

A Comparative Study of $\text{La}^{3+}\text{-F}_i^-$ Complexes in Three MF_2 Fluoride Crystals

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Thermal depolarization of defect dipoles has been studied in crystals of CaF_2 , SrF_2 , and BaF_2 doped with La^{3+} ions. $\text{CaF}_2:\text{La}^{3+}$ and $\text{SrF}_2:\text{La}^{3+}$ show only one depolarization peak which is attributed to type I, nearest-neighbor (nn) $\text{La}^{3+}\text{-F}_i^-$ dipoles. Three depolarization peaks were observed in $\text{BaF}_2:\text{La}^{3+}$. The 143 K peak is ascribed to type I dipoles because of the similarity in kinetic parameters to those for these dipoles in CaF_2 and SrF_2 . The small peak at 152 K is attributed to a small concentration of nn O^{2-} fluorine-ion vacancy complexes. The dominant peak at 194 K is due to type II, next-nn $\text{La}^{3+}\text{-F}_i^-$ dipoles. The activation energy for the reorientation of type I dipoles decreases linearly with increasing lattice constant in the series CaF_2 , SrF_2 , BaF_2 , and the relatively low activation energy for this process, compared with that for the jump of isolated interstitials in these crystals, is due to coulomb interactions with the substitutional impurity.

1. Introduction

With the discovery of the solid state laser, the impetus provided by the search for new and better laser materials led to an explosive growth in the study of rare-earth-doped alkaline-earth fluoride crystals after 1961 (1-3). These materials are relatively easy to grow in the form of large single crystals and they readily accept rare-earth dopants. The substitution of a rare-earth ion for a lattice cation in the fluorite structure can lead to either cubic or noncubic sites. The cubic sites are produced by isolated substitutional impurity ions with nonlocalized charge compensation; the noncubic sites comprise substitutional-interstitial pairs in which the rare-earth ions occupy normal cation sites in the fluorite lattice, with charge compensation provided by the incorporation of F^- anions as interstitials. The electrostatic attraction between defects of opposite effective charge

produces a defect complex or dipole, provided the temperature is not too high. Two types of noncubic centers are illustrated in Fig. 1. If the charge-compensating interstitial F^- ion is in one of the six nearest-neighbor (nn) sites along $\langle 100 \rangle$, the complex thus formed is designated as type I and has tetragonal symmetry (C_{4v}). If the interstitial F^- ion is in one of the eight next-nearest-neighbor (nnn) positions along $\langle 111 \rangle$ directions, the center has trigonal (C_{3v}) symmetry and is designated type II.

Detailed information about the defect structure of trivalent-ion-doped alkaline-earth fluoride has been obtained from the ENDOR measurements of Baker *et al.* (4). These studies show that hyperfine spectra occur that are characteristic both of cubic and of tetragonal symmetry for the environment of the paramagnetic cation. Weak trigonal spectra also have been detected by Voron'ko *et al.* (5) and Rector *et al.* (6). It

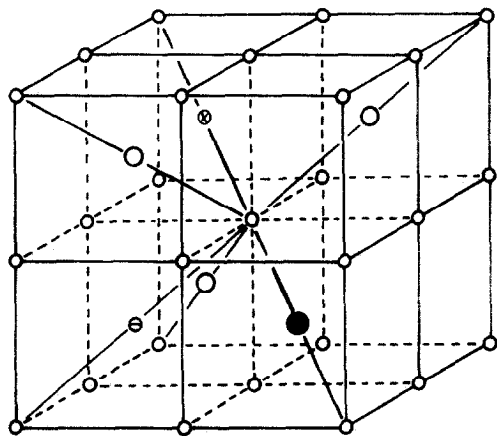


FIG. 1. The structure of tetragonal (type I) and trigonal (type II) $R^{3+}-F_i^-$ complexes in fluorite crystals. \circ , F^- ; \odot , M^{2+} ; \bullet , RE^{3+} ; \ominus , $nn F_i^-$; \otimes , $nnn F_i^-$.

has been shown by Sierro (7) and Ranon and Yaniv (8) that the trigonal defects become important in doped SrF_2 ; and these latter workers together with Boatner *et al.* (9) suggest that such defects are predominant in doped BaF_2 .

