ACTIVATION ENERGY OF VARIOUS STRUCTURAL DEFECTS IN PURE AND ErF$_3$ DOPED CaF$_2$

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Abstract
Pure and Erbium-doped calcium fluoride crystals have been grown using the vertical Bridgman method. The real and imaginary parts of the complex dielectric constant have been measured at five audio-frequencies over the temperature range 150–300 K. From the observed relaxation processes the activation energy for various structural defects has been determined.
Keywords: Defects, Calcium compounds, Dielectric materials.

1. Introduction

Information on impurity-defect aggregates in the alkaline-earth fluorides can be obtained from spectroscopic and dielectric relaxation techniques the last being sensitive to aggregates with a dipole moment which can reorientate through migration of the anions. The alkaline-earth fluorides (MF$_2$, M = Ca, Ba, Sr) crystals doped with rare-earth fluorides (RF$_3$, R = La, Er, Yb, etc.) are good laser crystals. The excess charge on the R ion is compensated by an interstitial fluoride ion in order to preserve charge neutrality. The resultant dipolar complexes can reorient (relax) by "jumps" of one of the charges to other lattice sites. Temperature and frequency dependence of the complex dielectric constant give information about the relaxation processes and permits the determination of the activation energy and the reciprocal frequency factor of the relaxation time [1-5]. In this paper we report a study of energy activation of various structural defects in pure and Erbium-doped calcium fluoride crystals. Temperature and frequency dependence of the complex dielectric constant have been measured and the activation energy have been calculated.

2. Experiment

Pure and various ErF$_3$ concentrations doped calcium fluoride crystals have been grown using the vertical Bridgman method [6]. Capacitance C, conductance G, dielectric loss D and

loss angle θ measurements were performed on 0.6mm thick samples using a RLC Meter ZM 2355, NF Corporation, Japan, over the temperature range 150–300 K, at five audio-frequencies 1–100 kHz; for more details see [7]. The real part of the dielectric constant, ε', has been calculated from the measured capacitance. The ε'' has been then calculated from $D = \varepsilon'' / \varepsilon'$. Room temperature optical absorption spectra were recorded by a Shimadzu 1650 PC and FTIR Nexus 470 spectrophotometers.

The objectives of this study are: to analyze the effect of erbium ions on the dielectric spectrum of CaF_2 crystals, to determine the activation energy of various structural defects in pure and ErF_3 doped calcium fluoride crystals.

3. Results and Discussions

In alkaline-earth fluoride crystal containing trivalent Er^{3+} ions, the extra positive charge is usually compensated by interstitial fluorine ions (F_i^-) in order to preserve charge neutrality. Besides the tetragonal (C_{4v}) symmetry of the predominant dipolar complex, many other simple type configurations or cluster formations appear [7] (Fig. 1). The absorption spectra of ErF_3-doped crystals in the near-IR region are shown in Fig. 2. The absorption peaks correspond to transitions specified in the figure. These spectra are characterized by a very broad band, corresponding to the $^4I_{15/2} - {}^4I_{13/2}$ transition. The structure of the band is due to the crystal-field split, field with various symmetries generated by several types of charge compensation. These possible types of charge compensation induce dipole formation whose relaxation process can be observed in the dielectric spectra of the crystals.
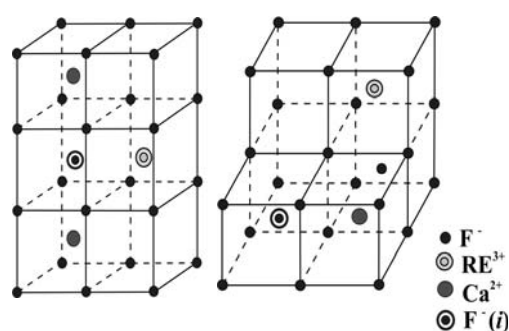

