

Electric dipole relaxation of mixed clusters in double-doped CaF_2

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Audio-frequency dielectric relaxation measurements from 150 to 400 K and ionic-thermocurrent measurements from 90 to 290 K have been used to study the relaxation of dipolar defects in several calcium-fluoride samples doped with two rare-earth species. In particular, the region containing the R_{IV} relaxation for the corresponding singly doped samples has been investigated. The R_{IV} relaxation is distinguished by an activation energy that is a strong function of the ionic radius of the rare-earth dopant, varying from about 0.5 eV (for $\text{CaF}_2:\text{Tm}$) to about 0.9 eV (for $\text{CaF}_2:\text{Pr}$). In each doubly doped sample, relaxations are observed similar to those observed in the singly doped samples. In addition, a new relaxation is found which falls between the R_{IV} relaxation peaks of the two constituents. This suggests that the R_{IV} relaxation is associated with a cluster including two rare earths (a dimer) and that the new peak is associated with a cluster including two different rare earths (a mixed dimer). Since the existence of an electrical relaxation requires that the dimer be dipolar, the results cannot be explained by the usual dimer models. In addition, the data indicate that the rare-earth ions do not share equally in the reorientation process.

I. INTRODUCTION

In the past few years, it has become apparent that clustering is significant in rare-earth-doped calcium fluoride at rather low concentrations. Aggregation has, in fact, been observed using dielectric relaxation,^{1,2} ionic thermocurrents,³ selective laser excitation,⁴ nuclear magnetic resonance,⁵ optical,⁶ Mössbauer,⁷ neutron diffraction,⁸ and electron-spin-resonance⁹ techniques. In addition, aggregation has been treated theoretically.¹⁰ Of particular interest here is a center with a relaxation energy of from 0.5 eV (for $\text{CaF}_2:\text{Tm}$) to 0.9 eV (for $\text{CaF}_2:\text{Pr}$) designated the R_{IV} center by Andeen *et al.*² The activation energy was observed to correlate strongly with dopant ion size. There has been evidence that the R_{IV} center is some form of cluster.^{2,3,11}

In this paper we report a study of the R_{IV} relaxation region in samples of doubly doped CaF_2 using dielectric relaxation and ionic thermocurrent (ITC) techniques. We have found that, for each system studied, a new relaxation appears between those of the R_{IV} centers associated with each of the constituent dopants providing strong evidence that the R_{IV} relaxation is associated with two rare earths (a dimer). The results are discussed in terms of models for dimers already existing in the literature.

II. EXPERIMENT

Samples of calcium fluoride doped with 0.05 mol% each of erbium and samarium, 0.05 mol% each of neodymium and dysprosium, 0.05 mol% each of neodymium and terbium, and 0.3 mol% each of terbium and thulium were obtained from Optovac, Inc.

Three terminal capacitance C and conductance divided by the frequency G/ω measurements were performed on the samples using a specially modified General Radio 1615 bridge. The samples were 25.4-mm-diam disks 1.5-mm thick that had aluminum electrodes evaporated onto their surfaces in the standard three-terminal configuration. The measurements were performed isothermally at five audio frequencies from 10^2 to 10^4 Hz at various temperatures from 150 to 380 K. Further details of the apparatus are given elsewhere.²

In the present work, the real part of the dielectric constant ϵ' at 300 K and 1000 Hz was taken to be 6.915 for all samples. ϵ' at 300 K and frequencies other than 1000 Hz was then calculated assuming that the relative change in dielectric constant with frequency is equal to the relative change in capacitance. The real part of the dielectric constant at temperatures other than 300 K for each frequency was then determined from

$$\frac{\epsilon'_T}{\epsilon'_{300}} = \frac{C_T}{C_{300}} \exp\left(-\int_{300}^T \alpha_p dT\right), \quad (1)$$

where α_p is the isobaric linear thermal expansion coefficient taken to be equal to that for pure calcium fluoride¹² due to a lack of values for rare-earth-doped samples. Finally, the imaginary part of the dielectric constant, ϵ'' , was calculated from the equation

$$\epsilon'' = \epsilon'G/\omega C. \quad (2)$$

Ionic-thermocurrent spectra were measured from 90 to 290 K at heating rates of 3–5 K/min. During all ITC experiments the sample chamber was filled with a 1-atm helium exchange gas to minimize thermal gradients. The ITC experiment was performed according to the method developed by Bucci *et al.*^{13,14} Polarizing fields of about 8 kV/cm were used, and depolarization currents were measured using a Cary 401 vibrating-reed electrometer. Peak currents were about 10^{-13} A, with a background noise level of about 10^{-15} A. Linear heating rates of 3–5 K/min were employed.

