JOURNAL OF MATERIALS SCIENCE 16 (1981) 2571–2574

Dielectric properties of LiF single crystals

H. B. GON, N. VEERAIAH
Department of Physics IIT, Kharagpur, India

The dielectric constant, ϵ, loss, tan δ, and a.c. conductivity, σ, of high quality single crystals of LiF have been measured in the frequency range 10^2 to 10^5 Hz and in the temperature range 30 to 400° C. ϵ of LiF at 30° C is 8.3 and is frequency independent; tan δ was below detection level (tan $\delta < 0.0001$). ϵ increases slowly with temperature up to about 150° C (frequency independent region) beyond which it rises rapidly, being frequency dependent with larger values at lower frequencies. A similar behaviour is exhibited by tan δ. The activation energy for conduction in the high temperature region is calculated to be 0.93 eV from log σ against $1/T$ graphs. Log ($\Delta\epsilon$) against $1/T$ plots (where $\Delta\epsilon$ is the difference between the dielectric constant at any temperature and the value at room temperature, ~ 30° C) yields an activation energy value of 1.0 eV in the high temperature region. This activation energy is found to be independent of frequency. This agreement between the two activation energy values, one for the a.c. conductivity and the other for the ϵ increase with temperature. This suggests that the same charge carriers are responsible for the two processes in the high temperature region.

1. Introduction

A study of the dielectric properties of solids gives a good insight into the electrical field distribution in them. By studying the dielectric constant, ϵ, loss, tan δ, and conductivity, σ, as a function of frequency and temperature, it is possible to obtain an understanding of the various polarization mechanisms in solids and also estimate the defect concentration in them. Work along these lines was carried out on a variety of solids, for example, alkali halides [1–4] giving valuable information.

The dielectric properties and refractive index of LiF have previously been studied [5, 6]. Generally the dielectric properties of ionic crystals, including LiF, have been measured at one frequency and at about room temperature. As far as the authors know a study of the detailed influence of frequency and temperature on the dielectric properties of LiF has not been reported until now. It is the aim of this paper to present our measurements of dielectric constants and loss of high quality LiF single crystals in the frequency range 10^2 to 10^5 Hz and in the temperature range 30 to 400° C.

2. Experimental methods

The LiF crystals used in the present measurements were a gift from the Crystal Physics Laboratory, MIT, USA.* The impurity concentration of these crystals was less than 2 ppm. The dimensions of the samples were about 1 cm × 1 cm × 0.1 cm. Silver paint was applied to electrodes on either side of the samples. The dielectric measurements were carried out on a GR 716 type capacitance bridge. The accuracy of the measurements on several samples of LiF studied was 2% for ϵ and about 5% for tan δ.

3. Results

The dielectric constant, ϵ, of these LiF crystals at 30° C was measured to be 8.3 and was independent of frequency; the dielectric loss, tan δ, was below detection level (tan $\delta < 0.0001$) in this frequency region.

The variation of ϵ with temperature at different frequencies is shown in Fig. 1. ϵ increases slowly up to about 150° C (frequency independent region); beyond this temperature ϵ rises rapidly

---

*The authors are grateful to Professor A. Smakula, Director of the Crystal Physics Laboratory, for kindly sparing these samples.

0022–2461/81/092571–04$02.40/0

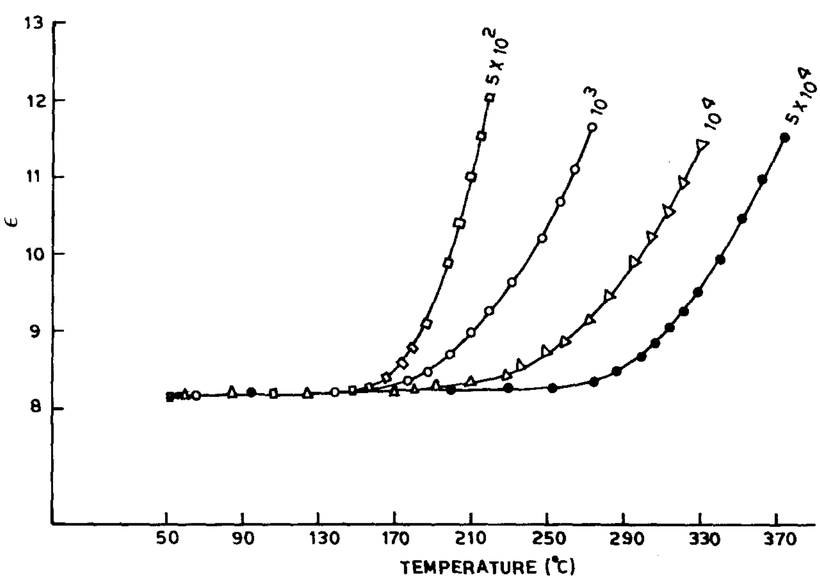

Figure 1 Variation of dielectric constant, ϵ, of LiF single crystals with temperature at different frequencies.

