

# Dielectric Behavior Of $\beta$ – Lead Fluoride

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**Abstract--** A detailed study of effect of temperature and frequency on dielectric constant ( $\epsilon$ ) and loss ( $\tan \delta$ ) of  $\beta$ -PbF<sub>2</sub> was performed. The measurements were taken from the frequency range of 10<sup>2</sup>Hz to 5x10<sup>7</sup>Hz and in the temperature range of -180<sup>0</sup>C to 240<sup>0</sup>C. The value of static dielectric constant at room temperature is 28.00. The value of ac conductivity is calculated from the relation,  $\sigma = \epsilon \omega \tan \delta$  where  $\epsilon_0$  is the permittivity of the free space and  $\omega$  is the angular frequency. The activation energy for conduction in the intrinsic region of the plot  $\sigma$  versus reciprocal of temperature is calculated to be 0.92 eV.

**Keywords-** Dielectric constant, dielectric loss, electrical conductivity, activation energy.

## 1. INTRODUCTION

Lead fluoride can found either is cubic structure with four molecules per unit cell ( $\beta$ -PbF<sub>2</sub>) or in orthorhombic phase ( $\alpha$ -PbF<sub>2</sub>) at high temperatures [1]. Cubic phase becomes a 'super ionic conductor' at high temperatures. The conductivity of  $\beta$ -PbF<sub>2</sub> is one of the highest values for any known solid ionic conductors [2]. As it exhibits a variety of interesting physical properties like radiation resistance [3], high ionic conductivity at a relatively low temperature, associated specific heat anomaly, behaving as an extrinsic semiconductor [4] attracted considerable recent attention.

Denham et al [5] has derived the dielectric properties of lead fluoride from experimental studies on infra-red and Raman spectra. Direct measurement of dielectric properties has been reported by Axe et al [6]. Samara [7] studied the effect of temperature and pressure on dielectric properties of cubic and orthorhombic modifications of lead fluoride over the range of 4K to 350K. Complex admittance study on  $\beta$ -PbF<sub>2</sub> was done by Bonn and Schoonman [8].

Schoonman et al [9] reported the ionic and electronic conductivity in very limited temperature region (325K- 410K). The measurement of dielectric constant ( $\epsilon$ ) and loss ( $\tan \delta$ ) of  $\beta$ -PbF<sub>2</sub> in a wide range of frequency and at higher temperatures is not reported so far.

In the present investigation, dielectric properties of  $\beta$ -PbF<sub>2</sub> have been measured in the temperature range of -180<sup>0</sup>C to 240<sup>0</sup>C and in the frequency range of 10<sup>2</sup>Hz to 5x10<sup>7</sup>Hz.

## 2. EXPERIMENTAL

A pure colorless single crystal of  $\beta$ -PbF<sub>2</sub>, supplied by M/S Optovac Inc., was used for the present investigation. A plate of 5mm diameter and 2mm thick was cut from the crystal with a diamond cutter. Silver paint was applied on either side of the sample, after grinding and polishing with carborundum powder and emery paper, to ensure good contact and to remove air gaps between the sample and electrodes. The sample was dried before taking the measurements.

Measurements of dielectric constant ( $\epsilon$ ) and loss ( $\tan \delta$ ) were made with GR 716C capacitance bridge in the frequency range 10<sup>2</sup>Hz to 5x10<sup>5</sup>Hz and with Marconi circuit Magnification Meter TF 329G in conjunction with laboratory built sample holder in the range of the frequency 10<sup>5</sup>Hz to 10<sup>7</sup>Hz. Temperature measurements were carried out in the range of -180<sup>0</sup>C to 240<sup>0</sup>C. The following procedure was used for the low temperature measurements:

The sample holder with sample was inserted in to liquid nitrogen bath and allowed to remain until a steady temperature was reached, which was checked by constant reading of the millivolt meter. For taking

measurements at different temperatures the sample holder was slowly lifted out of the bath allowing the temperature to rise steadily. Readings were recorded at intervals of 10K.

The temperature measurement was accurate to  $\pm 1^{\circ}\text{C}$ . ( $\epsilon$ ) and ( $\tan \delta$ ) are measured with accuracies of 3% and 5% respectively.

### 3. RESULTS AND DISCUSSION

The variation of dielectric constant ( $\epsilon$ ) with frequency for  $\beta$ -PbF<sub>2</sub> is shown in Fig.1.