III. RESULTS

The results for the imaginary part of the dielectric constant over the temperature range 150–380 K are plotted in Figs. 1–4 along with previous results for the corresponding singly doped samples.²

In Figs. 1–4 the R_{IV} relaxation is the most prominent peak above 200 K for all singly doped samples. In each case the following trend is observed for the doubly doped samples: the expected lower temperature R_{IV} relaxation (small rare earth) is not readily observable in the dielectric loss spectrum, a new relaxation appears

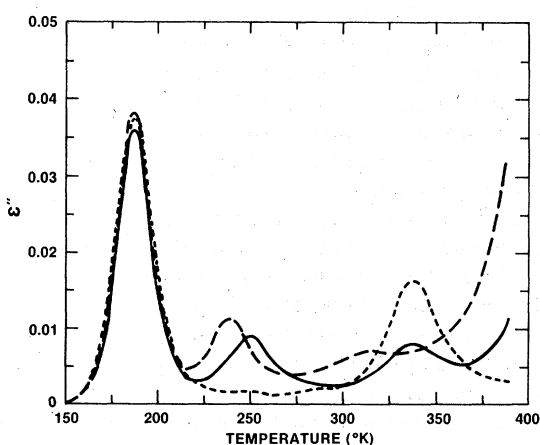


FIG. 1. ϵ'' temperature for various samples of rare-earth-doped calcium fluoride. — CaF_2 :Er, Sm, 0.05 mol % each; - - CaF_2 :Er, 0.1 mol %; - · - CaF_2 :Sm, 0.1 mol %.

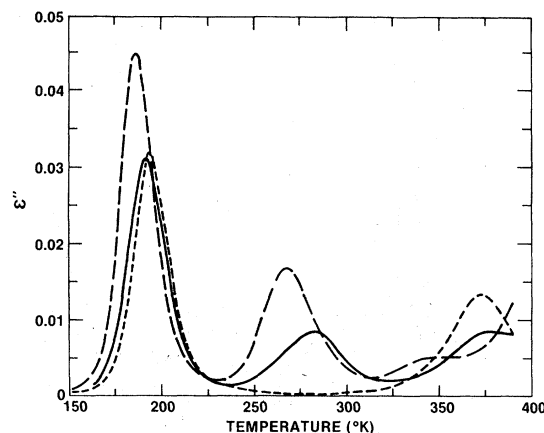


FIG. 2. ϵ'' temperature for various samples of rare-earth-doped calcium fluoride. — CaF_2 :Dy, Nd 0.05 mol % each; - - CaF_2 :Dy 0.1 mol %; - · - CaF_2 :Nd 0.1 mol %.

at a slightly higher temperature, and the expected higher temperature relaxation (larger rare earth) is observed.

A comparison of the various relaxations is given quantitatively in Table I where activation energies E and reciprocal frequency factors τ_0 are tabulated. The values of E and τ_0 were determined as follows. First, each peak was fitted to the Debye equation for ϵ'' :

$$\epsilon'' = (\epsilon'_L - \epsilon'_H)\omega\tau / (1 + \omega^2\tau^2), \quad (3)$$

where ϵ'_L and ϵ'_H are the “low”- and “high”-frequency limits of the dielectric constant where “low” and “high” mean relative to the dispersion produced by the relaxation only. τ is the relaxa-

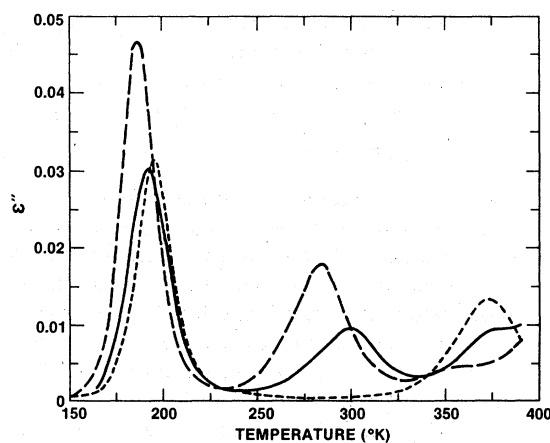


FIG. 3. ϵ'' temperature for various samples of rare-earth-doped calcium fluoride. — CaF_2 :Nd, Tb 0.05 mol % each; - - CaF_2 :Nd 0.1 mol %; - · - CaF_2 :Tb 0.1 mol %.

