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# ELECTRICAL CONDUCTION IN $GeO_2$ / BaO GLASSES

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**Abstract:** The electrical measurements have been carried out in a number of germanate glasses described by the equation x mol % $GeO_2$ + (100-x) mol % BaO. The samples were prepared using melt quench technique. D.C. electrical conduction of the glass specimens at room temperature was studied using the two probe method. The electrical conduction mechanism was found to be Poole-Frenkel. The Poole Frenkel coefficient of barrier lowering was found to lie in the range $5.82\times10^{-5}$ to $8.45 \times 10^{-5}$ eV $m^{1/2}$ $V^{-1/2}$. The electrical conductivity was found to decrease with the increasing value of the former to modifier weight ratio. The activation energy was also calculated by observing the temperature dependence of the conductivity.

**Keywords:** Activation energy, electrical conduction, glasses.

## INTRODUCTION

The amorphous solid state is of topical interest and the experiments are normally performed on glasses or on amorphous thin films. Many investigations have been reported on the optical and electrical properties of non-crystalline materials, such as inorganic glasses prepared with glass formers like oxides of Boron, Germanium and Silicon etc. [Kumar And Chakravorty 1980, El-Egili and Oraby 1996, Pal 1997, Tsuboj 2004, Sanghi *et al*. 2004, Doweidar and Meikhail 2004, Jianrong *et al*. 2004], measured at room temperature and with a change of temperature. One important difference between the optical properties of amorphous solids compared with crystalline solids is that whereas in crystalline non-metallic solids there is a sharp, well - defined lattice absorption edge but in amorphous materials the absorption edge is less sharp and not well defined. A discussion of the various forms of optical absorption edge and other electronic properties of amorphous solids was first given by Tauc [1966] and later on generalized by Davis and Mott [1970]. They suggested an equation involving $E_{opt}$, the energy of photons involved and the absorption coefficient α(ω):

$$\alpha(\omega) = A\,(\hbar\omega - E_{opt})^n / \hbar\omega \qquad (1)$$

where the value of n lies between 0.5 and 3.0 depending upon the type of transition involved. Eq. (1) with n=2 has been successfully applied by many researchers in oxides [Moridi and Hograth 1977], chalcogenides [Rockstad 1970], phosphate [Chaudhry and Altaf 1991] glasses and evaporated thin films [Nadeem and Ahmed 2000]. With reference to the optical properties mostly refractive index and optical band gap have been studied for the Phosphate, Silicate, Borate and Germanate glasses [Kumar And Chakravorty 1980, El-Egili and Oraby 1996, Pal 1997, Tsuboj 2004, Sanghi *et al*. 2004, Doweidar and Meikhail 2004, Jianrong *et al*.

2004 ]. Germanate glasses have advantages on Silicates due to low melting point and can transmit longer wavelength in the infra-red region [Rawson 1967]. Electrical conduction in metals at room temperature obeys only the Ohm's law but in amorphous materials several types of conduction mechanisms are possible. These include ohmic, space-charge-limited, ionic, Schottky and Poole-Frenkel conduction [Schottky 1914, Frenkel 1938, Lamb 1967, Maissel and Glang 1970]. At high fields (typically ~ $10^4$ V $cm^{-1}$) most probable of these are the later two.

## SCHOTTKY EMISSION

This mechanism, which is analogous to thermionic emission except that the applied field F lowers the barrier height, corresponds to the activation of electrons over the metal-insulator barrier. This conduction is described by the relation:

$$J = A_1 T^2 \exp(-\varphi_o / k_B T) \exp(\beta_s F^{1/2} / k_B T) \qquad (2)$$

where $\beta_s$ (Schottky coefficient of barrier lowering) is given by:

$$\beta_s = [e^3 / (4\pi\varepsilon_0 K_1)]^{1/2} \qquad (3)$$

$K_1$ is high frequency dielectric constant and $\varphi_o$ is the barrier height at zero applied field. This mechanism is, therefore, characterized by a linear dependence of log I versus $V^{1/2}$ (Eq. 2).

