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ORIGINAL ARTICLE

FREQUENCY DEPENDENCE OF AC CONDUCTIVITY OF DIVALENT OXALATE CRYSTALOXALATE SINGLE CRYSTALS

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Abstract:

Characterization of the grown cadmium oxalate single crystals is an essential requirement to describe, confront and explain their various properties. Cadmium oxalate trihydrate (CdC2O4·3H2O) single crystals suitable for the present investigation were grown using controlled diffusion process in silica gels. The investigation on electrical parameters of cadmium oxalate has been carried out to understand the mechanism of charge transport. The crystal shows a very prominent sharp peak at 385 K. This confirms to the dehydration temperature. The dielectric constant for (001) planes remain almost temperature independent upto 450K. It is difficult to distinguish the variation with frequency. The temperature 450K corresponds to generation of complete dehydrated sample of cadmium oxalate, in confirmation of thermal analysis

KEY WORDS:

Gel Method, Oxalate Crystal, Dc Conductivity, Activation Energy, Etc

INTRODUCTION

In recent years, owing to a number of practical applications in the field of micro-electronics and opto-electronics a great deal of interest has been shown in the study of the dielectric and conduction behaviour of various materials1-5). From measurements of the dielectric constant and the dielectric loss as a function of frequency and temperature, various polarization mechanisms in solids (such as atomic polarization of lattice, orientational polarization of dipoles, space charge polarization) and the electric field distribution can be understood6,7) . A typical variation in dielectric constant with frequency has been attributed to the defect structure of the nanophase such as AgI8), Ag2HgI49). The investigation on electrical parameters of cadmium oxalate has been studied to understand the mechanism of charge transport at different temperatures and frequencies.

EXPERIMENTAL

The electrical conductivity measurements were carried out in the temperature range 300 to 600K for ten different input frequencies in the range 800 Hz to 1 MHz. The specimens were mounted between two stainless steel electrodes and it was then put into the resistance-heated furnace and the temperature of the sample was monitored using a chromel-alumel thermocouple. The temperature of the furnace was gradually increased by regulating the input power through a dimmerstat (AE; 0-270 V, 9 amp), so as to maintain constant heating rate during the whole experiment. The frequency dependent resistance was determined using a precision type 'Hewlett Packard' 4284 A LCR meter in the range 20 Hz to 1MHz. The values of capacitance and dissipation factor at different temperatures were converted into electrical conductivity (σac). The dielectric constant is calculated using the relation $\varepsilon' = Ct/\varepsilon_0 A$ where C is the measured capacitance of the sample, t is the sample thickness, ε0 is the free space permittivity and A is area of cross section of the sample inserted between the parallel electrodes.

RESULT AND DISCUSSION:

AC CONDUCTIVITY

The ac conductivity measurements have attracted the most attention because they are widely used for understanding the nature of conduction and defects in materials. The most familiar equation proposed to explain this type of conduction is

$$\sigma(\omega) = A\,\omega^{s} \qquad (1)$$

Several models such as Quantum Mechanical Tunneling (QMT) model10,11), Correlated Barrier Hopping (CBH)model12,13) and Overlapping Large Polaron Tunneling (OLPT) model14) have been proposed to interpret the mechanism of ac conduction. The ac conductivity σ is calculated at different temperatures using the equation

$$\sigma = \omega \varepsilon_0 \varepsilon' \tan \delta \qquad (2)$$

where ε_0 is the vacuum dielectric constant.

The plot of $\ln\sigma$ against 1000/T as obtained at different frequencies is shown in Fig.1.The dc conductivity has also been included in the plot for ready reference and comparison. The ac conductivity in Fig.1 show a lesser temperature dependence with increasing frequency, but it is more at higher temperature. The shape of the curves in Fig.1 suggests two different regimes, one with weak temperature dependence and other with relatively stronger temperature dependence. Overall, the ac component of the frequency dependent conductivity $\sigma_{ac}(\omega)$ can be expressed as the sum of the two different conduction mechanisms15)

$$\sigma_{ac}(\omega) = \sigma_f + \sigma_s \qquad (3)$$

where σ_f represents the relatively weak temperature dependent mechanism which is to be interpreted as being due to hopping between localized states at the Fermi level, and σ_s represents the strong temperature dependence component of ac conductivity and is numerically obtained by subtracting σ_f from $\sigma_{ac}(\omega)$ and this mechanism may be interpreted as being due to hopping between localized states near band edges (edges of the valence and/or the conduction band). This conjecture agrees with that obtained before by Rockstad15).
The ac conductivity $\sigma_{ac}(\omega)$ can also be expressed as 15)

$$\sigma_{ac}(\omega) = \sigma_t(\omega) + \sigma_{dc} \qquad (4)$$

where σ_{dc} is the dc part of the total conductivity. The resolution of $\sigma_t(\omega)$ into σ_{dc} and $\sigma_t(\omega)$ mostly arise from different processes in different states, since σ_{dc} is due to extended states and σ_{ac} due to localized states15-18).