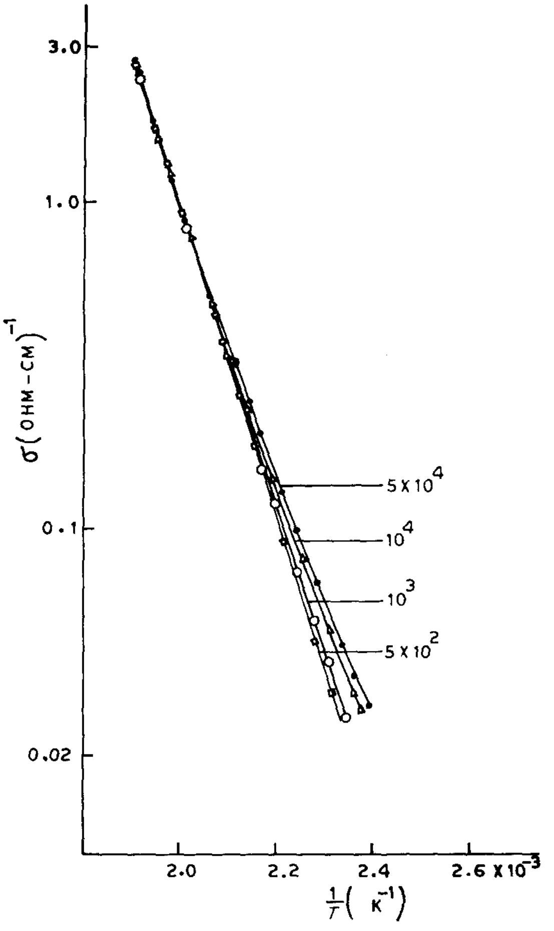

Figure 2 A.c. conductivity, σ against $1/T$ at different frequencies for LiF crystals.

and is very frequency dependent with larger values at lower frequencies. Similar behaviour is exhibited by $\tan\delta$ and hence the graph is not shown. Using the values of ϵ and $\tan\delta$, the value of a.c. conductivity has been calculated using $\sigma = \omega \tan\delta\, \epsilon_0$, where ϵ_0 is vacuum dielectric constant. Log σ against $1/T$ graphs were plotted at different frequencies and are shown in Fig. 2. These graphs merge into a straight line beyond about 150° C. The activation energy for conduction in this region was calculated to be 0.93 eV.

4. Discussion

The dielectric constant of a material is due to electric, ionic, dipolar and space-charge polarizations. All these are active at low frequencies. In fact the nature of the variation of ϵ with frequency indicates which types of contributions are present.

The space-charge contribution will depend on the purity and perfection of the crystals. The influence is negligible at very low temperatures and is noticeable in the low frequency region. The dipolar orientational effect can sometimes be seen in some materials even up to 10^{10} Hz. The ionic and electronic polarization always exist below 10^{13} Hz.

The dielectric constant value of 8.3 at 30° C for LiF crystals measured in the present work is in good agreement with the literature value [7]. The frequency independence of ϵ (at room temperature) in this crystal shows that only electronic and

