

Dielectric properties of cobalt doped cadmium oxalate crystals

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Abstract. $\text{Co}_x\text{Cd}_{1-x}\text{C}_2\text{O}_4\cdot 4\text{H}_2\text{O}$ crystals grown by gel technique are characterized for dielectric properties by optical absorption measurements. Loss curve shows a relaxation peak at 500 KHz corresponding to a relaxation time of $0.3 \mu\text{s}$. Cole–Cole diagrams give exponent of universal power law to be equal to 0.22. Optical absorption shows peaks due to Co^{+2} ion and water of hydration. An attempt is made to understand the results.

Keywords. Gel growth; dielectric properties; optical absorption; relaxation time; non Debye type; universal power law.

1. Introduction

Oxalate crystals are insoluble in water and they decompose before melting. Therefore, single crystals of these materials cannot be grown by either slow solvent evaporation or melt techniques. Cadmium oxalate crystals grown from gel technique have been investigated by X-ray methods from which lattice constants and space group were determined (Volkova *et al* 1985). Barium, cadmium and their mixed oxalate crystals were grown by gel technique (Dharma Prakash and Mohan Rao 1986). Cadmium oxalate trihydrate single crystals were grown in silica gel employing various nucleation controlling procedures (Arora and Abraham 1981) by adding impurities such as Li^+ , K^+ , NH_4^+ etc. (Pella *et al* 1984) and divalent impurities like Co^{+2} , Ca^{+2} , Ni^{+2} , Zn^{+2} etc (Jagannatha and Mohan Rao 1993). Addition of impurities suppressed the nucleation density and increased the size of the crystal. Thermogravimetry and differential thermal analysis of various oxalates have also been reported (Dolhimore and Griffiths 1970; Dharma Prakash and Mohan Rao 1989). Since in these crystals Co^{+2} are present in a very small proportion (0.4% of the total volume), these impurities are expected to affect the properties of the crystals in general and dielectric properties in particular. Hence we present in this paper the dielectric behaviour of gel grown Cd–Co oxalate single crystals $\text{Co}_x\text{Cd}_{1-x}\text{C}_2\text{O}_4\cdot 4\text{H}_2\text{O}$.

2. Experimental

Gel was allowed to set in a corning glass tube (length 200 mm and dia 25 mm) using sodium meta silicate (specific gravity $1.04 \text{ g}\cdot\text{cm}^{-3}$) and oxalic acid (0.5 M) in 10:8 volume ratio. The observed pH of gel solution was 3.8. Gel formation took about a week. A mixture of cadmium and cobalt chloride solutions was then added slowly along the walls of the glass tube. The chloride solution diffused deep into the gel as indicated by the Liesegang rings and their movements. Well formed pinkish coloured Co–Cd oxalate crystals of $\sim 7 \times 2 \times 1 \text{ mm}^3$ size were obtained in about ten days deep in the gel. Chemical analysis of these crystals indicated the composition to be 36.3%, Cd^{+2} ; 0.400%, Co^{+2} ; 36.900%, oxalate and 26.400%, water. Using these values, the value of x can be shown to be 0.01.

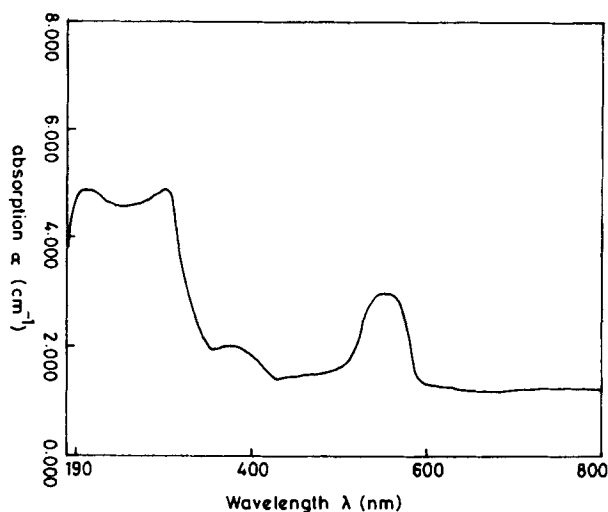


Figure 1. Optical absorption spectrum of Co-Cd oxalate.

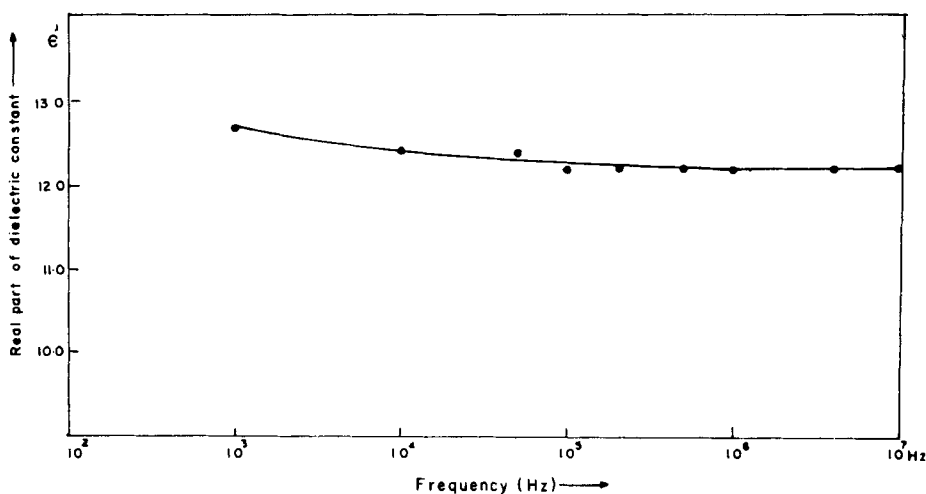


Figure 2. Real part of dielectric constant (ϵ') as a function of frequency.