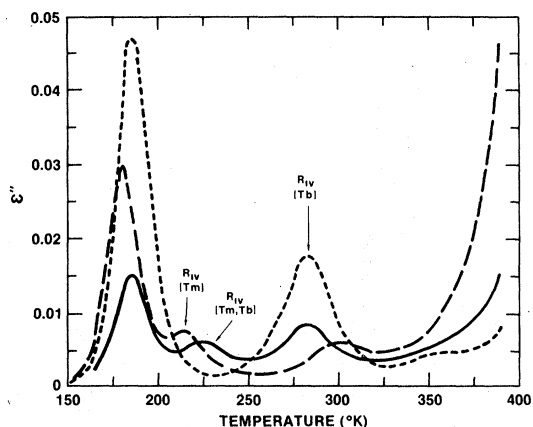


FIG. 4. ϵ'' temperature for various samples of rare-earth-doped calcium fluoride. — CaF_2 :Tm, Tb 0.3 mol% each; - - - CaF_2 :Tm 0.1 mol%; - · - · CaF_2 :Tb 0.1 mol%.

tion time of the dipole assumed to be given by an Arrhenius equation of the form

$$\tau = \tau_0 e^{E/kT}, \quad (4)$$

where T is the absolute temperature and k is Boltzmann's constant. In addition, it is assumed that

$$\epsilon'_L - \epsilon'_H = A/T, \quad (5)$$

where the constant

$$A = Np^2/3\epsilon_0 k \quad (6)$$

is known as the dipole strength, N is the dipole concentration, p is the dipole moment, and ϵ_0 is the permittivity of free space. Fits were made for all five frequencies and the results were used to determine the approximate temperature at which $\omega\tau = 1$ for each of the five frequencies. The activation parameters quoted in Table I were then found from a best fit to the equation

$$\ln(\omega) = -E/kT - \ln(\tau_0). \quad (7)$$

The activation parameters for singly doped CaF_2 :Tm were determined in the present paper after subtracting off an estimated contribution due to the R_I relaxation. Consequently, these values are more uncertain than those for R_{IV} in most of the other materials. However, the values are considered better than the estimate given in Ref. 2 based on the peak position at 100 Hz.

It is seen in Table I that both E and τ_0 for the new relaxation in the doubly doped samples are slightly larger than the corresponding activation parameters for R_{IV} for the smaller rare earth. Because of the interference of dielectric loss due

TABLE I. Activation parameters for the R_{IV} and associated mixed-cluster relaxations in rare-earth-doped CaF_2 . The estimated error in E and $\ln\tau_0$ is about 1%.

Dopant (mol%)	E (eV)	τ_0 (10^{-15} sec)
0.1% Er ^a	0.543	5.51
0.05% Er-0.05% Sm	0.558	9.11
0.1% Sm ^a	0.793	2.47
0.1% Dy ^a	0.604	7.64
0.05% Dy-0.05% Nd	0.631	9.04
0.1% Nd ^a	0.89	
0.1% Tb ^a	0.645	5.35
0.05% Tb-0.05% Nd	0.671	7.86
0.1% Nd ^a	0.89	
0.1% Tm	0.463	26
0.3% Tm-0.3% Tb	0.478	30
0.3% Tm-0.3% Tb	0.638	7.2
0.1% Tb ^a	0.645	5.4

^aReference 2.

to other relaxations or high temperature dc conductivity, it was only possible to obtain activation parameters for the higher temperature relaxation in the doubly doped samples for the Tm-Tb sample. It is seen that to within experimental error the peak is the same as R_{IV} for the larger rare earth. It is interesting to note that terbium was studied both as the larger (Tb-Tm) and the smaller (Tb-Nd) rare earth.