## POOLE – FRENKEL EMISSION

This is the bulk analogue of Schottky effect and is exhibited when the current is bulk limited and is described by:

$$J = J_o F \exp[\beta_{PF} F^{1/2} / (2k_B T)] \qquad (4)$$

where $\beta_{PF} = [e^3 / (\pi\varepsilon_0 K_1)]^{1/2}$ (5)

We, thus, note that in this case a plot of log (I/V) against V gives a straight line with a slope

$$m_{PF} = \beta_{PF} (\log e) / (k_B T d^{1/2}) \qquad (6)$$

A lot of work has been carried out on the optical and electrical properties of $SiO_2$ in thin film [Illyas and Hogarth 1983] form as well as in the bulk (glass) form [Mazurin *et al*. 1983]. However, work on $GeO_2$ based glass system is quite meager. Hogarth and Nadeem [1981, 1982] have published some work on $GeO_2$/BaO complexes in thin film form. The higher thermal expansion coefficient of germanate glasses compared to silica and boron anhydride make these glasses useful for high vacuum seal applications with brass or copper [Takahashi and Sugimoto 1984]. They have also been drawn into optical fibers because of higher thermal stability. These photosensitive glasses represent a fruitful area for potential applications in optical communications and photonics. Today photosensitive fibers and planer wave-guides are being used for the fabrication of many devices used by the telecommunication industry. They can also be used to form active devices since their low phonon energy enables them to become excellent hosts for laser active dopants and laser action in the infrared spectral region [Takahashi and Sugimoto 1984].

In the present work we have investigated electrical conduction in a number of germanate glasses described by the equation (x mol% $GeO_2$ + (100-x) mol% BaO, where x = 60, 65, 70). We have also evaluated the activation energy involved in the conduction process.

## MATERIALS AND METHODS

### SAMPLE PREPARATION

A chain of glass samples were prepared by melt-quench technique in the laboratory. The relative amounts of the reagent grade oxide and carbonate materials ($GeO_2$ and $BaCO_3$; purity > 99.99%) were calculated for 5 grams samples using molar weight percentage formula. The mixture was then put in a platinum crucible which was placed in electrically pre-heated Muffle furnace at 1400$^oC$ for an hour. The molten form of the material was then cast in a stainless steel die. To avoid any stresses in the prepared glass matrix the casting dies were pre-heated and the samples were annealed at 200$^oC$ for an hour. During the preparation process $CO_2$ evolved from $BaCO_3$ and mixed with $GeO_2$ to give us the ultimate required composition $GeO_2$-BaO of the glass.

### ELECTRICAL MEASUREMENTS

The d. c. electrical measurements were carried out using two probe method. An ORTECH DC Regulated Power Supply having a range of 3kV was used for the applied bias and KEITHLEY 610C Electrometer (capable of measuring currents as low as $10^{-14}$ amperes) for the measurement of the resulting d. c. current.

## RESULTS AND DISCUSSION

### ELECTRICAL PROPERTIES

The electrical conductivity of these glasses was measured at room temperature and at 200V by using two-probe method. The plot of conductivity versus composition ($GeO_2$ /BaO) ratio was traced in Fig. 1 to examine the variation of conductivity with changing ratio of components. It is noted from the plot that conductivity decreases with increasing BaO concentration.

In order to check the possibility of ohmic or any other power law dependence, log I was plotted against log V typically for one of the compositions i.e. 65% $GeO_2$ + 35% BaO in Fig. 2. We noticed a non-linear behavior which eliminates the possibility of any power law dependence.

To check the possibility of Schottky conduction, Log I was plotted against $V^{1/2}$ (Eq. 2) for the three compositions as shown in Figs. 3-5. These curves were seen to be linear in the high field region. Slope of the straight part of these curves using following relation (as derived from Eq. 2):

$$\text{slope} = m_s = [\beta_s(\log e)]/[k_B T d^{1/2}]$$

furnishes the experimental values of $\beta_s$. These values of $\beta_s$ are given in Table 1 for the three compositions. The experimental values of Schottky dielectric constant $K_s$ were then evaluated using Eq. 3 (with $K_1 = K_s$) and are also given in Table 1. Theoretical values of the dielectric constant $K_{th}$ were estimated using relation $K = n^2$ [Maissel and Glang 1970] where n is the refractive index of prepared glasses measured by apparent depth method. These values for the three compositions are also given in Table 1 for comparison with the experimental ones. We note here that the theoretical $K_{th}$ and the experimental $K_s$ do not match for any of the three compositions. This eliminates the possibility of Schottky emission as the conduction process in our samples.

