Dielectric properties of $\text{Bi}_4(\text{GeO}_4)_3$ and $\text{Bi}_4(\text{SiO}_4)_3$

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Abstract. Dielectric constant, dielectric loss and conductivity of $\text{Bi}_4(\text{GeO}_4)_3$ and $\text{Bi}_4(\text{SiO}_4)_3$ single crystals have been measured as a function of frequency and in the temperature range from liquid nitrogen temperature to 400° C. The values of the static dielectric constant at room temperature are 16·4 and 13·7 for $\text{Bi}_4(\text{GeO}_4)_3$ and $\text{Bi}_4(\text{SiO}_4)_3$ respectively. The plots of $\log(\sigma)$ against reciprocal temperature at different frequencies of these crystals merge into a straight line beyond 250° C and the activation energies calculated in this region are found to be 0·95 eV and 1·2 eV for $\text{Bi}_4(\text{GeO}_4)_3$ and $\text{Bi}_4(\text{SiO}_4)_3$ respectively.

Keywords. Dielectric constant ; dielectric loss ; dielectric conductivity ; activation energy.

1. Introduction

Eulytite-type compounds $\text{Bi}_4(\text{GeO}_4)_3$ and $\text{Bi}_4(\text{SiO}_4)_3$ belong to the cubic space group 143 *d* with four molecules per unit cell (Wyckoff 1968). Kuzminov *et al* (1969) measured the lattice parameters, electrical conductivity, infrared transmission, micro-hardness, electrooptical properties and dielectric permittivity of $\text{Bi}_4(\text{GeO}_4)_3$. Schweppe (1969) has reported the measurements of electrooptical properties of $\text{Bi}_4(\text{GeO}_4)_3$ at 20° C. Crystal growth and measurement of various crystal properties along with dielectric constant measurement on $\text{Bi}_4(\text{SiO}_4)_3$ have been reported by Rehwald and Widmer (1973). Recently, Gopalakrishnan *et al* (1976) concluded from a study of nuclear quadrupole resonance that the bonding in these crystals cannot be purely ionic.

In view of the limited data available on the dielectric properties of these compounds it was considered worthwhile to carry out a systematic study of the dielectric constant (ϵ) and dielectric loss ($\tan \delta$) over a wide range of frequency and temperature.

2. Experimental

Single crystals of $\text{Bi}_4(\text{GeO}_4)_3$ and $\text{Bi}_4(\text{SiO}_4)_3$ were received as a gift from RCA Laboratories, Zurich. Samples of $\text{Bi}_4(\text{GeO}_4)_3$ and $\text{Bi}_4(\text{SiO}_4)_3$ with dimensions $1.5 \times 1.5 \times 0.4 \text{ cm}^3$ were cut with a diamond cutter. They were ground carefully with corborundum powder and polished with emery polishing paper. Silver paint was applied on either side of the samples to ensure good contact and to remove

air gaps between the sample and electrodes. The samples were dried before making measurements.

Dielectric measurements were made with a GR 716C capacitance bridge in the frequency range 10^2 – 10^5 Hz and temperature range -180°C to 400°C . In the high frequency range 10^5 – 10^7 Hz a Marconi circuit magnification meter TF 329 G was used in conjunction with laboratory-built sample holders. The accuracy in temperature measurement is about 4°C throughout the range. ϵ is measured to an accuracy of 3% and $\tan \delta$ to an accuracy of 5%.

3. Results and discussion

Plots of ϵ versus frequency (ω) for $\text{Bi}_4(\text{GeO}_4)_3$ and $\text{Bi}_4(\text{SiO}_4)_3$ are shown in figure 1. For $\text{Bi}_4(\text{GeO}_4)_3$ the value of ϵ at 10^2 Hz is 22.2 and it decreases continuously upto a value of 16.4 at 10^5 Hz, and beyond this frequency ϵ is frequency-independent. In $\text{Bi}_4(\text{SiO}_4)_3$, ϵ is frequency-independent throughout the range covered in the investigation. The frequency-independent ϵ values are 16.4 and 13.7 for $\text{Bi}_4(\text{GeO}_4)_3$ and $\text{Bi}_4(\text{SiO}_4)_3$ respectively. The value of the static ϵ at room temperatures for $\text{Bi}_4(\text{GeO}_4)_3$ agrees with the value of 16.0 reported by Schweppe (1969). In $\text{Bi}_4(\text{SiO}_4)_3$, the value obtained in this work is lower than the value of 16.2 obtained by Rehwald and Widmer (1973). Variation of $\tan \delta$ with frequency is also shown in figure 1. It can be seen that $\tan \delta$ decreases with frequency for both the samples and the value of $\tan \delta$ at 10^7 Hz is of the order of 10^{-4} .

Figure 1. Variation of ϵ and $\tan \delta$ with frequency for $\text{Bi}_4(\text{GeO}_4)_3$ (●) and $\text{Bi}_4(\text{SiO}_4)_3$ (○).

The variation of ϵ and $\tan \delta$ with temperature at different frequencies for $\text{Bi}_4(\text{GeO}_4)_3$ and $\text{Bi}_4(\text{SiO}_4)_3$ are shown in figures 2 and 3 respectively. Although the measurements were made in temperature range of -180°C to 400°C , the data below room temperature is not shown in the figures since no appreciable variation was observed below room temperature. The increase of ϵ with temperature takes place in two stages : (i) ϵ rises slowly upto 180°C for all frequencies (ii) a fast frequency dependent increase is observed beyond 180°C .