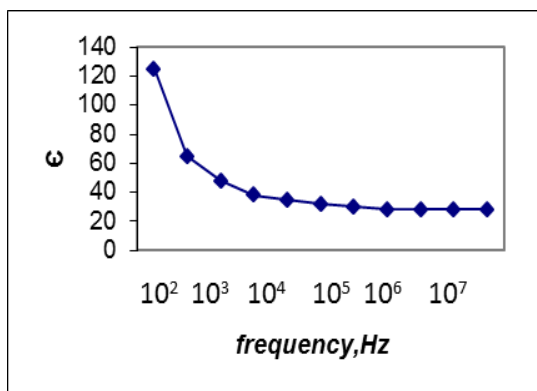


Fig.1.Variation of dielectric constant with frequency

The value of  $\epsilon$  is at  $10^2$  Hz is 125. A fast decrease in the dielectric constant is observed up to a frequency of  $10^5$  Hz beyond which it is constant. The frequency independent value is 28.00 and is taken as static dielectric constant. The value of static dielectric constant of the present work and the earlier reported values are shown in Table 1.

The value of dielectric constant of  $\beta$ -lead fluoride is nearly four times the value for other fluorite structures. For alkaline earth fluorides [10-12] and EuF<sub>2</sub> [13], the values of dielectric constant range from 6.00 to 8.00. The high value in  $\beta$ -PbF<sub>2</sub> is attributed by samara [7] as being due to several causes like i) a large value of electronic enhancement factor,  $[(\epsilon_0 + 2)/3]^2$  where  $\epsilon_0$  is the optical dielectric constant, ii) abnormally small value of resonance frequency and iii) large value of polarizability of lead.

Table.1.Values of  $\epsilon$  and  $\tan \delta$  of  $\beta$ -PbF<sub>2</sub> at room temperature and at a frequency of  $10^6$ .Hz

$\epsilon$	$\tan \delta$	source
29.30	-	Samara [7]
27.40(cal.)	-	Axe et al [6]
26.30	-	Axe et al [6]
28.00	$10^{-3}$	present work

The variation of dielectric loss ( $\tan \delta$ ) with frequency at room temperature is measured for the first time and is shown in Fig.2.

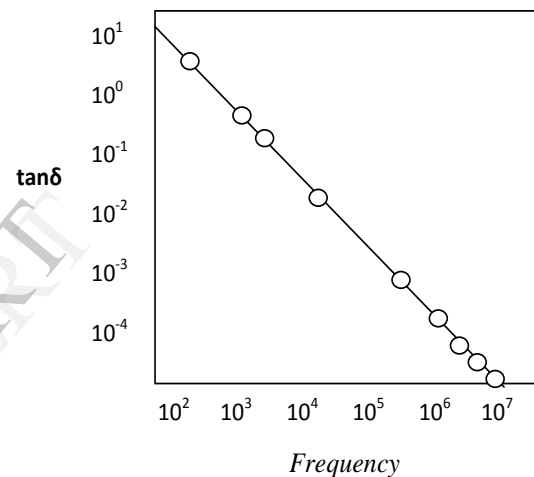


Fig.2.variation of  $\tan \delta$  with frequency

The value of  $\tan \delta$  is very high at  $10^2$  Hz and decreases to a value of  $10^{-4}$  at  $10^7$  Hz.

The dielectric constant at low frequencies depends on electronic, ionic, dipolar orientation and space charge polarization. Contributions due to electronic and ionic polarization are frequency- independent where are dipolar orientation and space-charge contributions are frequency dependent. Fig.1 & 2 shows that  $\epsilon$  and  $\tan \delta$  are frequency dependent in the low frequency region. This behavior can be attributed to the presence of space charge polarization due to unknown impurities and other imperfections, which would be negligible at higher frequencies [14]. The low loss value of  $\tan \delta$  of the order of  $10^{-4}$  indicated high grade purity of the sample used for the present investigation.

The variation of  $\epsilon$  with temperature from 30°C to 240°C at various frequencies is shown Figure 3.