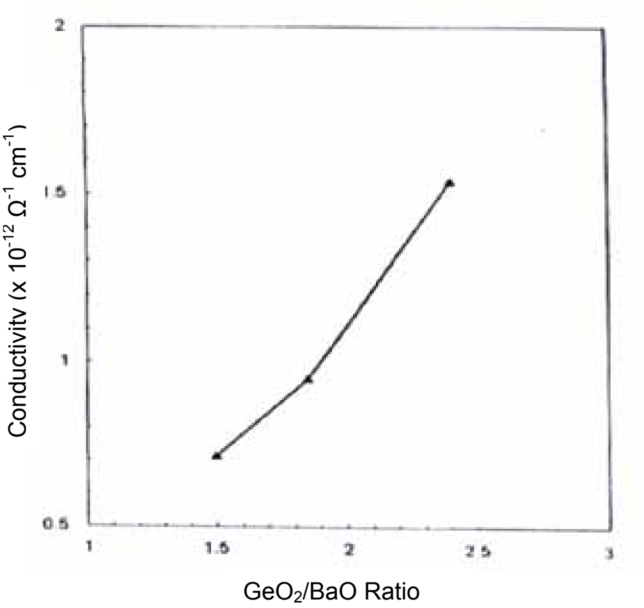

**Fig. 1:** Variation of electrical conductivity with $GeO_2$/BaO ratio in germanate glasses.

Next step was to ascertain the Poole-Frenkel effect to be involved in the conduction phenomenon in our glasses. In accordance with the Poole-Frenkel equation (Eq. 4) we trace log (I /V) versus $V^{1/2}$ with a slope (from Eq. 6)

**Table 1:** Conduction parameters for germanate glasses.

| Composition mol % | $K_{th}$ | $\beta_S$ ($\times10^{-5}$ eV m$^{1/2}$ V$^{-1/2}$) | $K_s$ | $\beta_{PF}$ ($\times10^{-5}$ eV m$^{1/2}$ V$^{-1/2}$) | $K_{PF}$ | ΔE (eV) |
|---|---|---|---|---|---|---|
| 70%$GeO_2$ + 30% BaO | 1.56 | 4.40 | 85.0 | 8.95 | 1.20 | 0.20 |
| 65%$GeO_2$ + 35% BaO | 1.24 | 3.40 | 38.3 | 6.59 | 1.45 | 0.25 |
| 60%$GeO_2$ + 40% BaO | 1.50 | 3.04 | 18.8 | 5.82 | 1.12 | 0.29 |