The relationship between the ac conductivity and the applied frequency at different constant temperature values are shown in Fig.2. The frequency dependence of ac conductivity, which rises almost linearly (Fig.2), is most likely due to hopping of electrons between two pairs of localized states. The frequency exponent s (refer to equation (1)) is calculated from the slopes of ln σ_{ac} versus ln f graphs. The dependence of the frequency exponent s on temperature as obtained is shown in Fi.g3 .The graphs show increase in 's' upto the water liberating temperature, which matches with the data obtained from DTA – TGA, and then decreases with an increases of temperature through frequency and temperature ranges. The fact that the frequency exponent s is temperature dependent indicates that the bipolaron conduction is a thermally activated process which takes place under the assistance of phonons. In other words, one can conclude that the exponent s is somewhat temperature sensitive and agrees with the Correlated Barrier

Hopping model (CBH)18). The numerical values of s lie in the range 0.5< s < 0.9 and hence are closely associated with the established carrier transport19).

CONCLUSIONS:

The frequency dependence of ac conductivity, which rises almost linearly, is most likely due to hopping of electrons between two pairs of localized states. The frequency exponent s is temperature dependent indicates that the bipolaron conduction is a thermally activated process which takes place under the assistance of phonons. In other words, one can conclude that the exponent s is somewhat temperature sensitive and agrees with the Correlated Barrier Hopping model (CBH)18).

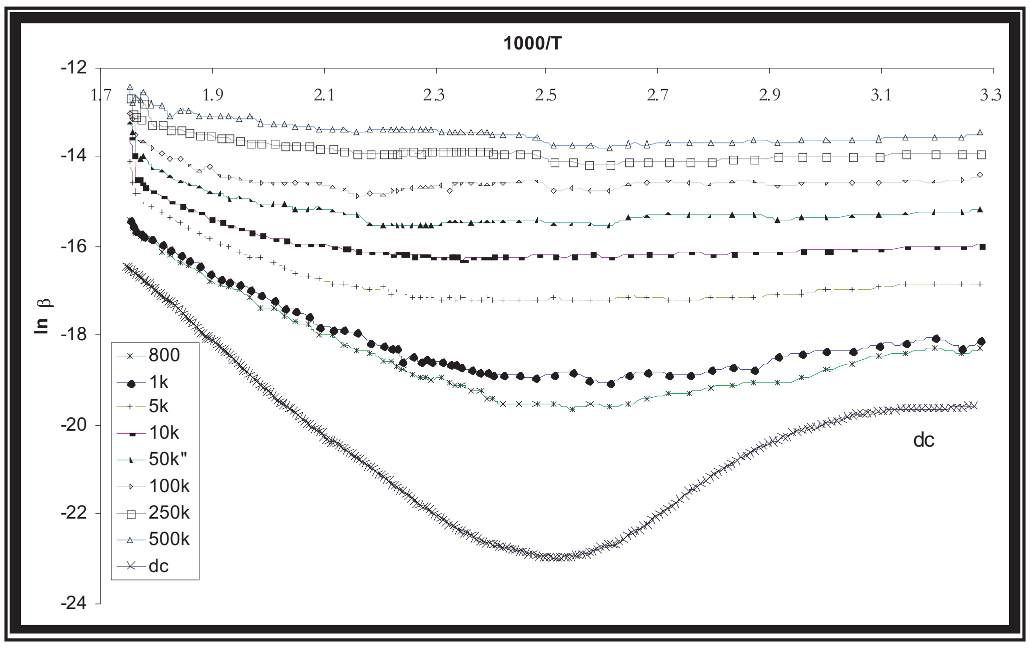

Fig.1 Plot of lnσ versus 1000/T for (001) plane of the crystal.