Using Shimadzu spectrophotometer Model No: 3100, optical absorption characteristics of grown crystals were studied as a function of wavelength in the range 200–800 nm. Impedance spectroscopy studies were carried out using Hewlett-Packard impedance analyser No. 4192 A. The measurements were done at room temperature (30°C) in the frequency range 100 Hz to 10 MHz. The large area faces of the sample were painted with silver paint which served as electrodes.

3. Results

These crystals showed a low absorption coefficient of 1.2 cm^{-1} at 800 nm which increased to 1.8 cm^{-1} as the wavelength decreased to 350 nm. Such low absorption

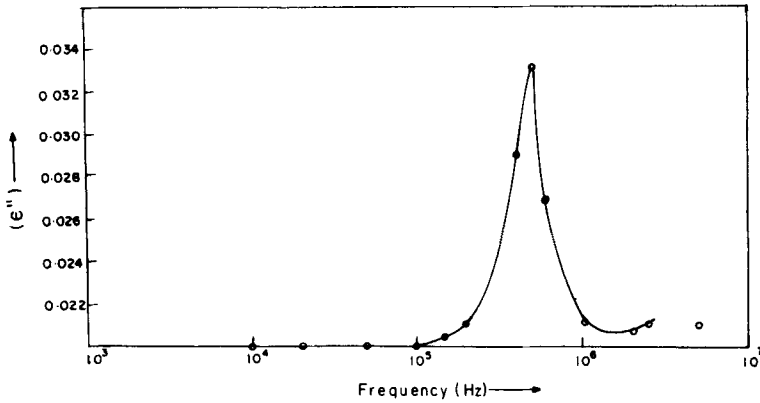


Figure 3. Imaginary part of dielectric constant (ϵ'') as a function of frequency.

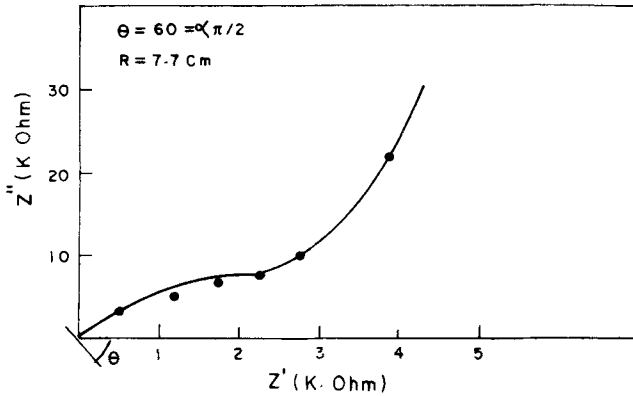


Figure 4. Real part of impedance (Z') and imaginary part of impedance (Z'') vs frequency.

values indicate that the crystals grown are of moderately high quality (Gupta and Rao 1979). In optical absorption spectrum (figure 1) a broad peak is observed at 550 nm. This peak appears to be due to Co^{+2} ion electronic transitions, since Cd-oxalate crystals are known to be transparent. Figure 2 presents the variation of real part of dielectric constant (ϵ') as a function of frequency for Cd-Co oxalate crystals. The value of ϵ' shows a very small decrease with increase in frequency attaining a constant value at higher frequencies. The value of ϵ' at 10^6 Hz is 12.5. Variation of imaginary part of dielectric constant (ϵ'') as a function of frequency for Cd-Co oxalate crystals is presented in figure 3. We observe a peak at about 500 KHz in this curve. Figure 4 gives the imaginary part of impedance (Z'') as a function of real part of the impedance (Z'). We observe this to be almost a semi-circle. In figure 5 we present the variation of $\log(G'/\omega)$ and $\log(G''/\omega)$ (where G' and G'' are real and imaginary parts of conductance) as a function of frequency. $\log(G''/\omega)$ vs $\log(\omega)$ curve is a straight line almost parallel to the frequency axis indicating linear dependence of G'' on ω . $\log(G'/\omega)$ curve is assumed to be a straight line and the slope of this line is 0.22.

