₃ crystal with hexagonal symmetry. (a) general arrangement of the cell,
(b) crystalline axis A pointed toward reader, (c) crystalline axis C pointed toward reader. F1 is a vacancy located on the line connecting two lanthanum atoms, F2 is a vacancy located in plane with lanthanum

When one of the lanthanums is replaced with a rare-earth ion, following vacancy options are possible: F1 vacancy located on a straight line connecting two lanthanums, and F2 vacancy located in plane with lanthanum. For

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the tysonite structure, another possible position of the vacancy exists - F3 shifted out of plane with lanthanum atoms.

To gather a better understanding of energy transfer processes within fluoride crystals, comprehensive theoretical and experimental study of their geometrical and electronic structures is necessary.

EXPERIMENT

A series of dielectric measurements of lanthanum fluoride crystals both nominally pure and doped with impurities of Eu^{2+} , Sm^{2+} , and Yb^{2+} were conducted. The LaF₃ crystals under study were grown by the Stockbarger method, the concentration of rare-earth fluoride impurities was 0.01, 0.1 and 0.3 mol. % [11].

Crystals containing RE^{3+} and also crystals with significant fraction of trivalent samarium and ytterbium ions converted to the divalent form were used for study. In crystals doped with EuF₃, all europium ions were converted to divalent form. The LaF₃ samples doped with Ba²⁺ ions were used as a control group (the measurement results were reported by Roos et al. [1]).

Table 1 contains the most consistent results of the activation energy study obtained by different methods including data for different concentrations obtained by ionic conductivity method [12] and data obtained by thermally stimulated polarization current (TSPC) and thermally stimulated depolarization current (TSDC) techniques [2].

TABLE 1. Generalized research data on the energy an	d enthalpy of activation of	f crystals doped with Ba ²⁺ .
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Impurity Concentration (mol. %)		Activation energy (eV)	Method of measurement	
	0.003	0.357		
DeE	0.009	0.373	Bulk ionic conductivity	
Dar_2	0.027	0.37	Temperature range of	
$La_{1-x}Ba_xF_{3-x}$	0.05	0.388	measurements is from 100	
(X from 0 to 0.1)	0.078	0.36	to 1000 K [12]	
	0.1	0.427		
Ba^{2+}	0.012	0.32 (±0.02)	TSDC [2]	
Impurity	Concentration (mol. %)	Delta Enthalpy(eV)	Method of measurement	
	Pure	0.43		
	0.30	0.36		
	0.79	0.4		
BaF_2	1.30	0.37	TSPC and TSDC	
La _{1-x} Ba _x F _{3-x}	2.10	0.38	Temperature range of	
(x from 0 to 7)	7.10	0.38	te 1200 K [2]	
	9.52	0.37	10 1300 K [3]	
	6.72	0.4		
	7.93	0.36		

Data on activation energies for nominally pure LaF_3 crystals investigated by several groups using nuclear magnetic resonance (NMR), thermally stimulated depolarization current, dielectric loss, and spectroscopic impedance methods, are also available as well as data on the activation energy for crystals with CaF₂ impurity [4,13–17].

It's worth mentioning that the data obtained by different methods do not agree well with each other. It can be attributed to the doping of studied crystals and the temperature range of measurements.

Impurity Concentration (mol. %)		Activation energy (eV)	Method of measurement	
	0.01	0.457		
C-2+	0.03	0.457	a-relaxation and association-	
Ca	0.1	0.462	region direct current (DC)	
	0.3	0.512	conductivity [15]	
CaF_2	0.5	0.19	TSPC and TSDC [14]	
LaF ₃	Pure	0.30	465–670 K [4]	
C-E	Defect association	0.48	273–325 K [4]	
CaF_2	Dissociation Ca ²⁺	0.43	325–465 K [4]	
1.2 mol. %	Defect migration	0.31	465–670 K [4]	
I-E	Pure	0.28	Impedance spectroscopy	
Lar ₃	Relaxation energy	0.31	(least-squares method) [15]	
LaF ₃	Pure 0.5 Cap		Capacitance and dielectric	
			loss measurements [16]	
LaF ₃	Pure	0.29	NMR Energy for F1 [17]	
Sr^{2+}	²⁺ 0.03 0.20 (±0.02)		NMR [17]	

TABLE 2. Generalized research data on the energy and enthalpy of activation of crystals doped with Ba²⁺.

In our experiments we performed measurements using the dielectric loss method on E7-20 impedance meter, spectra were recorded at frequencies from 25 Hz to 1 MHz, with gradual cooling of samples in the temperature range from 300 to 240 K. Electrodes were covered in silver (Kettler epoxy). The diameter of the electrodes was about 5 mm with samples thickness of about 2 mm.

RESULTS

Measurement of the temperature dependence of the dielectric loss tangent reveals the peak associated with the reorientation of dipoles (Fig. 2).



