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# Dielectric relaxation in yttrium- and lanthanum-doped calcium fluoride

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The complex dielectric constant has been measured at five audio frequencies over the temperature range 5.5–400 K for 0.1 mol% of yttrium and lanthanum in calcium fluoride. Five relaxations are observed in the yttrium-doped material and one is observed for lanthanum. These results are consistent with trends with ion size observed previously for rare earths in calcium fluoride and emphasize that ion size is the primary factor determining defect formation in calcium fluoride doped with trivalent ions.

## INTRODUCTION

In a recent paper,[1] dielectric relaxation spectra for thirteen rare earths in calcium fluoride were presented. In the present note, the work is extended to yttrium- and lanthanum-doped calcium fluoride.

## EXPERIMENT AND RESULTS

Samples of 0.1-mol% yttrium- and lanthanum-doped calcium fluoride were obtained from Optovac, Inc. in the form of 25.4-mm-diam discs 1.5 mm thick. Three-terminal audio-frequency capacitance and conductance measurements were then carried out on the samples over the temperature range 5.5–400 K using a specially modified General Radio 1615 bridge. Further details of the experiment along with the procedure used to transform the capacitance and conductance data to complex dielectric constants are given elsewhere.[1] The results for the imaginary part of the dielectric constant at 100 Hz for yttrium and lanthanum in calcium fluoride are shown in Figs. 1 and 2.

Five peaks are observed in $CaF_2$:Y and are labeled $R_I$–$R_V$ by analogy with previous results for the rare earths.[1] Only one peak, the $R_I$ relaxation, is observed in $CaF_2$:La. Each peak represents the reorientation of a dipolar complex and it is assumed that such a process can be characterized by a relaxation time $\tau$ given by an Arrhenius equation of the form

$$\tau = \tau_0 \exp(E/kT) , \tag{1}$$

where $\tau_0$ is referred to as the reciprocal frequency factor, $E$ is the activation energy, $k$ is Boltzmann's constant, and $T$ is the absolute temperature. Values for $E$ and $\tau_0$ were determined for each relaxation as described previously[1] and the results for each relaxation are tabulated in Table I. Apparently, literature values exist only for the $R_I$ relaxation in $Y$ and those results are also tabulated in Table I. It is seen that the agreement

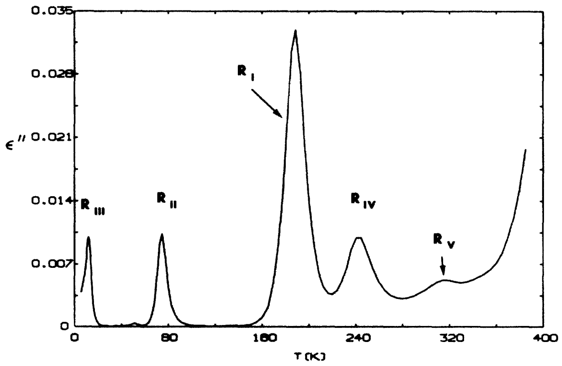

FIG. 1. Imaginary part of the dielectric constant $\epsilon''$ at 100 Hz for calcium fluoride doped with 0.1 mol% of yttrium. The curve was generated by connecting the data points.

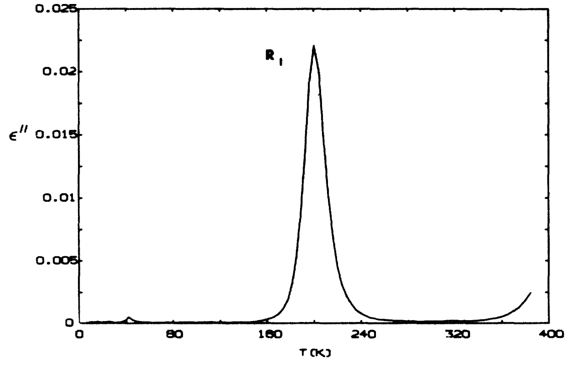

FIG. 2. Imaginary part of the dielectric constant $\epsilon''$ at 100 Hz for calcium fluoride doped with 0.1 mol% of lanthanum. The curve was generated by connecting the data points.

TABLE I. Activation parameters for yttrium- and lanthanum-doped calcium fluoride. The uncertainty in $E$ and $\ln(\tau_0)$ is estimated to be on the order of 1%.

| $CaF_2$:Y | $E$ (eV) | $\tau_0$ (sec) |
|---|---|---|
| $R_I$ | 0.409 | $1.8\times10^{-14}$ |
| | $0.412^{a}$ | $3.0\times10^{-15\,a}$ |
| | $0.41^{b}$ | $2.3\times10^{-14\,b}$ |
| $R_{II}$ | 0.148 | $1.6\times10^{-13}$ |
| $R_{IV}$ | 0.552 | $5.7\times10^{-15}$ |
| $R_V$ | 0.68 | $1.7\times10^{-14}$ |
| $CaF_2$:La | | |
| $R_I$ | 0.443 | $1.2\times10^{-14}$ |

[a] E. L. Kitts, Jr. and J. H. Crawford, Jr., Phys. Rev. B 9, 5264 (1974).