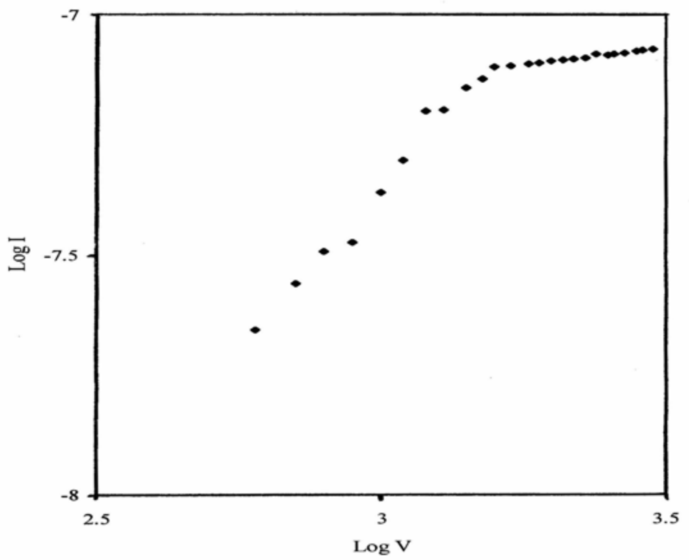

**Fig. 2:** Logarithmic current plotted against logarithmic voltage for a typical 65% $GeO_2$ + 35 % BaO sample.

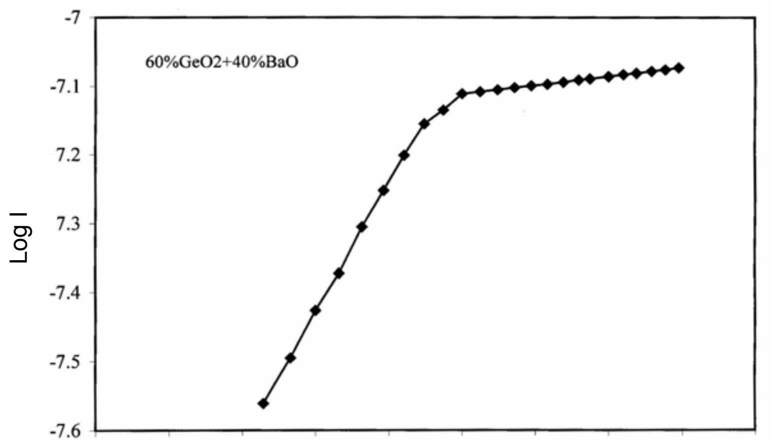

**Fig. 3:** Logarithmic I plotted against $V^{1/2}$ for the 60% $GeO_2$ + 40% BaO Glass sample.

$$\text{Slope} = m_{PF} = \beta_{PF}\,(\log e)/\,(k_B\, T\, d^{1/2})$$

Figs. 6-8 were, therefore, drawn to estimate the experimental values of $\beta_{PF}$ for the three compositions. Experimental values of Poole-Frenkel dielectric constant $K_{PF}$ were then evaluated using Eq. 5 and the experimental values of $\beta_{PF}$ and are reported in Table 1. Now we see a reasonable match between theory ($K_{th}$) and experiment ($K_{PF}$). So it can be said that Poole-Frenkel emission is the dominant conduction mechanism in the present germanate glasses. This result is, however, in contrast to the conduction in thin film samples of similar compositions [Hogarth and Nadeem 1982] where it was found to be Schottky. It can be explained on the ground that glass samples are more bulky as compared to thin films and Poole-Frenkel conduction mechanism is bulk-limited [Morey 1960] so it is more likely in our glass samples.