Dielectric relaxation in solid materials may be detected by means of isothermal measurements of charging and discharging currents, dielectric and anelastic relaxation, nuclear magnetic resonance (NMR), electron paramagnetic resonance (EPR), and thermal depolarization (TD), the latter often being called ionic thermoconductivity (ITC) (10). Of these techniques, TD is the most recent but it has become a very popular method of studying dipolar relaxation in ionic crystals. This is due not only to its inherent sensitivity, but also because it gives a complete picture of the temperature-dependent relaxations and allows the kinetic parameters (i.e., the activation energy, E , and the preexponential factor in the relaxation time, τ_0) to be obtained from a single measurement. Another important advantage of TD is its ability to resolve relaxation processes arising from sets of dipoles with only slightly different reorientation energies and to detect a small concentration of dipoles

whose relaxation is masked by other dominant relaxation processes (10).

There have been extensive studies of alkaline-earth fluorides doped with various trivalent ions by TD (11-15) and dielectric relaxation (16). In this study, we have concentrated on the relatively large ion lanthanum, doped into the three alkaline-earth fluoride crystals. The dipolar complexes $La^{3+}-F_i^-$ that are formed in these crystals were studied by TD measurements and the relaxation kinetic parameters E and τ_0 thus obtained will be compared with results from other workers. Special consideration will be given to a comparative study of the $La^{3+}-F_i^-$ type I complex in the three fluorides.

2. Experimental

Crystals doped with a nominal La^{3+} content of 0.1 mole% in CaF_2 , SrF_2 , and BaF_2 , and 1 mole% in BaF_2 were obtained from Dr. A. V. Chadwick, who has successfully developed the technique of growing good quality fluorite single crystals at the University of Kent Chemical Laboratory. For TD measurements, the smallest separation between the two cleavage faces is desirable. The samples were therefore cleaved so as to have the following dimensions: 0.5-1.0 cm^2 in cross-sectional area and about 1 mm in thickness. GC Electronic silver paint was then applied to the two large faces to function as electrodes.

The TD cell and the detailed experimental procedure can be found elsewhere (17-18). The sample was polarized in a static electric field, E , ranging from 2000 to 5000 $V\ cm^{-1}$, in 700 Torr of dry He at an appropriate temperature, T_p , for the polarizing time, t_p , and then cooled down to the temperature, T_0 , where the dipoles remain oriented. The applied field was then removed and the sample was warmed up at a constant rate (usually 4 K/min) controlled by a Stanton Redcroft Model 681 linear temperature

programmer. As the sample is warmed up, the dipole relaxation time for reorientation becomes shorter and shorter, and eventually the randomization of the dipoles gives rise to a thermally induced depolarization current given by the equation (10)

$$I(T) = (Q_0/\tau_0) \exp(-E/kT) \exp\left\{(-b\tau_0)^{-1} \times \int_{T_0}^T \exp(-E/kT') dT'\right\}, \quad (1)$$

where b is the heating rate, Q_0 is the total stored charge, and $\tau = \tau_0 \exp(E/kT)$ is the relaxation time. The depolarization currents, ranging from 5×10^{-15} to 10^{-12} A, were measured with a Model 401 Cary vibrating reed electrometer and the chromel–alumel thermocouple and the electrometer outputs were displayed on a two-pen Hewlett–Packard chart recorder.

In BaF₂ peak 1 and peak 2 are partially overlapping. Peak cleaning techniques (10) were then applied. Each of the experimentally observed TD peaks was fitted to Eq. (1) over the whole temperature range to yield the activation energy E , the total stored charge Q_0 , and the characteristic relaxation time τ_0 associated with the reorienting dipoles.

3. Results and Discussion

3.1. TD of CaF₂:La³⁺

The dipolar relaxation of La³⁺–F_i[–] complexes in CaF₂ is reported for the first time in this study. A single peak is detected in the CaF₂:La³⁺ spectrum (Fig. 2) and this is attributed to jumps of a nn interstitial charge compensator between equivalent sites. The peak position is at 146 K (Fig. 2) with activation energy $E = 0.475$ eV and $\tau_0 = 3.53 \times 10^{-15}$ sec. The circles show the experimental points and the solid line is the calculated best fit to these data, using Eq. (1). Annealing at 1100 K under vacuum and then quenching in liquid nitrogen did not change the spectrum significantly.