Fig.1. Er^{3+} ions sites in CaF_2 crystals: dipolar complex (a) type I or NN (C_{4v} symmetry), (b) type II or NNN (C_{3v}).
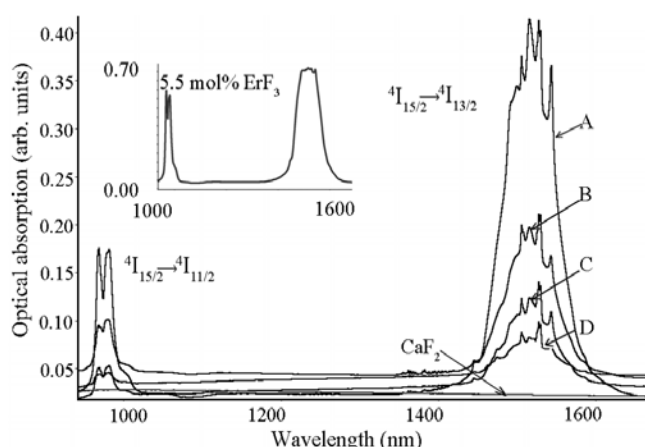
Fig. 2. Absorption spectra of ErF_3 doped CaF_2 crystals: A- 1 mol% ErF_3, B- 0.6 mol% ErF_3, C- 0.3 mol% ErF_3, D- 0.1 mol% ErF_3.

relaxation time, τ, given by $\tau = \tau_0 \exp(E/kT)$, where E is the activation energy for reorientation of the specific defect and τ_0 can be determined from the slope and intercept of a plot of T_{max}^{-1} versus logarithm of the angular frequency, ω. Temperature and frequency dependence of ε'' for CaF_2 is shown in Fig. 3 and the various defects activation energies calculated are given in Table 1.
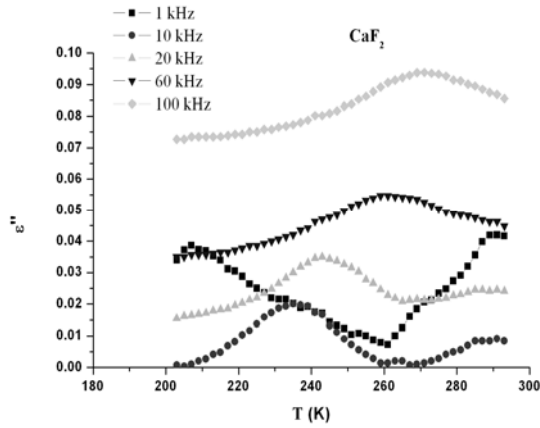

Fig. 3. Temperature and frequency dependence of
the imaginary part of the complex dielectric constant.

Table I. Anion vacancy and interstitial activation energy.

Vacancy activation energy (eV)	
Calculated	Experimental
0.35 (a)	0.355 0.55(b)
Interstitial activation energy (eV)	
0.91(a)	0.988 1.0 (b)

(a)C.Catlow, et al., J.Phys:S.S. Phys 10 (1977) 1627
(b) W. Bollmann et al., P. S. Solidi (a) 2 (1970) 157

The peak occurring in all Er-doped samples around 200 K is associated with R_I, Debye-like relaxation with activation energy of 0.3-0.4 eV [see Table 2]. The R_{IV} relaxation, in contrast with R_I, increases as the concentration increases (Fig. 4).
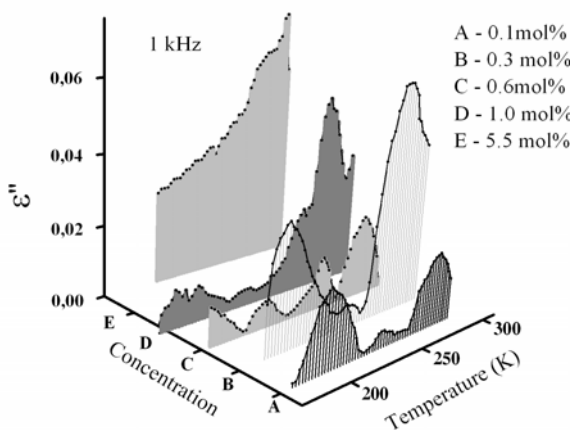