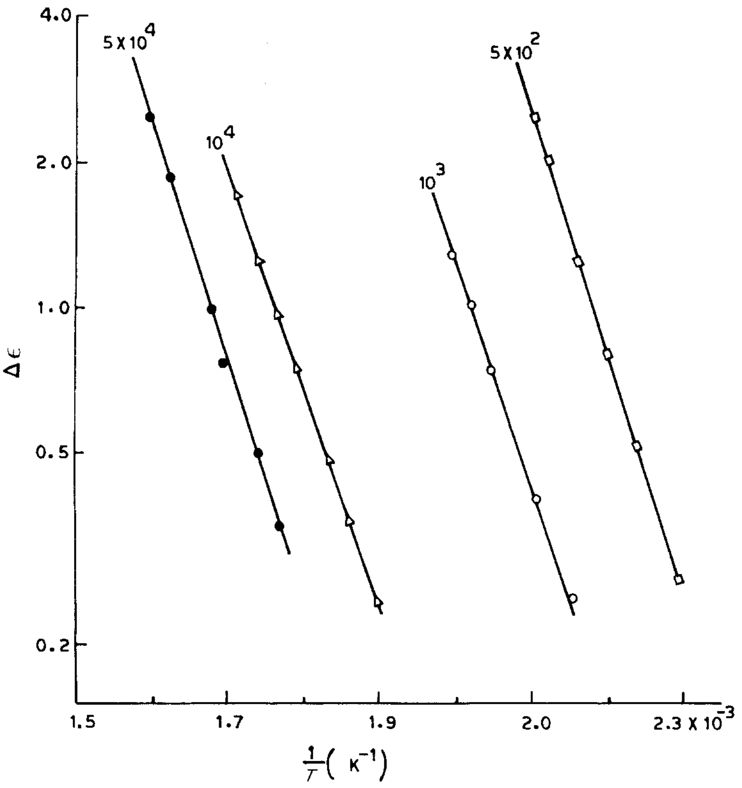

Figure 3 $\Delta\epsilon$ against $1/T$ at different frequencies for LiF crystals.

ionic polarizations are present. The concentration of crystal defects contributing to space-charge polarization is negligible. This is also borne out by the fact that the tan δ values for these samples even at 10^2 Hz and 30° C is very low (tan $\delta < 0.0001$).

The temperature has a complicated influence on the dielectric constant. Generally, increasing temperature of the crystal decreases the electronic polarization. The increase of ionic distance due to the temperature influences the ionic and electronic polarizations. The decrease in electronic dielectric constant for many solids is found to be less than 3% for a temperature change of about 400° C [8, 9]. Similarly it appears that the changes in ionic polarization are not very large. Even assuming the presence of a small number of dipoles and their contributions to dielectric constant, we know from Debye's theory that ϵ is inversely proportional to temperature. As such, it is expected that the dielectric constant of LiF crystals should not change considerably with increase in temperature. However, we found a large increase in ϵ. The crystal defects can only increase with temperature making space-charge polarization dominant; hence ϵ increases with temperature [3, 4]. The changes in ϵ with temperature are smaller at higher frequency as this type of polarization decreases appreciably at such frequencies [10]. The frequency independent increase in ϵ is apparently due to an increase in ionic polarization of the samples.

It is interesting to find that the nature of variation of ϵ and tan δ (of LiF crystals) with temperature at different frequencies is similar. The variation of ϵ with temperature can be connected to frequency through modified Debye equations, as reported earlier [3, 4]. A plot of log ($\Delta\epsilon$) against $1/T$ (where $\Delta\epsilon$ is the difference between dielectric constant value at any temperature T and that at room temperature) at different frequencies for these crystals is shown in Fig. 3. The graphs are straight lines from about 150° C having about the same slope for all frequencies. The computed activation energy is 1.0 eV. This value is practically the same as the value of activation energy for a.c. conduction, σ, in these samples in the same temperature region. This seems to suggest that the charge carriers responsible for the changes in ϵ and σ are the same. Although it is not possible to understand the nature of the charge carriers responsible for the conduction in this solid (in this temperature region) from the present measurements, the activation energy value of 0.93 eV seems to be connected to the mobility of cationic vacancies [11].

Acknowledgements

The authors are grateful to Professor K. V. Rao for his continuous interest and helpful discussions.

References

1. C. WAGNER and P. HANTLEMAN, *J. Chem. Phys.* **18** (1950) 72.
2. H. KELTING and H. WILT, *Z. Physik* **126** (1949) 697.
3. K. V. RAO and A. SMAKULA, *J. Appl. Phys.* **36** (1965) 3953.
4. *Idem, ibid.* **37** (1966) 319.
5. K. KAMIYOSHI and Y. NIGARA, *Phys. Stat. Sol. (a)* **3** (1970) 735.
6. K. R. MAHMUD, *Phil. Mag.* **23** (1971) 665.
7. C. KITTEL, "Introduction to the Solid State Physics" (John Wiley and Sons, New York, 1953).
8. M. BARBRON, *Ann. Phys. (Paris)* **6** (1951) 899.
9. T. RADHAKRISHNAN, *Proc. Indian Acad. Sci. A.* **33** (1951) 2234.
10. A. K. JONSCHER, *Phil. Mag.* **B38** (1978) 587.
11. R. J. DRIAUF, S. O. MORGAN and W. J. MARZ, "American Institute of Physics Handbook" 2 edn (McGraw-Hill, New York, 1963).

Received 23 December 1980 and accepted 19 March 1981.