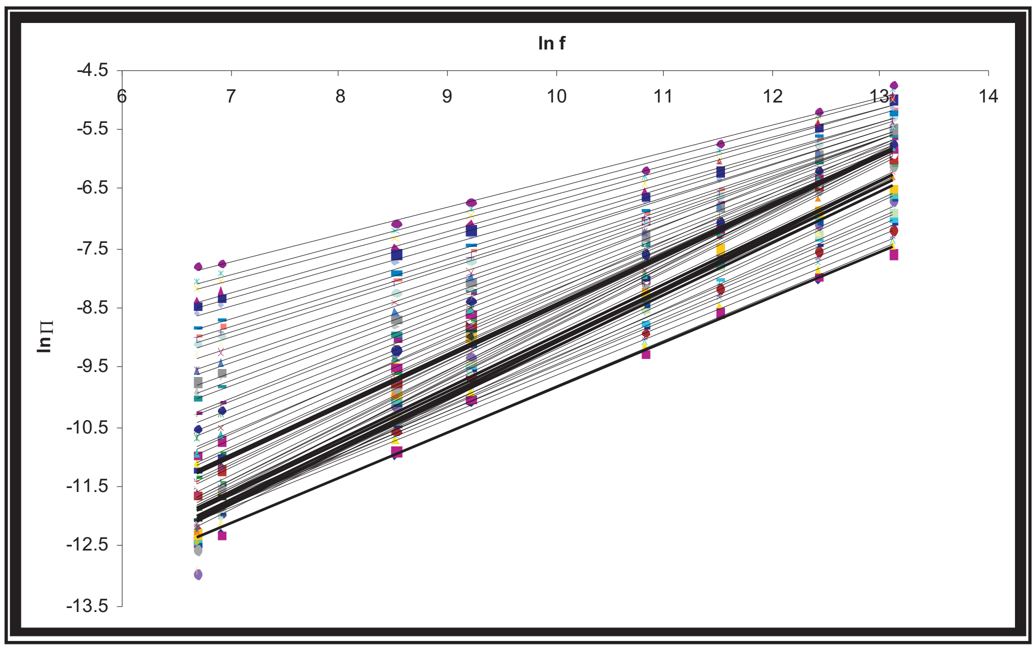

Fig.2 Plot of lnσ versus ln f for (001) plane of the crystal.

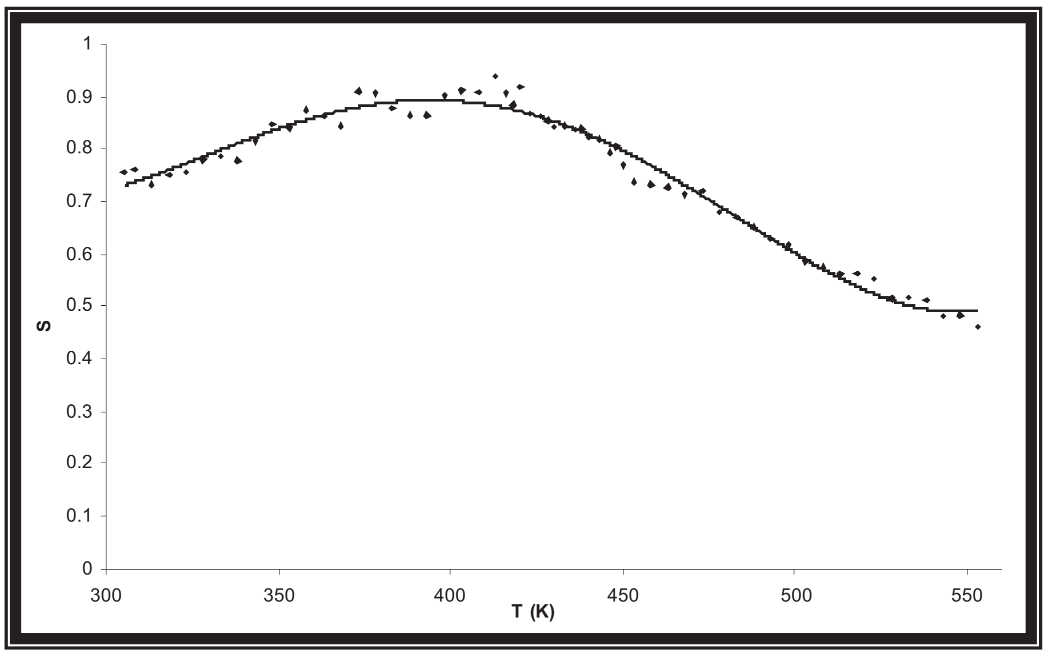

Fig.3 Plot of S versus T for (001) plane of the crystal.

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