Since the new relaxation is displaced only slightly in all cases from the position of the R_{IV} relaxation of the smaller rare earth, ITC was used as a probe for the presence in the relaxation spectrum of the peak due to the smaller rare earth in the low-temperature shoulder of the new peak. The ITC experiment is ideally suited to this purpose, since "peak-cleaning" techniques, involving selective polarization and/or depolarization at temperatures in the vicinity of the peak of interest, can greatly reduce the intensity of nearby peaks, while only slightly attenuating the peak of interest. Such measurements were made on the CaF_2 :Er, Sm samples, and revealed the presence of the peak associated with the R_{IV} relaxation of Er, the smaller rare-earth, as illustrated in Fig. 5. The ITC data shown as a solid curve were taken without peak-cleaning procedures. The dashed curve was taken on the same sample, but with polarization procedures chosen to enhance the Er-associated R_{IV} relaxation. Similarly, peak cleaning of the new peak in the CaF_2 :Tb, Nd sample showed the presence of the Tb R_{IV} relaxation as shown in Fig. 6. In each case, the peak associated with the smaller of the rare earths is about one-third the intensity of the newly observed peak.

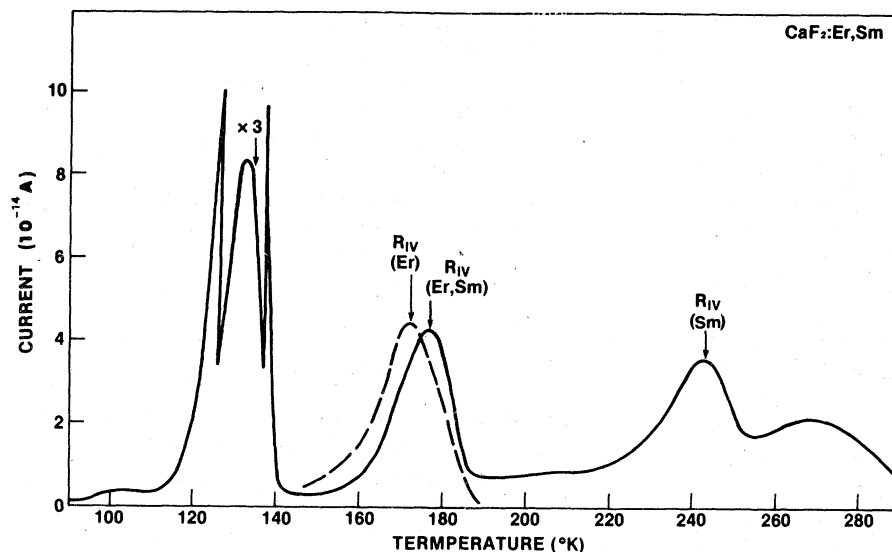


FIG. 5. Ionic thermocurrent results for $\text{CaF}_2:\text{Er}, \text{Sm}$, 0.05 mol% each. - No peak cleaning; -- Peak-cleaning techniques used to enhance the 172-K peak.

IV. DISCUSSION

These results strongly suggest that the R_{IV} relaxation is due to a cluster containing more than one rare earth. Furthermore, since only one new peak is observed, it appears likely that only two rare earths are involved in the cluster, the new peak representing a mixed dimer.

Dimers have been observed previously in rare-earth-doped calcium fluoride using techniques other than electrical relaxation. For example, various dimer models have been proposed to explain optical,⁶ neutron diffraction,⁸ electron-spin-

resonance,⁹ and selective laser excitation⁴ data. However, Booth *et al.*⁵ have recently reported dimer-associated nuclear magnetic resonance data that cannot be explained by any dimer models in the literature. The results of the present work also are inconsistent with most of the models in the literature for the following reason. In order for a dimer to relax electrically, it must have a dipole moment. Consequently, neither the dimer with a nearest neighbor pair of rare earths along the [110] direction (see Fig. 1 of Ref. 5, for example) nor the 2-2-2 cluster of Cheetham *et al.*⁸ as developed theoretically by Catlow¹⁰ would be