FIGURE 2. Frequency dependence of the dielectric loss tangent tg δ of LaF₃-0.3% EuF₃ (Eu²⁺) crystals at different temperatures

The peak was observed in graph of temperature dependence of $tg\delta$ for all divalent ions – Ba^{2+} , Sm^{2+} , Eu^{2+} , and Yb^{2+} (Fig. 3–6).



FIGURE 3. Arrhenius plot for LaF₃ crystals doped with divalent barium with concentration of 0.01%, and 0.3% (two samples for each concentration, respectively); it represents dependence of the natural logarithm of the dipole reorientation time on the reciprocal temperature

Now we have ability to compare results of our calculations for LaF_3 -BaF₂ (Table 3) with similar concentrations obtained by the methods of ionic conductivity, TSDC and TSPC.

TABLE 3. Comparison of our calculation results and previously	y obtained values of activation energy of LaF3 crystals doped with
Ba	$3a^{2+}$.

		Activation energy (eV)			
Concentration of Ba ²⁺ ions (mol. %)	Dielectric loss measurements 300– 240 K	Bulk ionic conductivity 100– 1100 K [12]	TSDC 300-1100 K [2]	TSPC 293-1300 K [3]	
~ 0.01	0.578; 0.54	0.373	0.22 (±0.02)		
0.1	0.52	0.427			
0.3	0.542; 0.49			0.36	



FIGURE 4. Arrhenius plot for LaF₃ crystals doped with divalent samarium with concentration of 0.01%, 0.1% and 0.3%, respectively



FIGURE 5. Arrhenius plot for LaF3 crystals doped with divalent europium with concentration of 0.1% and 0.3%, respectively



FIGURE 6. Arrhenius plot for LaF₃ crystals doped with divalent ytterbium with concentration of 0.01%.

The frequency of reorientation of the dipoles is naturally decreasing with increase of the radius of impurity ion, since rotation of the anion vacancy around the ion becomes constrained with increasing size of the ion. Building on the results of performed measurements of temperature peaks, we can calculate the reorientation energies for RE^{2+} dipoles in LaF₃ (Table 4).

TABLE 4. Generalized data on the reorientation energies of RE ²⁺ dipoles in LaF ₃ .	

Impunity	Reorientation energy (eV),		Reorientation energy (eV), Impurity concentration 0.1 %		Reorientation energy (eV), Impurity concentration 0.3 %	
Impurity	Impurity concentration 0.01 %					
Ba^{2+}	0.578	0.55		0.52	0.496	0.542
Sm^{2+}	0.49	0.561	0.556		0.52	0.562
Eu^{2+}			0.557	0.517	0.532	
Yb ²⁺	0.5	84				

DISCUSSION

Tangent of dielectric loss is mainly dependant on the expenditure of field energy for the reorientation of dipoles with the lowest vacancy migration energy in the studied temperature range, since the time of reorientation of the dipoles with higher energies becomes longer than the time of the field exposure. According to earlier studies by NMR methods for nominally pure LaF₃ crystals, the energy of vacancy migration in the F1 position is of the order of 0.36 eV, while the energy for vacancies in the F2 and F3 positions is much higher, more than 0.6 eV. Such types of migrations make a significant contribution only at temperatures above 500 K. For NMR in the temperature range from 240 to 400 K, movement is mainly limited by ions in the F1 sublattice, while F ions in the F2 and F3 sublattices are slow, with ion movement correlation time $\tau > 10^{-3}$ s. Taking into account the obtained energy values, the temperature range of measurements, and the bonds structure in the crystal lattice, we can conclude that we observe a jump of the anionic fluorine vacancies located in the F1 position.

Slight decrease in the reorientation energies was observed in LaF_3 crystals activated by Ba^{2+} , Eu^{2+} ions together with a significant increase in the concentration of impurity bivalent ions. (Fig. 3 and Fig. 5).

The values of the activation energies of vacancies obtained in this work are slightly higher than the values for samples previously studied by Roos et al. [2,3] and are close to the values obtained by other methods of investigation in a similar temperature range [12]. Values of activation energies obtained in modern studies aimed at investigating the dielectric conductivity of pure crystals are also higher than that in results of earlier studies in the low-temperature segment [18]. The reasons for this discrepancy are currently unclear.

CONCLUSIONS

The ground state of RE^{2+} centers in LaF₃ is described by the configuration of the RE^{2+} -anion vacancy. Transitions of a vacancy near the RE^{2+} impurity center (with a dipole reorientation energy of 0.49, 0.55, 0.56, 0.58 eV for Ba²⁺, Sm²⁺, Eu²⁺, Yb²⁺) result in dielectric loss peak. Most likely, rotation of the fluorine anionic vacancy located in the F1 position occurs.

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