[b] I. Kunze and P. Müller, Phys. Status Solidi A 13, 197 (1972).

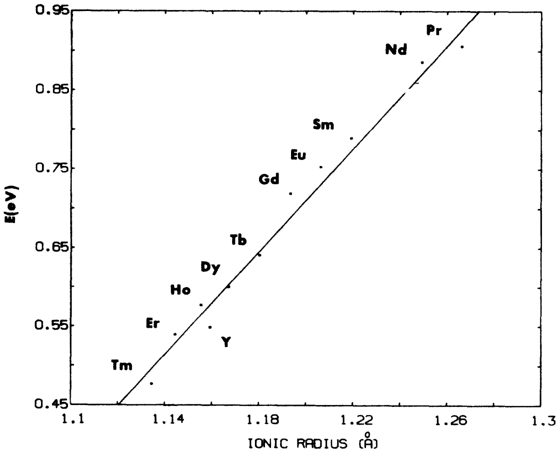

FIG. 3. Activation energy vs rare-earth ion size (Ref. 3) for the $R_{IV}$ relaxation.

with other workers for this relaxation is reasonable.

## DISCUSSION

The essential features of the dielectric spectra for lanthanum- and yttrium-doped calcium fluoride can be predicted from previous work[1] solely on the basis of ion-size considerations.

### A. $CaF_2$:La

For example, it has been found that $R_{II}$ and $R_{III}$ do not exist for large rare-earth ions in as-received samples of calcium fluoride from two different manufacturers.[1,2] Since a trivalent lanthanum ion is larger than any trivalent rare-earth ion,[3] neither relaxation would be expected in $CaF_2$:La. Both of these low-temperature relaxations have been tentatively assigned to clusters,[1,4] and the general conclusion is that the larger the ion, the more difficult it is to form certain types of clusters. Perhaps the formation of these clusters is diffusion limited since larger rare-earth ions would probably have smaller diffusion coefficients.

The $R_{IV}$ and $R_V$ relaxations are probably not observed in $CaF_2$:La for a different reason. It was shown previously[1] that the positions of these peaks depend strongly upon the size of rare-earth ions, shifting to higher temperatures for larger ions. The trends observed in that work suggest that both $R_{IV}$ and $R_V$ for $CaF_2$:La should occur at temperatures well above the range of the present experiment.

Finally, the activation energy for $R_I$ in $CaF_2$:La is slightly larger than for any rare earth in calcium fluoride. This is once again consistent with ion-size considerations since it is known[1] that the activation energy for $R_I$ for rare earths in calcium fluoride generally increases slightly as the size of the ion increases.

### B. $CaF_2$:Y

The dielectric spectrum for $CaF_2$:Y is also consistent with ion-size considerations. In particular, yttrium is approximately the same size as holmium,[3] and the similarity between Fig. 1 and the dielectric spectrum for $CaF_2$:Ho (Ref. 1) is quite striking. In fact, the activation parameters for $R_I$ in $CaF_2$:Y and $CaF_2$:Ho are almost identical and those for $R_{II}$ and $R_V$ are quite similar. In order to compare the values for $R_{IV}$, a plot of activation energy versus ionic radius for the rare earths and yttrium has been made in Fig. 3. A similar plot was made previously for the rare earths,[1] however, it is of interest to replot the data since revised values for the ionic radii have recently become available.[3] It is seen that the approximately linear dependence of activation energy on ion size is preserved and that yttrium lies reasonably close to the line.

Finally, it is noted that $R_{III}$ in $CaF_2$:Y and $CaF_2$:Ho are somewhat different. Specifically, $R_{III}$ in $CaF_2$:Y occurs at lower temperatures and is less Debye-like than $R_{III}$ in $CaF_2$:Ho. In fact, the shape of $R_{III}$ in $CaF_2$:Y is sufficiently non-Debye-like that activation parameters are not reported in the present note. These differences are not particularly surprising since no strong trends have been noted for $R_{III}$ other than its appearance only for ion sizes smaller than gadolinium.

## CONCLUSIONS

In summary, then, the dielectric spectra for yttrium- and lanthanum-doped calcium fluoride are found to be consistent with simple ion-size considerations by comparison with similar results for rare-earth doped calcium fluoride. Consequently, it is concluded that defect formation in calcium fluoride doped with trivalent ions is determined primarily by the size of the ion.

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[1] C. Andeen, D. Link, and J. Fontanella, Phys. Rev. B 16, 3762 (1977).

[2] C. Andeen and J. Fontanella, J. Phys. Chem. Solids 38, 237 (1977).

[3] R. D. Shannon, Acta Crystallogr. A 32, 751 (1976).

[4] J. Fontanella and C. Andeen, J. Phys. C 9, 1055 (1976).