Fig. 4. Influence of ErF_3 concentration
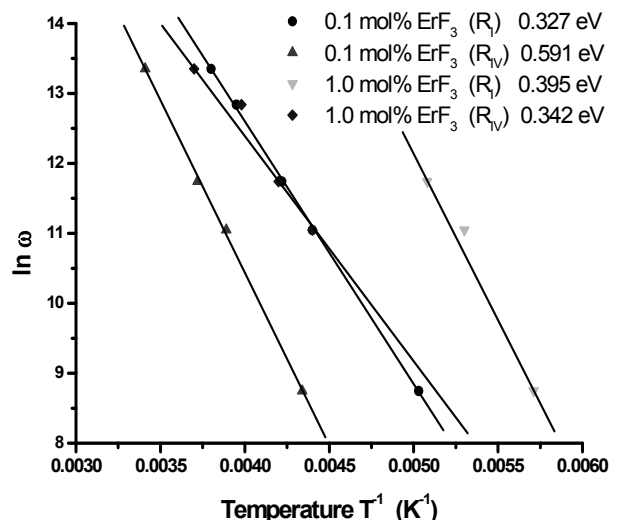on the dielectric spectrum.

Fig.5. Dependence of on ln ω ($\omega=2\pi f$).

An additional, new relaxation (R_A with high activation energy) has been observed around 280 K, which becomes predominant as the concentration increases.

The 0.3-0.4 eV relaxation is associated with the relaxation of Er^{3+} - F^- (i) complexes in which the F^- occupies the NN interstitial position with respect to the RE^{3+} ion (complex type I, Fig. 1a.).The position of the R_{IV} relaxation is found [2] to depend strongly upon the nature of the RE and is not as Debye-like as the R_I. Previously [9,10], this relaxation has been attributed to the reorientation of a NNN interstitial F^-. Because the R_{IV} relaxation increases and the R_I decreases as the concentration increases, and the ratio R_{IV} / R_I should be independent of concentration, it is concluded that the R_{IV} relaxation is not NNN associated [2]. This relaxation may be cluster associated; a possible model is a positive dimer ion [11]. The additional, new relaxation (R_A) that appears at concentration > 0.1 mol % ErF_3 with high activation energy (> 2 eV) can be associated with other complex defects.

The activation energy and τ_0 frequency factor for various relaxation types are given in Table II and compared with other published works.

Table II. Activation energy of various types observed defects.

RF$_3$ concentration in CaF$_2$	R$_I$ type or NN				R$_{IV}$ type			R$_A$
	E (eV)	τ_0 (sec) 10^{-13}	E (eV)	τ_0 (sec) 10^{-14}	E (eV)	τ_0 (sec) 10^{-15}	E (eV) τ_0 (sec) 10^{-15}	E (eV)
0.1 mol%ErF$_3$	0.327	8	0.406 [2] 0.4 [8]	1.88 [2] 0.4 [8]	0.601	2.10^{-2}	0.54 5.5 [2,4]	-
0.3 mol%ErF$_3$	0.339	3.8	0.404 [1]	1.97 [1]	0.575	$5.4\,10^{-2}$	0.53 8.7 [1]	2.6
1.0 mol%ErF$_3$	0.395	0.5	0.401 [1]	2.65 [1]	0.34	2.01	0.52 15.4 [1]	1.49
5.5 mol%ErF$_3$	-	-	-	-	-	-	-	2.22

4. Conclusions

The dependence of real and imaginary parts of the complex dielectric constant on the temperature at various frequencies for pure and ErF_3 – doped CaF_2 crystals has been studied. Our investigation reveals the two types of relaxations, R_I and R_{IV}, characteristic for RE doped CaF_2, approximately at the same temperature and activation energy as reported in other published works. The observed difference of the relaxation behavior of the studied crystals confirms the observation that the crystals properties depend strongly upon the growth conditions.   An additional, new relaxation, R_A, has been observed around 280K, which

becomes predominant as the concentration increases. In order to determine the nature of these relaxations, the symmetry of the RE centers and the structure of the complex defects, additional measurements are necessary.

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