The dielectric constant slowly increases from 30°C to certain temperature and the variation above that temperature is rapid. This behavior is similar to the

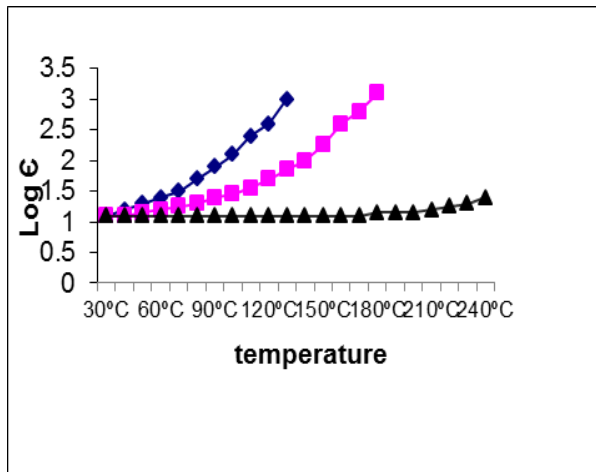


Fig.3. variation of  $\epsilon$  with temperature

variation of other crystals of fluorite structure [15, 13]. The temperature variation of the dielectric constant is frequency dependent. The value of dielectric constant is high at low frequencies for the same temperature. At  $10^6$  Hz, the increase in dielectric constant is linear from 30°C to 140°C and above 140°C the rise in  $\epsilon$  is rapid. The dependence of the high temperature dielectric constant on frequency may be attributed to the creation and destruction of the dipoles at such temperatures [10].

The variation of  $\epsilon$  with temperature from -180°C to 30°C is shown in Figure 4.

There is a departure from the usual trend in the low temperature region. A slow decrease of dielectric constant was observed from -180°C to room temperature.  $\beta$ -Lead fluoride behaves as an extrinsic semiconductor [16] in the low temperature region; predominantly it contains n-type electronic conductivity. The electronic conductivity behavior of  $\beta$ -lead fluoride would show a gradual change from n-type to p-type conductivity; whereas the magnitude of the electronic component of the electrical conductivity would decrease with increasing temperature [17], may be attributed for this behavior of  $\epsilon$  in the low temperatures.

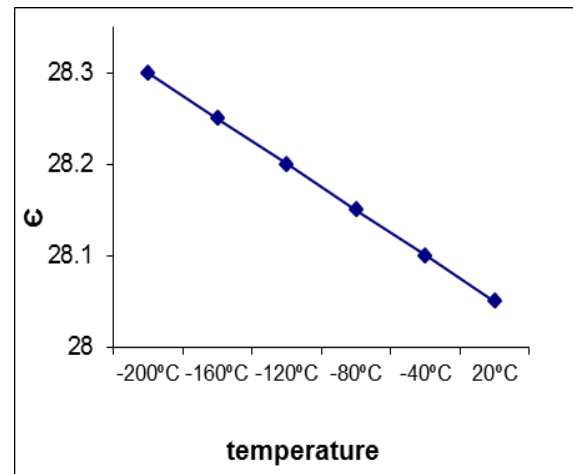


Fig.4. variation of  $\epsilon$  with temperature from -180°C to 30°C

An attempt was made to fit the experimental values of the static dielectric constant with temperature at a frequency of  $10^6$  Hz to an empirical equation. Several forms of equations were tried but it was found that no single equation can represent the data over the entire region of temperature satisfactorily. However the data in different temperature ranges could be represented by the following equations:

$$i) \quad \epsilon = 28.08 - 1.05 \times 10^{-3} t \quad \dots (1)$$

in the temperature region -180°C to 30°C

$$ii) \quad \epsilon = 26.93 + 3.16 \times 10^{-2} t \quad \dots (2)$$

in the temperature region -180°C to 30°C.

$$iii) \quad \epsilon = 66.22 - 54.41 \times 10^{-2} t + 2.139 \times 10^{-3} t^2 \quad \dots (3)$$

In the temperature region 147°C to 240°C

In all the above equations  $t$  is the temperature in °C.

The variation of  $\tan \delta$  with temperature at different frequencies is shown in the Figure.5.

The values of  $\tan \delta$  are higher at low frequencies and high temperatures. This behavior is due to defects arising out of thermally generated charge carriers.