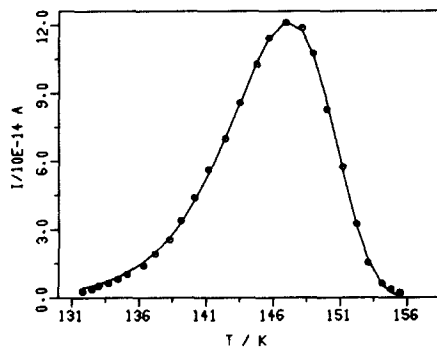


FIG. 2. The peak for CaF₂:La³⁺. The circles show the experimental data and the solid line is the computer fit to Eq. (1).

3.2. TD of SrF₂:La³⁺

The reorientation of dipoles in SrF₂:R³⁺ reported by Lenting *et al.* (15) indicates that type I dipoles are predominant in the first part of the series of lanthanides while type II complexes are found for the heavier R³⁺ ions. On the other hand both types of relaxations were detected simultaneously in samples doped with Gd³⁺, Tb³⁺, or Dy³⁺. In this study, only a single peak was seen in the SrF₂:La³⁺ spectrum (Fig. 3) and this is assigned to the relaxation of type I dipoles. The relaxation parameters agree well with those published by Lenting *et al.* (15). We find the following values: $E = 0.444$ eV, $\tau_0 = 8.58 \times 10^{-13}$ sec, and $T_M = 159$ K for the

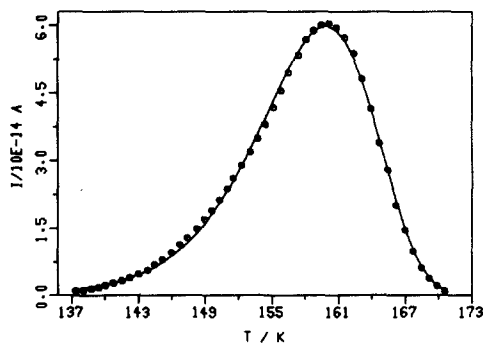


FIG. 3. TD peak for SrF₂:La³⁺. Circles show experimental data and the solid line is the computer fit to Eq. (1).

activation energy, the characteristic relaxation time and the temperature corresponding to the maximum depolarization current, respectively. The corresponding values obtained by Lenting *et al.* (15) are 0.44 eV, 4.68×10^{-13} sec, and 151 K.

3.3. TD of $\text{BaF}_2:\text{La}^{3+}$

In $\text{BaF}_2:\text{La}^{3+}$ three clear relaxation peaks were observed (Fig. 4). Qualitative studies showed that the "as grown" crystals containing a nominal concentration of 0.1 and 1 mole% La^{3+} displayed the same type of spectrum. However, the polarization increases with increasing concentration of dopant, as expected. The final results of computer fitting are presented in Table I. After this work had been submitted for publication a paper by Laredo *et al.* (19) on relaxation processes in $\text{BaF}_2:\text{La}^{3+}$ appeared in the literature. These authors observed a three-peak spectrum with depolarization maxima occurring at 141, 194, and 287 K. We also observed the high-temperature depolarization but did not report it as a dipole relaxation phenomenon because strong depolarization in this temperature range is commonly associated with the decay of macroscopic space charge. Indeed the shape of the peak, its shift to lower temperature with increasing concentration of La^{3+} impurity, and the variations in activation energy (0.85–0.65 eV) all lead us to suspect that this high-temperature peak is associated with the decay of macroscopic space charge.

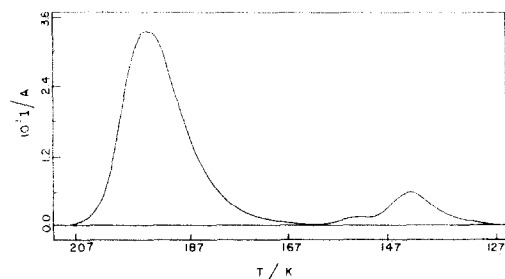


FIG. 4. TD spectrum of $\text{BaF}_2:\text{La}^{3+}$.