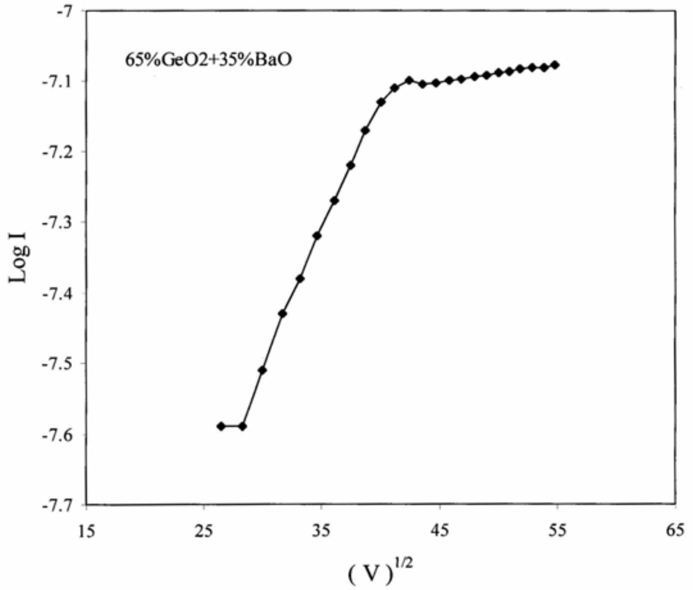

**Fig. 4:** Logarithmic I plotted against $V^{1/2}$ for the 65% $GeO_2$ + 35% BaO glass sample.

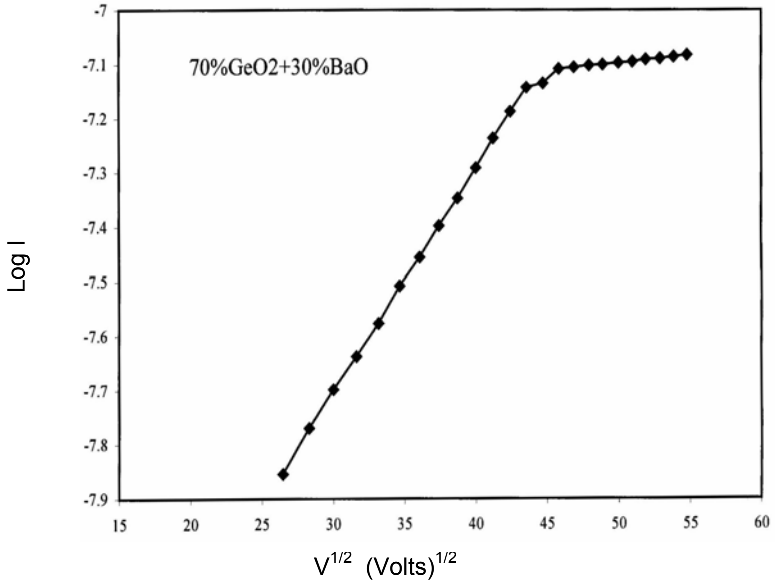

**Fig. 5:** Logarithmic I plotted against $V^{1/2}$ for the 70% $GeO_2$ + 30 % BaO sample.

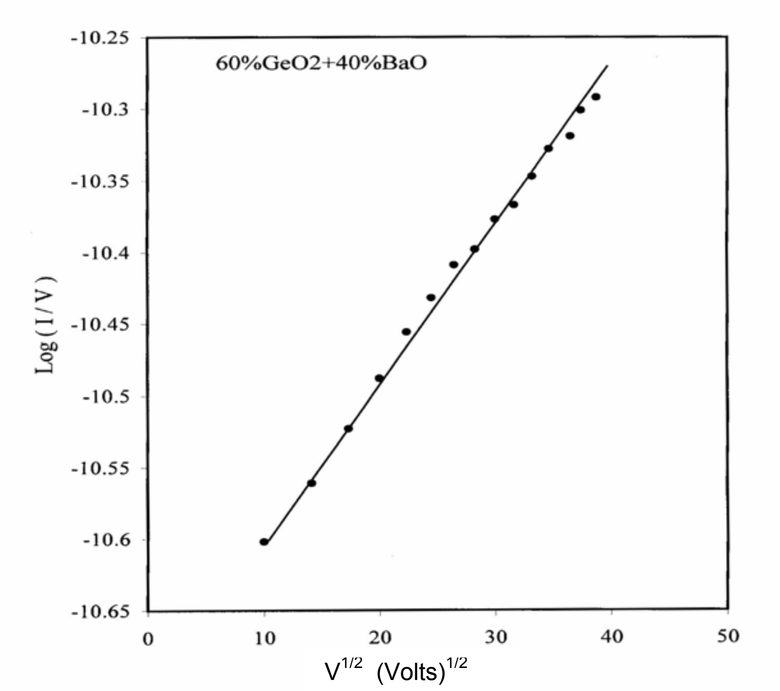

**Fig. 6:** Log (I/V) Vs. $V^{1/2}$ for the 60%$GeO_2$ + 40% BaO glass sample required by Poole-Frenkel emission.

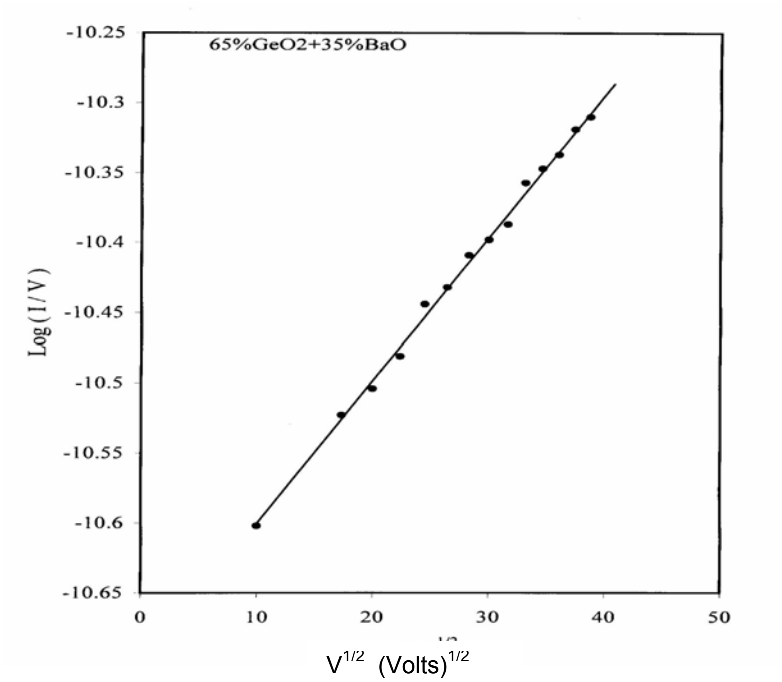

**Fig. 7:** Log (I/V) Vs. $V^{1/2}$ for the 65%$GeO_2$ + 35 % BaO glass sample as required by Poole-Frenkel emission.

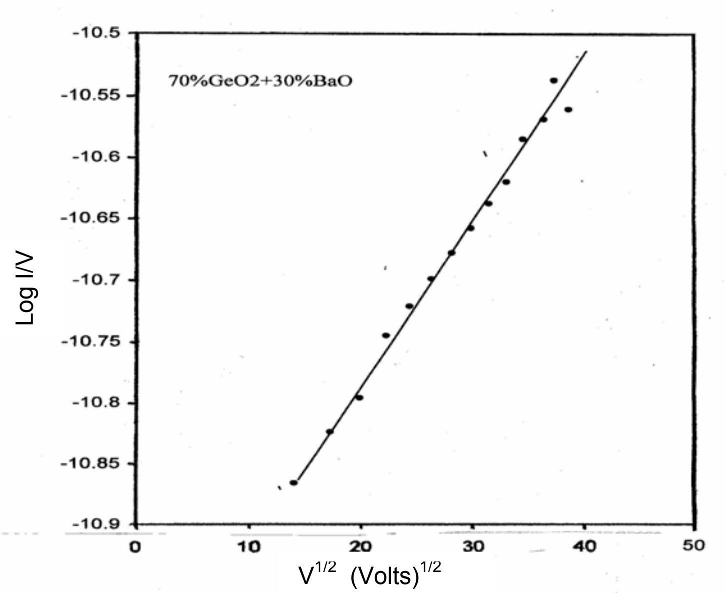

