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STUDIES ON SOME ELECTRICAL PROPERTIES OF POLYCRYSTALLINE CALCIUM FLUORIDE AT HIGH TEMPERATURES

S Shakeel Ahmad* and S Wajahat Ali Rizvi

PCSIR Laboratories Complex, Off University Road, Karachi - 75280, Pakisktan

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The electrical conductivity σ and the dielectric constant ε′ were measured at a frequency of 1 KHz on pressed pellet of CaF_2 in the temperature range 373-873°K. The pressure applied for preparing the sample varied from 3 to 5 tons/cm^2 on circular disk of 2.5 cm diameter and 0.45 cm thickness by hydraulic press. In the temperature range investigated the conductivity data exhibited to activate regions yielding activation energies of 0.532 ev and 0.42 ev. The region I called intrinsic region and region II is extrinsic region. The effect of temperature and the hydrostatic pressure on the real and imaginary part of the dielectric constant for this sample has been studied. The dielectric constant curve shows a slow increase of dielectric constant up to temperature 473°K and above this temperature, a fast increase in ε′, which may be attributed to lattice expansion and polarizability of constituent ions. At high temperature in the dielectric, two points of phase transition are attained. In the present study, it has been found that within the reported temperature range the dielectric constant and dielectric loss are predominately determined by the motion of the defects. The activation energy deduced from the dielectric studies is in good agreement with that obtained from the present electrical conductivity data.

Key words**:** Ionic conductivity, Dielectric constant, Phase, Activation energy.

Introduction

Currently there is considerable interest in materials with high ionic conductivity, solid electrolytes or fast ionic conductors (Perram 1983, Suresh 1973). The fluorite structure of alkaline earth metal fluorides exhibit super ionic behavior at high temperatures, and they have been attracting particular attention because they have important potential applications as electrolyte in high energy density batteries and other devices. The superionic conductors, because of their remarkable physical properties, are used in electrochemical devices (Vashista *et al* 1979)

Trnorcorn (1998) studied on mixing of isovalent cationic effect in multi components fluorite structured fluorides, the static permittivity and the diffusivity in concentrated solutions of alkaline earth fluorite which are rare earth flouride. With this, the influence of mixing the physical properties of super ionic conductor was also studied. The fast ionic conduction is found in $Ba_{0.7-x}SrLaF$, a single crystal of barium station lanthanum flouride.

There exists an essential characteristic of all super ionic conductors, due to which almost complete crystal disorder of one species of ions raises several important questions. First of all as the number of defects become equal to the number of ions, it becomes important to identify the vacancies and interstitials. There are no regular lattice sites in such conductors. This difficulty can be resolved by treating all the ions as interstitial with more than one available sites.

Thus electrical properties of the alkaline earth fluorides are of considerable interest. One of most basic form of the properties of solids is the static dielectric constant ε′ and the loss factor ε″. The value of dielectric constant plays a key role in the lattice dynamics of ionic crystal (Liang 1973), while considering the effect of electronic interaction on the transport of matter or charges in ionic crystals, a knowledge of dielectric constant is needed. The rate of increase of dielectric constant with temperature change dε′/dT is expected to be faster at high temperature in ionic crystals (Oberschmidt *et al* 1980). So, it was considered worth while to measure the dielectric properties of polycrystalline CaF_2 at high temperatures. From the application point of view it is easier to use well pressed powder in the form of pellets. Also to evaluate the electrical conductivity of well pressed powder as a function of temperature and to determine the transport parameters and compare their results with data those obtained by single crystal. (Oberschmidt *et al* 1980). The dielectric constant and its change with temperature is calculated from the measured sample capacitance C, by applying corrections for changes in sample diamensions. Due to the thermal expansion in an isotropic medium, Samara (1968) has given the following equation for the change in dielectric constant with temperature, at constant pressure:

$$I/\varepsilon_\circ (d\varepsilon/dT)_p = 1/C_\circ (dC/dT)_p - 1/3V_\circ (dV/dT)_p \text{.........} (1)$$

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*Author for correspondence

Where ε_o, C and V_o are the values for dielectric constant, capacitance and volume at atmospheric pressure. At sufficiently high temperature, the loss factor is dominated by the conductivity of the sample which is given by equation (2):

$$\tan\delta = \varepsilon''/\varepsilon' = 4\pi\sigma/\varepsilon'' \quad \text{(2)}$$

Where ε'' is the imaginary part of the dielectric constant and ε' is the real part and σ is the conductivity of the sample and ω is the measuring frequency. The conductivity can also be written by equation (3):

$$\sigma = \sigma_o \exp(-E/2KT) \quad \text{(3)}$$

From this equation we can calculate the activation energy E at a particular temperature and σ is the DC conductivity and σ_o is a constant. Here we intend to study the ionic or electrical conductivity and the dielectric properties of pure and dispersed alkaline earth fluoride structured compound, CaF_2 at high temperature starting from 373°K, with a view to determine precisely the transport parameters and studying the defect mechanism for the flow of charge at these temperatures.