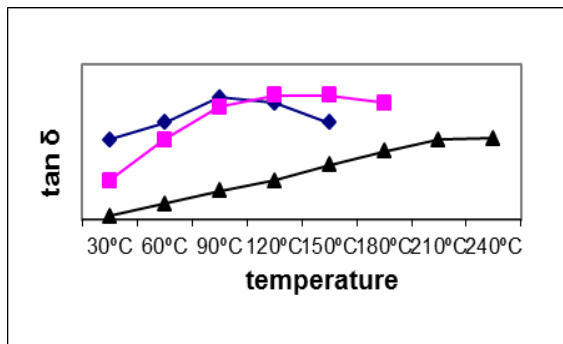


Fig.5. variation of  $\tan \delta$  with temperature at various frequencies

At  $10^4$  Hz,  $\tan \delta$  increases with temperature up to  $95^\circ\text{C}$  and then decreases slightly, showing a Debye-type relaxation peak at  $95^\circ\text{C}$ . Similar peaks are observed at  $120^\circ\text{C}$  and  $220^\circ\text{C}$  for frequencies  $10^5$  Hz and  $10^6$  Hz respectively. The peaks shift towards higher temperature for higher frequencies. Such peaks have been observed by Agrawal [18] in the same range of temperature and frequencies in the case of  $\text{CaF}_2$  when doped with either Mn or Na as impurity. Presence of such impurities which is not uncommon might be responsible for the occurrence of relaxation peaks. In the present work the peaks may be due to dipoles formed by unidentified impurities.

The activation energy for the rotation of the dipoles in the crystal have been calculated using the following relation

$$f = f_0 e^{-E/KT} \quad \dots (4)$$

where  $f$  is the frequency of the relaxation peak at a temperature  $T$ .  $f_0$  is constant,  $K$  is the Boltzmann constant and  $E$  is the activation energy. The input data for the calculation of activation energy for the rotation of the dipoles is given in table 2.

Table.2: Temperature at which the relaxation peaks are observed for  $\beta$ -Lead fluoride.

S.No	Frequency	temperature
1.	$10^4$ Hz	$95^\circ\text{C}$
2.	$10^5$ Hz	$120^\circ\text{C}$
3.	$10^6$ Hz	$220^\circ\text{C}$

The calculated value of activation energy for the rotation of dipoles is 0.06eV.

The experimental data on variation of  $\epsilon$  and  $\tan \delta$  with temperature have been used to obtain the values of dielectric conductivity  $\sigma$  by the equation

$$\sigma = \epsilon \epsilon_0 \omega \tan \delta \quad \dots (5)$$

where  $\epsilon_0$  is the vacuum dielectric constant and  $\omega$  is the angular frequency. The plot of  $\sigma$  against reciprocal temperature at various frequencies is shown in figure 6.

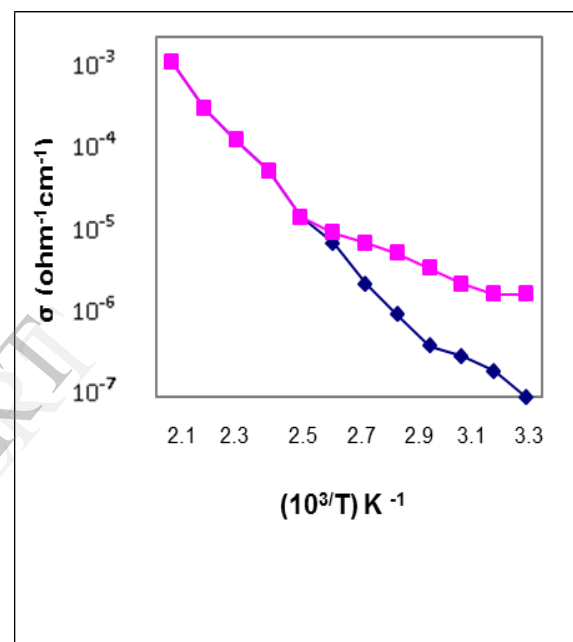


Fig.6. Plot of  $\log \sigma$  against  $(10^3/T) \text{K}^{-1}$

At higher temperature the variation is linear and frequency independent. The variation of conductivity  $\sigma$  with temperature is given by the equation

$$\sigma = A e^{-E/KT} \quad \dots (6)$$

where  $E$  is the activation energy. The activation energy has two different values  $E_e$  and  $E_i$  at moderate temperatures (extrinsic region) and at high temperatures (intrinsic region), respectively. These values can be calculated from the slope of the curves at their respective regions.

$$\text{Further } E_e = W_m \quad \dots (7)$$

$$\text{And } E_i = W_m + W_f/2 \quad \dots (8)$$

where  $W_m$  and  $W_f$  are the energy of mobility of defects and formation energy of defects, respectively. The calculated values of energies are listed in Table.3.

Table 3: Values of  $W_m$ ,  $E_i$ , and  $W_f$  of  $\beta$ -Lead fluoride

Crystal	$W_m$ (eV)	$E_i$ (eV)	$W_f$ (eV)
$\beta$ -PbF <sub>2</sub>	0.32	0.78	0.92

It is not possible, in this temperature region, to understand the nature of the charge carriers responsible for conduction from the present measurements.

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