TABLE I
RELAXATION PARAMETERS FOR $\text{BaF}_2:\text{La}^{3+}$

Peak No.	T_m (K)	τ_0 (sec)	E (eV)
1	143	1.08×10^{-12}	0.391
2	152	3.26×10^{-15}	0.492
3	194	6.83×10^{-13}	0.544

Our peak 2, $T_M = 152$ K, is clearly evident in the TD spectra reported by Laredo *et al.* but was not resolved by these authors as a separate depolarization. The relaxation parameters reported in Table I, which were derived by computer fitting the whole depolarization curve, are in good agreement with those reported by Laredo *et al.* (peak 1 \equiv peak A; peak 3 \equiv peak B), who determined E and τ_0 from the initial rise of the depolarization current.

The EPR spectrum (7–9) of $\text{BaF}_2:\text{R}^{3+}$ is dominated by the trigonal spectrum associated with the type II complexes. It is logical, therefore, to assign the largest peak at 194 K to type II dipoles. Indeed, the peak position is identical with that observed by Kitts *et al.* (14); also the activation energies found in the two studies agree well. In a recent study of thermally stimulated polarization (TSP) and TD in $\text{BaF}_2:\text{Tb}^{3+}$, Kristianpoller and Kirsh (20) observed a single dipole relaxation peak at 194 K with $E = 0.52$ eV. T_M is identical with, and E very similar to, the corresponding quantities for the dominant peak 3 in $\text{BaF}_2:\text{La}^{3+}$ TD spectrum. As only one peak is found for $\text{BaF}_2:\text{Tb}^{3+}$, this must be due to type II nnn $\text{R}_s^{3+}\text{F}_i^-$ complexes, in agreement with our assignment.

In their study of $\text{BaF}_2:\text{Gd}^{3+}$, Kitts *et al.* (14) observed initially one large TD peak which was then resolved into two clearly separated components. They assumed that the high-temperature peak at 194 K was due to type II dipoles and the low-temperature peak at 173 K to type I dipoles. In the

present study, the lowest temperature peak in the spectrum of BaF₂:La³⁺ was observed at 142 K and by comparison with the results of CaF₂:R³⁺ (21, 22) it seems most likely that this is due to the relaxation of the type I dipole. The large temperature difference of 30 K for the relaxation of nn dipoles in the two systems, BaF₂:La³⁺ and BaF₂:Gd³⁺, seems surprising and further work is required to elucidate this problem. The ratio r of the peak height for the nn relaxation in BaF₂:La³⁺ to that for the relaxation of nnn F_i⁻ is 0.198 and 0.195 for two different specimens of nominal concentration 0.1% La³⁺ and is 0.193 for a crystal containing nominally 1% La³⁺. All three specimens were polarized at $T_p = 196$ K. The value of r is thus independent of concentration and has a mean value of 0.20. Laredo *et al.* (19) also found r to be independent of concentration with a mean value of 0.24 for $T_p = 295$ K. The small difference found in the two investigations for the concentration ratio of nn to nnn dipoles is probably due to differences in annealing procedures.

When the sample is polarized at 140 K, the high-temperature peak disappears and only the two lower-temperature peaks are displayed. The small second-lowest peak at $T_M = 152$ K has relaxation parameters (Table I) that are quite similar to those found (21) for the orientation of O²⁻F_v⁻ complexes ($E = 0.47$ eV, $\tau_0 = 6.8 \times 10^{-14}$ sec) and for T₁ complexes ($E = 0.48$ eV, $\tau_0 = 3.4 \times 10^{-13}$ sec) in crystals of CaF₂:Y³⁺ that have been doped with oxygen. It may, perhaps, seem somewhat surprising for local charge compensation of R_s³⁺ by F_i⁻ and of O_s²⁻ by F_v⁻ to exist in the same crystal when remote compensation of R_s³⁺ by O_s²⁻ would be the more stable state. However, the coexistence of these defects in CaF₂:Y³⁺ has been demonstrated (21) by showing that the nn Y_s³⁺ F_i⁻ complex is first removed on heating the crystal in oxygen and then reforms on quenching, while the O_s²⁻ F_v⁻ and T₁ peaks also grow on

quenching. Although a similar detailed study has not been performed on BaF₂:La³⁺ the similarity in activation energies suggests that the small peak 2 at 152 K in BaF₂:La³⁺ may be associated with either the T₁ complex or with O_s²⁻ F_v⁻ dipoles.

