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Temperature and frequency dependent conductivity and electric modulus formulation of manganese modified bismuth silicate glasses

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ABSTRACT

The ac conductivity and electric modulus formalism of bismuth silicate glasses containing manganese with compositions $x\mathrm{MnO_2}\cdot(60-x)\mathrm{Bi_2O_3}\cdot 40\mathrm{SiO_2}$, ($x = 0$, 5, 10, 15 and 20) have been studied in the frequency range 10^{-1} Hz to 1 MHz and temperature range 583 K to 703 K. The ac conductivity is found to increase with an increase in MnO_2 content. The frequency dependent conductivity for manganese doped bismuth silicate glassy system shows a single plateau for samples with $x = 0$ and 5, but for glasses with $x = 10$, 15 and 20, the temperature and frequency dependent conductivity shows a double plateau in the whole temperature range 583 K to 703 K. The observed dispersive behavior of ac conductivity of bismuth silicate glasses containing manganese is discussed in the framework of Jonscher's universal power law fitted to the experimental data of samples showing single as well as two plateau regions. The results show that the ac conductivity increases with the increase in the frequency of applied field. Further, it is observed that small polaron conduction mechanism is more or less suitable to explain the conduction in the present glass samples with $x = 10$, 15 and 20 in the high frequency region. However, the temperature dependent behavior of the frequency exponent s for glass samples with $x = 0$ and 5 seems to follow CBH conduction mechanism. The electrical relaxation is rationalized using the electric modulus formulation in the presently studied glasses at all the temperatures. The values of activation energy for dc conduction (E_A) and electric modulus (E_R) were estimated. For glass sample with $x = 0$ and 5, the activation energy associated with electric modulus is almost equal to that of the dc conductivity at the low frequency range, whereas for glass samples with $x = 10$, 15 and 20, the values of E_R are equal to the activation energy due to dc conduction in the high frequency region.

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1. Introduction

Glasses containing transition metal oxides (TMO) show semiconducting properties due to the presence of more than one valance state of the transition metal ions [1–9]. These glasses are technologically important due to their remarkable applications in switching and electrochromatic devices, fuel cells, solid state batteries, chemical sensors, etc. [10–16]. The charge transport in these glasses is believed to take place by hopping of electrons from the low valence state to high valence state of transition metal ions [1,2], for example, in glasses containing manganese, the electronic conduction occurs due to the hopping of a 3d electron from the Mn^{2+} to Mn^{3+} ion. The introduction of TMI, like manganese, to the bismuth silicate glasses is expected to improve their electrical and dielectric features. The conductivity of bismuth silicate [17,18] and manganese borate glasses [19,20] has been reported by many researchers, but there is hardly any report available in literature on electronic transport of manganese bismuth silicate glass system. The objective of the present study is to analyze a comprehensive overview of the electrical properties like ac conductivity and dc conductivity along with electric modulus formulation in manganese modified bismuth silicate glasses as a function of frequency and temperature.

2. Material and methods

Glass samples having compositions $x\mathrm{MnO_2}\cdot(60-x)\mathrm{Bi_2O_3}\cdot 40\mathrm{SiO_2}$, ($x = 0$, 5, 10, 15 and 20) were prepared using standard melt-quenching technique. The appropriate amounts of these chemicals were thoroughly mixed in an agate pestle–mortar. Silica crucible containing the mixture was put in an electrically heated muffle furnace and the temperature was raised slowly to a temperature between 1000 and 1150 °C depending on the composition. The temperature was maintained for 1 h and the melt was shaken frequently to ensure proper mixing and homogeneity. The melt was then poured onto a stainless steel block and was immediately pressed by another similar block, at room temperature. The amorphous nature of samples was confirmed by the absence of any sharp peak in the X-ray diffraction (XRD) patterns of the synthesized glass samples, recorded by using Rigaku Table-Top X-Ray Diffractometer. The prepared glass samples were cut into small pieces of rectangular shapes with thickness ~ 1 mm and

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their surfaces were smoothed and polished. For electrical measurements, both sides of the samples were coated with the silver paint so that they serve as electrodes. Conductivity measurements were carried out using Alpha-A High Resolution Dielectric, Conductivity, Impedance and Gain Phase Modular Measurement System (Novo control Technologies GmbH & Co. KG) in the frequency range of 10^{-1} Hz to 1 MHz and temperature ranging from 583 K to 703 K. The fitting of experimental data was done using linear and non-linear curve fitting modules of origin Pro 8.6 software and errors in different parameters have been estimated by fitting.

3. Results and discussion

3.1. Alternating current (AC) conductivity

The total frequency dependent conductivity ($\sigma'(\omega)$), of different glass compositions $40SiO_2$–$(60-x)Bi_2O_3$–$xMnO_2$ with $x = 0$, 5, 10, 15 and 20, measured in temperature range 583 K to 703 K and frequency range 10^{-1} Hz to 1 MHz, is found to increase with an increase in MnO_2 content. The frequency dependent conductivity of glass samples, presented in Fig. 1 at any particular temperature (683 K), is characterized by two regions: (i) a plateau region and (ii) dispersion region for glass samples with $x = 0$ and 5. But for higher manganese content i.e. $x = 10$, 15 and 20, it shows an additional plateau region at intermediate frequencies as shown in Fig. 1. The appearance of this additional plateau occurs not only at 683 K but at all the studied temperatures for glass samples with $x = 10$, 15 and 20. The width of the additional plateau is observed to decrease with increase in MnO_2 content. It is not an unexpected result in heterogeneous glasses like the present ones, as this second plateau is due to the heterogeneity (difference) in conductivities of manganese and silicate networks. This type of behavior of conductivity is also reported for other ionic glasses and ceramics having different phases [21]. Electrical conductivity in the present glasses increases with the increase in temperature as a result of the increase in drift mobility of the thermally activated charge carriers [22,23].