**Fig. 8:** Log (I/V) Vs $V^{1/2}$ for the 70%$GeO_2$ + 30% BaO glass sample as required by Poole-Frenkel emission.

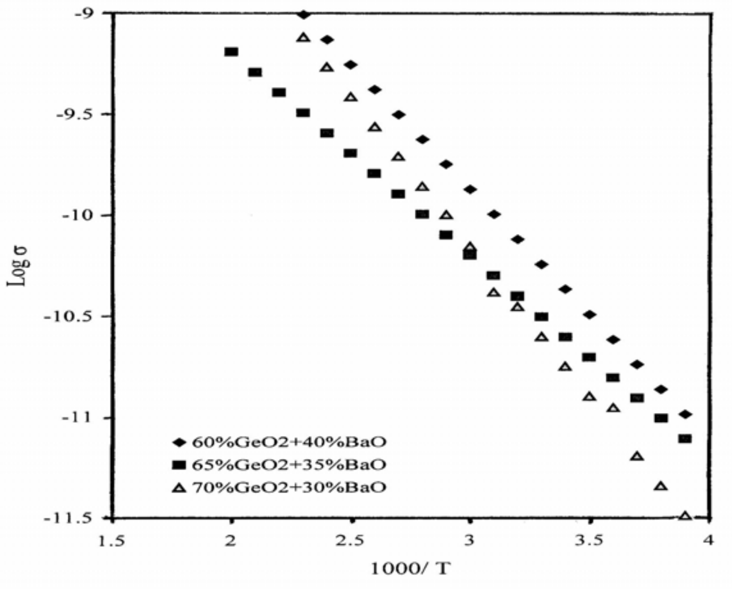

**Fig. 9:** Logarithmic conductivity plotted against reciprocal temperature for the calculation of activation energy.

## TEMPERATURE DEPENDENCE (ACTIVATION ENERGY)

Using temperature dependence of the conductivity we can estimate the activation energy through the equation:

$$\sigma = \sigma_o e^{-\Delta E / k_B T}$$

Thus, a plot of log σ versus 1000/T yields the value of activation energy ΔE involved. These plots are shown in Fig. 9 for the three compositions and calculated values of activation energy are again given in Table 1.

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