Dielectric constant is an important property in relation to the ionic conduction because the larger the value of dielectric constant of an ionic crystal, the lower energy formation for the lattice defect (Choudhry and Bichile 1986).

Experimental

Sources and preparation of sample. The powder sample of CaF_2 used in this work was obtained from M/s Koch Light Laboratories, France with specific purity of 99.99%. To obtain uniform particle size, the material were mortared in fine particles powder with a mesh size of 150 micron. The powder thus obtained were pressed and made in the form of pellet in a specially designed stainless steel die with plunger pressing with a hydraulic press which can read the pressure in Kbar or ton. For preparing such sample a pressure of 4 to 5 tons/cm^2 were applied. The density of pressed powder were obtained after pressing at different pressure. The typical diamension were 0.47 to 0.55cm thick. For measuring its electrical conductivity and the dielectric constant, the conducting electrodes were pasted on indium oxide paint and with a thin layer of graphite on them. Such electrodes were also used by Schoonman *et al* (1977). They obtained reproducible results on each thermal cycling.

Conductivity measurements. Following the ASTM standard 1983, the conductivity data were collected for the sample, kept in the holder has been designed and fabricated for this purpose. The AC conductivity or conductance G, were measured by Ogawa Seiki OSK 555 impedance bridge. It is a high resolution easy balancing bridge with three decades reading. It has built in variable frequency oscillator, IKHz tunable detector. It can give σ conductivity from 0.001μs - 120 S. Frequency dependent conductivity from 120Hz to 10KHz as well as the effect of applied voltage from 50mv to 1.5v A.C (Peak to Peak). The suitable frequency for measurement was 1KHz except at high temperature above 373°K where low frequency were selected. The measured resistance was independent of applied voltage.

Recording the temperature. A separate digital control unit was attached for recording the temperature. The internally heated system was driven by a thermocouple (Chromel-alumel thermocouple). The temperature can be controlled within an accuracy of ± 1%. This unit allowed the data to be taken at preset time interval as the sample was heated or cooled. The effect of heating rate was checked to see that the sample has sufficient time to equilibrate at rate of 10K/min sample was heated or cooled. The nominal heating rate was kept at 9K/min. During the cooling cycle, the a.c. conductivity was measured with an accuracy of ± 2%. This experiment was repeated three times for each sample at same temperature. Standard deviation for the three readings was taken to avoid the possible errors. Data obtained after several thermal cycling were found concordant and reproducible. The conductivity measurements were recorded during the cooling cycle. At high temperature > 700°K, it was observed that the sample was contaminated with oxygen of the atmosphere.

Measurement of dielectric parameters ε' and ε'' with temperatures. Capacitance and the dielectric loss measurements were made at a frequency of 1KHz employing transformer arm bridge OSK 555 impedance bridge which is equipped with three terminal cell (with connecting wires). Since the cell contains three terminal electrodes, the data were taken free from errors due to edges and the surface effects. The capacitance of the parallel plate is measured by depositing indium paint as electrodes on opposite sides on the specimen. The relative change in capacitance of the sample with temperature is equal to the relative change in permitivity, after applying the necessary edge corrections for the change in geometery of the sample. This instrument has a measuring accuracy of + 0.2 %. Shielded leads and specially designed sample holder is taken for the final results. The value of dielectric constant at room temperature were determined using standard geometrical technique in which the sample capacitance is calculated from the following formula:

$$C = \varepsilon' \varepsilon_o A / d \quad \text{(4)}$$

Where A is area of crossection, d is the thickness and ε_o is permitivity of free space.

From Equation (4) the dielectric constant ε' and its change with temperature is calculated from the measured sample capacitance C.