In general, the ac conductivity of hopping charges for many semiconducting amorphous materials exhibit Jonscher's power law [6,24,25]:

$$\sigma'(\omega) = \sigma_{dc}\left[1 + \left(\frac{\omega}{\omega_H}\right)^s\right] \quad (1)$$

where σ_{dc} is dc conductivity, ω_H is crossover frequency separating dc regime (plateau region) from the dispersive conduction and s is frequency exponent that lies between 0.5 and 1 [25,26]. The experimental data of glass samples with $x = 0$ and 5 are observed to obey single Jonscher's power law at all the temperatures. The typical fitting of Eq. (1) with experimental data for glass samples with $x = 5$ is shown in Fig. 2. For glass samples with $x = 10$, 15 and 20, where an additional plateau is also observed at intermediate higher frequencies, the ac conductivity cannot be accounted for by Eq. (1) only, rather two such formulae have been used in different frequency regions to explain the presence of two relaxation mechanisms [27]. The ac conductivity curve is, therefore, bifurcated into two parts and the experimental data of both parts are independently fitted with Jonscher's power law. In both regions the experimental data of conductivity show good fitting with the Eq. (1). Thus single Jonscher's power law is fitted to the experimental ac conductivity data of the present oxide glasses in both bifurcated regions of low as well as high frequencies for glass samples with $x = 10$ and 15. The values of σ_{dc}, ω_H, and s have been obtained for low and high frequency plateau regions independently, wherever observed.

The fitting of single Jonscher's power law with experimental data in low and high frequency regions for glass samples with $x = 10$ and 15 were similar and typical curves for a glass sample with $x = 10$ are shown in Fig. 3. For experimental data of sample with $x = 20$, as shown in Fig. 4, the first plateau does not seem to be complete in the studied frequency range, rather it appears that might appear at still lower frequencies and hence for this sample, single Jonscher's power law was applied for high frequency plateau region. The appearance of the second plateau in the intermediate/high frequency range in glass compositions with $x = 10$, 15 and 20 exhibiting heterogeneous structures with different phases, may be due to the Maxwell–Wagner effect. The Maxwell–Wagner effect is generally observed in the heterogeneous system where the difference in conductivity of the two phases is very high [21,28]. In the present system, the MnO_2 is added in the bismuth silicate matrix. Generally, silicate glasses are insulators but MnO_2 is semiconducting and hence there is a large difference of conductivity in manganese and silicate networks/phases [29,30]. So, the second plateau is observed in the glass samples with higher manganese concentration, wherein MnO_2 rich phase is expected to be formed.

If the conduction occurs via a defect mechanism then at a given instant only a fraction (n) of the total charge carriers (N) are mobile, which is given by [6,31]

$$n = N\exp\left(-\frac{G_f}{kT}\right) = N\exp\left(\frac{S_f}{k}\right) \times \exp\left(-\frac{H_f}{kT}\right) \quad (2)$$

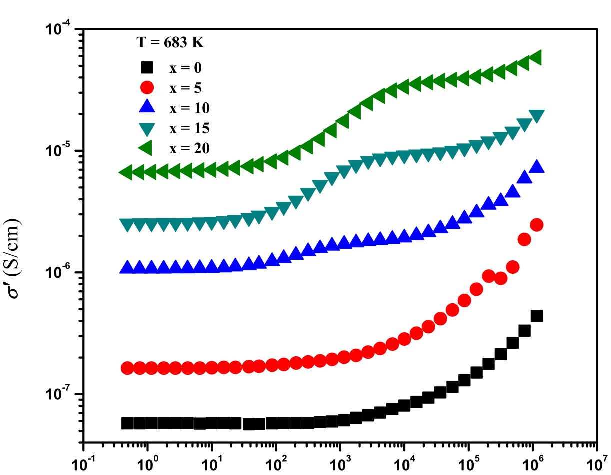

Fig. 1. Compositional variation of total ac conductivity ($\sigma'(\omega)$) of $xMnO_2\cdot(60-x)Bi_2O_3\cdot40SiO_2$ glass system at 683 K.

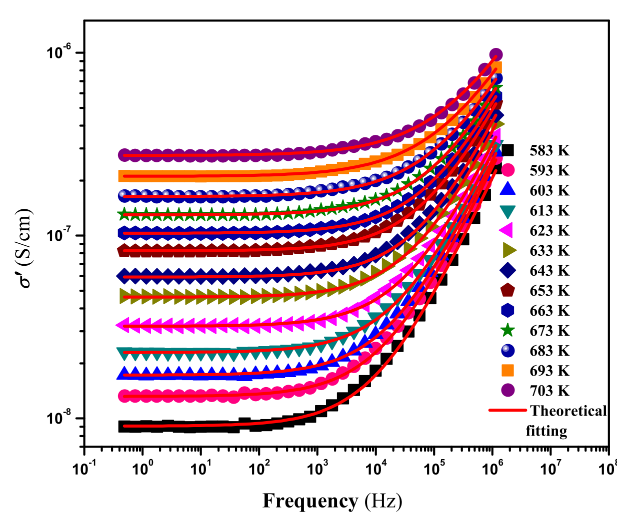

Fig. 2. Measured total ac conductivity ($\sigma'(\omega)$) versus frequency curves for $xMnO_2\cdot(60-x)Bi_2O_3\cdot40SiO_2$ with $x = 5$ at thirteen different temperatures. The solid lines in the figure are the best fits obtained from fitting of experimental data with Jonscher's power law.

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