The behaviour of $\tan \delta$ with temperature is similar to the behaviour of ϵ with temperature. $\tan \delta$ values increase with increasing temperature and higher values are observed for lower frequencies. Relaxation peaks are observed at 250°C , 300°C and 360°C for the frequencies at 10^3 Hz , 10^4 Hz and 10^5 Hz respectively for $\text{Bi}_4(\text{GeO}_4)_3$. Similar peaks appear for $\text{Bi}_4(\text{SiO}_4)_3$ at 270°C and 340°C for frequencies 10^3 Hz and 10^4 Hz respectively. The peaks are shifted to higher temperature region on increasing the frequency.

The equation $\sigma = \epsilon_0 \epsilon \omega \tan \delta$ (where ϵ_0 is the vacuum dielectric constant) gives the dielectric conductivity (σ) of a crystal. Using this relation, σ values have been calculated at different temperatures and frequencies. The plots of $\log \sigma$ versus $1/T$ are shown in figure 4 (A and B). The calculated values of activation energies in the range of temperature 250°C to 400°C for $\text{Bi}_4(\text{GeO}_4)_3$ and $\text{Bi}_4(\text{SiO}_4)_3$ are 0.95 eV and 1.2 eV respectively.

Figure 2. Variation of ϵ and $\tan \delta$ with temperature for $\text{Bi}_4(\text{GeO}_4)_3$ at different frequencies. $\circ$ — 10^3 Hz ; $\bullet$ — 10^4 Hz ; $\triangle$ — 10^5 Hz ; $\blacktriangle$ — 10^6 Hz .

Figure 3. Variation of ϵ and $\tan \delta$ with temperature for $\text{Bi}_4(\text{SiO}_4)_3$ at different frequencies. $\circ$ — 10^3 Hz; $\bullet$ — 10^4 Hz; $\triangle$ — 10^5 Hz; $\blacktriangle$ — 10^6 Hz.

Figure 4. Dielectric conductivity σ (ohm-cm^{-1}) against $(1/T)$ for $\text{Bi}_4(\text{GeO}_4)_3$ and $\text{Bi}_4(\text{SiO}_4)_3$ at different frequencies. $\circ$ — 10^3 Hz; $\square$ — 10^4 Hz; $\bullet$ — 10^5 Hz; $\triangle$ — 10^6 Hz.

The dielectric constant at low frequencies depends on electronic, ionic, dipole orientation and space charge polarisation. Contributions due to electronic and

ionic polarisation are frequency-independent whereas dipole orientation and space charge contributions are frequency-dependent. Figure 1 shows that ϵ is frequency-independent for $\text{Bi}_4(\text{SiO}_4)_3$ throughout the frequency range covered in this investigation. This behaviour indicates that only electronic and atomic contributions for polarisation are present (Rao and Snakula 1966). In $\text{Bi}_4(\text{GeO}_4)_3$ the increase in ϵ with increasing frequency can be attributed to the presence of space charge polarisation. The frequency-independent nature of ϵ for $\text{Bi}_4(\text{SiO}_4)_3$ indicates that the sample is of high purity. Choudhury and Rao (1969) while studying some oxides indicated that the dielectric loss of the order of 10^{-2} indicates low concentration of defects. The loss of about 10^{-4} for $\text{Bi}_4(\text{GeO}_4)_3$ and $\text{Bi}_4(\text{SiO}_4)_3$ at higher frequencies indicates that the crystals have very low concentration of defects. The presence of these defects show up in the measurement of ϵ and $\tan \delta$ at elevated temperatures.

Slow increase of ϵ upto certain temperature is characteristic of ionic solids (Smith 1955). ϵ increases slowly upto 180°C for both the samples and beyond 180°C the rise is rapid. The region where ϵ rises slowly with temperature is attributed to the increase of ionic polarisation with temperature and the rapid increase of ϵ with temperature is due to space charge polarisation of thermally generated charge carriers.

The dipolar relaxation peaks observed for both the samples in the curves showing the variation of $\tan \delta$ with temperature could be due to the minute impurities. The effect of these impurities may not be seen in the curves showing the relation between ϵ and frequency but may show up in the curve showing the variation in $\tan \delta$ with temperature. The activation energies for relaxation process are 0.23 eV and 0.25 eV respectively for $\text{Bi}_4(\text{GeO}_4)_3$ and $\text{Bi}_4(\text{SiO}_4)_3$. Similar peaks have been observed by Rao and Suryanarayana (1971) in the case of CoO and NiO single crystals with oxygen impurity.

The plots of $\log \sigma$ with reciprocal temperature ($1/T$) are straight lines at higher temperatures and are frequency-independent. In the low temperature region, the plots are frequency-dependent due to the impurities in the crystal (Brown 1967). The calculated activation energies are 0.95 eV and 1.2 eV for $\text{Bi}_4(\text{GeO}_4)_3$ and $\text{Bi}_4(\text{SiO}_4)_3$ respectively. It is not possible to understand the nature of the charge carriers responsible for conduction in these crystals, from the present measurements.

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