Table 1
Density of the sample at different applied pressure

S.No.	Hydrostatic pressure	Measured density gm/cm^3
1.	3.31 tons/inch^2	3.77
2.	3.85 tons/inch^2	3.88
3.	3.85 tons/inch^2	3.95
4.	4.4 tons/inch^2	3.91
5.	5.0 tons/inch^2	3.93
6.	5.4 tons/inch^2	3.93

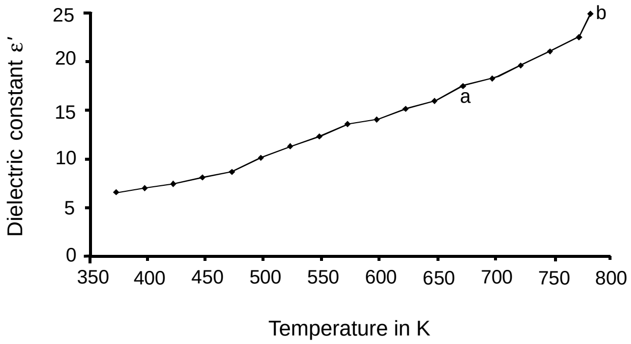

Fig 1. Variation of dielectric constant ε′ with temperature of pressed pellet of CaF_2.

Calculation of activation energy. From the equation given by Samara (1968), the activation energy can be determined from the slopes of the curve of Fig 3, at region I and II. It has also been calculated from equation (2) and (3) that the activation energy (E) is 0.532eV for region I and 0.423eV for region II, which is in accordance with the earlier studies. (Bone and Schoonman 1977). The CaF_2 compound has the following constants in the purest form at S.T.P:

CaF_2 Data

Mol. weight. 78.08, Refractive index =1.434,, . Density=3.18gm/cm^3, Melting point=1360°C, Boiling point 2500°C, Crystallographic phase = Cubic.

Results and Discussions

As shown in Fig 1, the dielectric constant of a CaF_2 pellet is 6.5 at 373°K, and at an elevated temperature of 773°K, it becomes 24.1. At temperature of 675°K and 773°K, the points a and b are the phase transition points from cubic to some other phase equilibrium. From 373°K to a temperature of 473°K, the dielectric constant is slowly increasing. At point b at a temperature of 800°K the dielectric constant is increasing to a value of 25. 1 there is dε′ /dT. Table 1 gives the values of density of the pressed sample after applying different hydrostatic pressures.

It is observed that the density of pressed CaF_2 is not changing after increasing the applied pressure of more than 5 tons/inch^2.

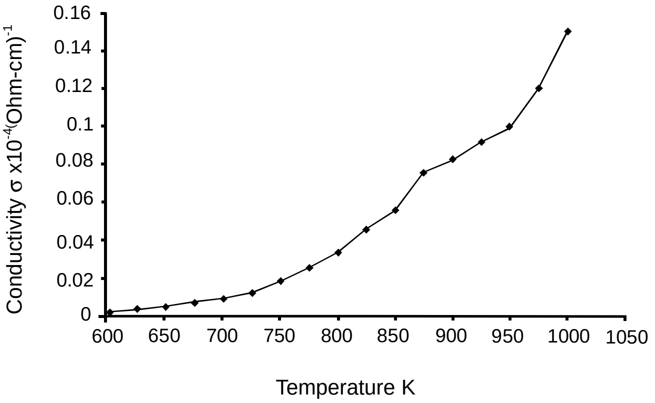

Fig 2. Variation of conductivity as a function of temperature.

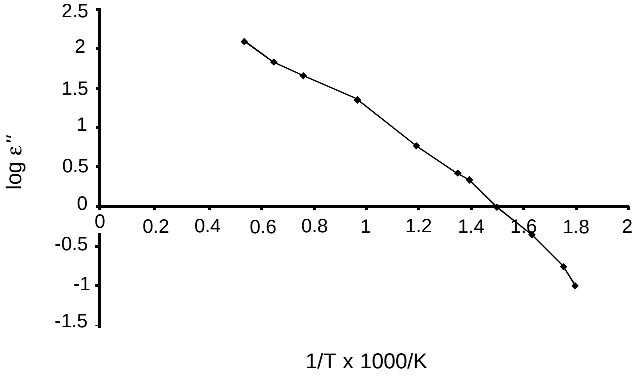

Fig 3. Plot of imaginary part of dielectric constant against inverse of temperature 1/T for CaF_2 (Pellet).

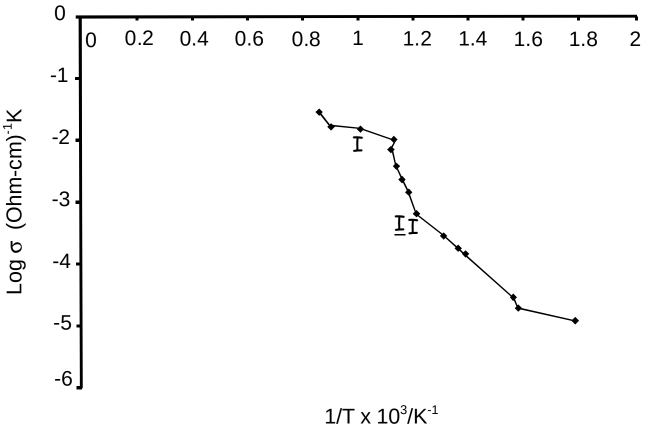

Fig 4. Curve between log σ vs 1/T for CaF_2 pellet 1/Tx 10^3/K^{-1}.