3.4. Comparative Study of the Type I Dipole in Three MF₂:La³⁺ Crystals

Figure 5 shows the complete TD spectra of the three MF₂:La³⁺ crystals. A comparative study of TD in the three La³⁺-doped fluorides is naturally limited to the tetragonal nn F_i⁻ compensated dipole complex, since nnn complexes were not observed in CaF₂:La³⁺ and SrF₂:La³⁺. The derived parameters are tabulated in Table II. The observed increases in τ_0 are qualitatively reasonable and consistent with the fact that the Debye frequency decreases in the series CaF₂ to SrF₂ to BaF₂. The reorientation activation energy decreases as the ionic radius of the host cation, and therefore the lattice constant of the host crystal, increases (Fig. 6). This reduction in activation energy shows the same trend as the migration energy of the free fluorine interstitial in the three fluorides (0.79 eV in CaF₂:La³⁺, 0.74 eV in SrF₂:La³⁺, and 0.72 eV in BaF₂:La³⁺) obtained from ionic conductivity measurements (21) and is clearly a result of the increased space available for the jumping interstitial ion. Thus the TD results justify the conclusion drawn from conductivity measurements (21) and the theoretical

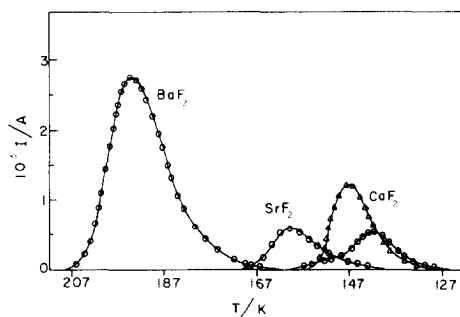


FIG. 5. TD spectra of MF₂:La³⁺.

TABLE II
COMPARATIVE STUDY OF TYPE I DIPOLAR
COMPLEXES IN $MF:La^{3+}$

Crystal	T_m (K)	τ_0 (sec)	E (eV)
$CaF_2:La^{3+}$	146	3.53×10^{-15}	0.475
$SrF_2:La^{3+}$	159	8.57×10^{-13}	0.444
$BaF_2:La^{3+}$	143	1.08×10^{-12}	0.391

calculations by Franklin (23), that the tendency to form charge-compensating anion interstitials should increase from CaF_2 to BaF_2 , if defect interactions are neglected. The difference in the dipolar reorientation energy and the migration energy of a free interstitial is understandable. Their mechanisms are entirely different. The free interstitial migrates by a concerted or interstitialcy mechanism in which a migrating ion replaces a lattice anion on a neighboring site, the displaced anion moving into a neighboring interstitial site. The reorientation activation energies for the complex $La^{3+}-F_i^-$ involve also the coulomb interaction between the substitutional La^{3+} and the jumping F_i^- ion in both the initial and saddle-point configurations. In either a direct ((110)) or noncollinear interstitialcy jump this coulomb interaction will be greater in the saddle-point configuration than in the initial

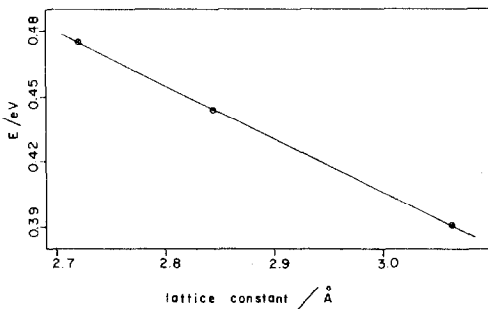


FIG. 6. Plot of the activation energy E for the reorientation of type I dipoles vs the lattice constant of the host crystal.

interstitial configuration and so the activation energy is lower than that for the isolated interstitial, as found experimentally.

4. Conclusions

The present study indicates that the reorientation activation energy of the type I dipole of $La^{3+}-F_i^-$ in the three fluorides decreases proportionally with the increase of the ionic radius of the host cation and the lattice constant of the host crystal. The relatively low activation energies of ~ 0.4 eV agree well with the majority of other TD measurements (11-15) and also are in agreement with the EPR line-broadening, dielectric, and anelastic relaxation results reported by Franklin *et al.* (24). It is now clear that the early results of higher reorientation energies obtained by Southgate (25) and Chen and McDonough (26) must be attributed to some process other than the orientation of type I dipoles. The mechanism for the type I dipole is that of a $nn \rightarrow nn$ interstitial jump around the substitutional trivalent cation and the relatively low activation energy is due to favorable coulomb interactions with the substitutional impurity.

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