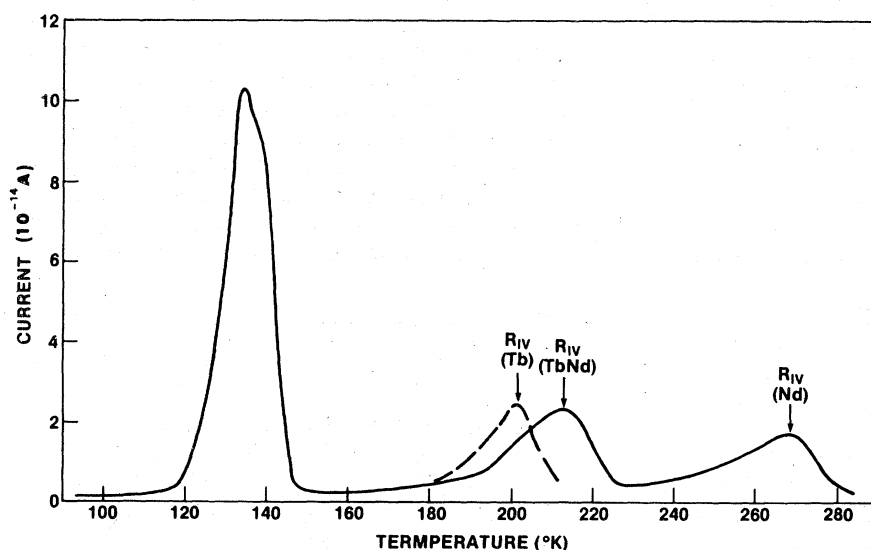


FIG. 6. Ionic thermocurrent results for $\text{CaF}_2:\text{Tb}, \text{Nd}$, 0.05 mol% each. - No peak cleaning; -- Peak cleaning techniques used to enhance the 202-K peak.

expected to relax electrically. Their existence can't be ruled out on the basis of the present work since they could exist in addition to the dimer reported here. There is, in fact, evidence that more than one type of dimer exists in rare-earth doped calcium fluoride.⁴ Furthermore, the dimer reported here may only be a slight modification of those clusters. For example, Andeen *et al.*² have speculated that perhaps the dimer is such that the rare earth sits off center. It should be kept in mind that this suggestion was made in an attempt to account for the fact that the activation energy for R_{IV} is strongly dependent upon the size of the rare earth.²

It is interesting that the results of the present work are consistent with the "gettering" model of Yaney *et al.*¹⁵ that was proposed to explain optical data in rare-earth-doped strontium fluoride. In that model a dimer extracts an additional interstitial fluoride ion from somewhere in the crystal. If the original dipole were one of the neutral dimers mentioned above, the new dimer would then most likely be endowed with a dipole moment and thus expected to relax electrically. Tallant *et al.*⁴ have also found evidence in support of the "gettering" model in rare-earth-doped calcium fluoride. The reason that this model is particularly attractive is that it can be used to explain the "anomalous" increase in cubic sites with increasing rare-earth concentration that is known to exist in $\text{CaF}_2:\text{Er}$.¹⁶⁻¹⁸ Specifically, an increase in cubic sites will occur if the dimer extracts its additional interstitial from tetragonal sites.

There are, however, still other ways to form dipolar dimers. For example, either of the "tetragonal" cluster sites proposed by Yaney *et al.*¹⁵ is dipolar though only the monoclinic modification contains equivalent sites necessary for dipolar reorientation. In addition, Andeen *et al.*² have speculated on the possible existence of positive dimer ions. While such an entity would seem rather unlikely from an electrostatic point of view, such a cluster has excess rare earths, which is an attractive feature for explaining the strong dependence of E for R_{IV} upon the size of the rare-earth ion.²

Finally, the results of the present work show

that the dipolar dimer exhibits one other "unusual" feature. It has been shown that the mixed cluster peak does not occur midway between the single specie peaks but is always only slightly shifted in temperature from the position of the peak associated with the smaller rare earth. Consequently, this suggests that the rare earths do not share equally in the reorientation process. This fact should be quite helpful in modeling the reorientation process once the actual structure of the dimer is determined.

V. CONCLUSIONS

In summary, then, it has been shown that in calcium fluoride doped with two different rare earths, a new relaxation is observed in addition to the R_{IV} relaxations observed in singly doped samples. This suggests that the R_{IV} relaxation is associated with a cluster involving two rare earths and that the new relaxation is due to a cluster involving two different rare earths. Since the existence of an electrical relaxation requires that the dimer be dipolar, the results cannot be explained by the usual dimer models. Finally, the data indicate that the rare-earth ions do not share equally in the reorientation process.

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