As shown in Fig 2, the ionic conductivity increases with temperature up to a temperature of 850°K, a sharp increase in the conductivity from 0.077x10^{-4}/Ohm/cm to 0.975x10^{-4}/Ohm/cm.

As shown in the curve of Fig 4, the graph between log σ and inverse of temperature 1/T exhibits two activated regions of

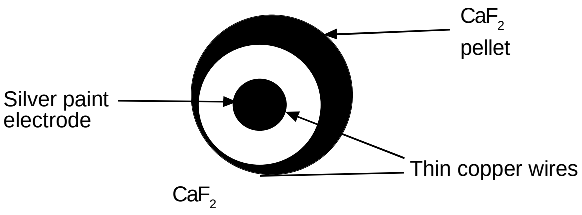

Fig 5. CaF_2 pressed pellet with silver electrodes used for the measurement of dielectric constant.

conductivity denoted by I and II. The data was fitted to a function by the analysis of method of least square. According to equation (3), the data is showing a transition from 830°K stage I to stage II. It is giving activation energy 0.532eV to 0.42eV respectively. This is the approximate method to calculate the energy required to create + ve ions vacancy or defect formation in ionic crystals.

Fig 3 illustrates log ε'' vs 1/T, for this material. It is seen that the temperature dependence loss as expected from equation 2 and 3. This graph shows a linear behavior, and by least square method of curve fitting, the data has been fitted to calculate the slope which is called the activation energy for the two regions in the curve. The density, dielectric constant and electrical conductivity were found to be depended on applied pressure. For pressure > 5tons /cm^2, the density and the related measured parameters do not remain constant and reproducible.

Conclusion

As we have seen the effect of applied pressure on the sample pellet of CaF_2 and its measured values of density, electrical conductivity and the static dielectric constant ε' these values are not different from the earlier studies (Perram 1983).

Fig 1 shows the variation of dielectric constant ε' with temperature of such CaF_2 pellet. It has been noticed that up to a temperature of 550°K, the dielectric constant ε' increases slowly as expected from the ionic solids (Smyth 1955).

However, this increase becomes very much fast above 559°K. This fast increase in ε' is due to lattice expansion, polarizability of the constituents ions. In addition to the polarization, another possible contribution to the static dielectric properties of a substance are the dipoles which are produced by the impurities and lattice defects. There are some factors which contribute to the temperature dependence of dielectric constant of a cubic crystal. For such a material, the temperature dependence of the dielectric constant at constant pressure is separated into volume dependent and volume independent contribution (Oberschmidt and Lazarus 1980). For such a material, the microscopic Clausius Mossotti Formula holds, depending upon the polarizability of the ions.

$$\varepsilon' - 1 / \varepsilon' + 2 = 4 / 3\pi\alpha_m / V \ldots\ldots\ldots\ldots (5)$$

Where α_m is the polarizability of microscopic, small sphere of volume C in vacuum (Bosman and Havings 1965). The following reasons are offered for the increase of ε at high temperatures.

i.) When the temperature rises, the number of polarizable particles per unit volume decreases as a result of volume expansion (Bosman and Havings 1965).

ii) Similarly as the temperature increases, the polarizability of a constant number of particles rises within an increase of available volume.

Ionic conductivity. As shown in Fig 2 which is in between ionic conductivity and temperature, the ionic conductivity is divided into two regions I and II that are analogous to the alkali halides. Region I identifies as extrinsic conduction region from 373°K to 573°K. Because the conduction occurs via extrinsic vacancies. The conductivity rises after heating the sample to high temperature and contaminate with the oxygen. The divalent oxygen ion replaces the monovalent fluorine atom and thus leaves one vacant anion site. Region II is identified as intrinsic region t in the range, 573-873°K and the doping experiment (Lian and Joshi 1975) shows that at this temperature the vacancies are more mobile than interstitials in CaF_2.

Frankel anion defects. As it is obvious from Fig 4, the transition from region I to region II results from a change of conduction from F ion by interstitial motion to ion vacancy motion (Kennedy *et al* 1973). The observed activation energy from stage I is 0.532eV in this stage and this energy is too small to be consistent with the formation and motion of defect with Frankel anion defect in the flourite structure. It has been explained by Schoonman *et al* (1973), that the formation energy for the Frankel defects required in CaF_2 is 2.2eV to 2.8eV.

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