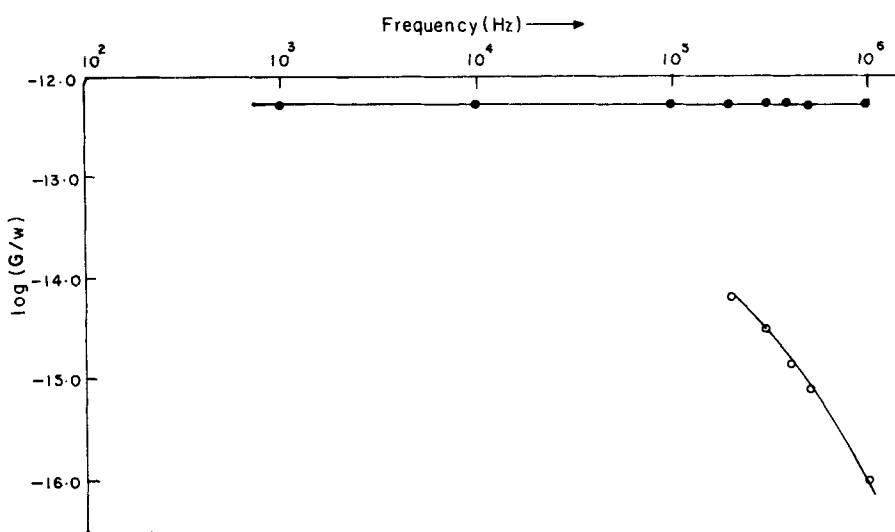


Figure 5. Variation of $\log(G'/\omega)$ and $\log(G''/\omega)$ with frequency: (a) $\log(G''/\omega)$ vs $\log \omega$ and (b) $\log(G'/\omega)$ vs $\log \omega$.

4. Discussion

In the present investigation, addition of Co^{+2} ions as CoCl_2 to supernatant solution of CdCl_2 suppresses the number of nucleation centres, facilitating the growth of larger crystals. Co^{+2} ions enter into the crystal lattice replacing Cd^{+2} ions. The Pauling radius of Co^{+2} is 0.97 \AA and that of Co^{+2} 0.72 \AA . Hydration energy enthalpy at 25°C is given by (Phillips and Williams 1965)

$$\Delta H = -699Z^2/r_{\text{eff}} \text{ kJ/mol,}$$

where Z is cation valency and r_{eff} the sum of Pauling radius of cation and anion. This is found to be -1654.44 kJ/mol for Co–Cd oxalate. For Cd-oxalate this value is -1441.24 kJ/mol . The ion distribution coefficient which is a measure of the Co^{+2} ions incorporated in the crystals is given by:

$$K_D = \frac{(C_{\text{Co}^{+2}}/C_{\text{Cd}^{+2}})_{\text{crystal}}}{(C_{\text{Co}^{+2}}/C_{\text{Cd}^{+2}})_{\text{solution}}},$$

where $C_{\text{Co}^{+2}}$ is concentration of Co^{+2} in a crystal and so on. The value of K_D is 1.037 for these crystals. From figure 2 it can be seen that the real part of dielectric constant (ϵ') has a value of about 12.8 at 1 KHz and it decreases with increase of frequency attaining a constant value of 12.5. This little variation of ϵ' with frequency indicates the absence of space charge polarization. Space charge polarization is generally active at lower frequencies and high temperatures and indicates the perfection of the crystal under study (Rao and Smakula 1965). This also confirms the finding of the optical absorption studies on these samples. In imaginary part of the dielectric constant (ϵ'') vs frequency curves, we obtain a sharp peak at about 500 KHz. Low values of ϵ'' also indicate that the crystals grown are of reasonably good quality (Rao and Smakula 1966). The loss peak observed corresponds to a relaxation time of about $0.30 \mu\text{s}$. This relaxation may be due

to heavy ions present in the crystals. When real and imaginary parts of impedance are plotted, we observe a semi-circle of radius making an angle of about $\pi/3$ radians with real axis. The value of constant α of Cole-Cole response function has been found to be equal to 0.67. The maximum of the semi-circle occurs at $\omega\tau = 1$ indicating $\tau = 1/\omega = 0.3 \mu\text{s}$. This relaxation time is very close to the value of τ obtained from ϵ'' vs frequency curve. These relaxations may be due to the Co^{+2} ion.

From admittance curves we have real part of admittance (G')

$$G'\alpha\omega^{n-1}.$$

Hence a plot of $\log(G'/\omega)$ vs ω must be a straight line with its slope equal to the value of exponent n . The exponent n of this universal power law gives an indication of the degree of disorder in the system. Our results indicate this value to be equal to 0.22. From Cole-Cole plots we have obtained a value of 0.67 for α . If we compare the exponents of Cole-Cole and power law we get

$$n = 1 - \alpha = 0.33.$$

This value is comparable to 0.22 which is obtained from the conductance curves. These low frequency relaxations may be attributed to the vacancies created in the lattice due to the non-stoichiometry introduced in the crystal because of the presence of dopant divalent cation.

5. Conclusions

The study of dielectric properties of gel grown Cd-Co oxalate crystals show a dielectric relaxation peak. The relaxation time is obtained to be equal to about $0.3 \mu\text{s}$. Cole-Cole plots are semi-circles. The exponent of Cole-Cole functions is 0.67. The conductance curves give the value of n to be 0.22. This value is comparable to that obtained from Cole-Cole plots.

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