Influence of modifier on dielectric and ferroelectric properties of aluminosilicate glasses

Bhupinder Kaur [a], K. Singh [a], O.P. Pandey [a], Samita Thakur [a,b,*]

[a] School of Physics and Materials Science, Thapar University, Patiala 147004, India
[b] Department of Chemistry, Panjab University, Chandigarh, India

ABSTRACT

Glasses with compositions SiO_2-CaO-Al_2O_3-TiO_2-Na_2O were prepared by conventional melt quench technique. The dielectric properties of these glasses with a variation in alkali content over a frequency range from 20 Hz to 1 MHz and temperature variation of 30–280 °C have been investigated. The electric modulus representation has been used to provide comparative analysis of the ion transport properties in these glasses. The conductivity isotherms show a transition from frequency independent dc region to dispersive region where the conductivity continuously increases with increasing frequency. The present glasses exhibit conductivity in the range of 10^{-5} to 10^{-3} S/m which is higher than the alkali containing silicate glasses. Hysteresis loop observed at room temperature confirms the ferroelectric nature of glasses.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Silicate glasses are of great importance and has an extremely wide spectrum of industrial applications ranging from laboratory glassware, encapsulation of radioactive waste to optical components and sealing materials [1–3]. Even these glassy materials are extensively studied in the last decades due to their ability to conduct electricity caused by ionic motion. This property of glasses is dominant in solid state electrolytes for rechargeable batteries/fuel cells, sensors, ion exchange membrane etc. [4–7].

Understanding of the conduction mechanism in the disordered glassy materials provide a more inclusive picture of the system dynamics and transport mechanism. The atomic structure of ionic glassy conductors is constituted of mainly two components; a relatively rigid matrix and ions of opposite charges occupying potential minima. These ions diffuse in the rigid matrix by means of thermal hopping between different potential minima [8]. The hopping or diffusion of ions can be broadly classified into two main processes depending on the frequency scale at which ionic conductivity is measured (1) long range redistribution of ions that give rise to ionic diffusion or dc conductivity at low frequencies (2) local short range ionic rearrangement causing dipolar intrinsic bulk polarization [9]. According to Barton-Nakajan-Namika observation, it can be concluded that conduction and polarization share same physical origin i.e. redistribution of ionic position. But the former (dc conduction) is more likely related to strongly coupled hops, the later (polarization) can be assumed as resulting from superposition of individual or localized ionic hops which are limited in a finite volume and taking place throughout the glassy network [10,11]. Therefore it is interesting to study the frequency and temperature dependent dynamic and relaxation mechanism of mobile ions in disordered ionic conductors by interpreting the frequency dependence properties in their dielectric response. Thus it is expected that analysis of bulk polarization and hopping mechanism can provide information about microscopic glassy structure.

The aim of the present study is to investigate the dielectric properties of NaO-CaO-SiO_2-TiO_2-Al_2O_3 glasses. In the present glass system, SiO_2 is the main glass former and other components have been chosen by considering the existing facts in the literature. The presence of NaO and CaO will generate the mixed alkali effect in the system [12]. According to dynamic structure model, the mismatch of individual ion sites may occur in alkali containing glasses because when a larger ion enters into the smaller site, site relaxation occurs to accommodate the larger ion. There are also possibilities that small interstitial sites which were previously vacant but will become typical ion sites if an ion resides there for a given time. These changes will make a fluctuating percolation pathway for migration of ions for both single and mixed ionically conducting glasses. The ions in mixed alkali glasses generate polarization by reorienting locally and are also responsible for conduction in lower frequencies by separating itself from immediate neighbourhood [13,14]. For TiO_2, It is well reported in literature that high ionic polarization of titanium results in long range interactions with the surroundings oxygen. It is also believed that high charge and small ionic radii of Ti^{4+} ion also influence the dielectric constant which is a measure of ionic polarization [15].

* Corresponding author at: Department of Chemistry, Panjab Unievrsity, Chandigarh, India.
E-mail address: samitasthakur@gmail.com (S. Thakur).

In the present study, a comprehensive overview of the electrical properties like ac and dc conductivity along with dielectric relaxation mechanism as a function of frequency and temperature has been studied. Along with the dielectric properties, the ferroelectric behaviour of these glasses has also been explored.

2. Experimental

Glasses with composition (60-X) SiO_2–15 CaO–10 Al_2O_3–5 TiO_2 - (10 + X) Na_2O (where X = 0, 5, 10, and 15 mol%) were prepared from high purity ingredients by conventional splat quenching technique and has been designated as N-10, N-15, N-20 and N-25. The details of glass preparation are given elsewhere [16].The resultant glass samples were observed to transform from transparent white to yellow colour by addition of the sodium content. These glasses were annealed at 400 °C for 12 h to remove stresses. The annealed glasses were cut in rectangular bar using diamond cutter (IsoMet® Low Speed Saw, Buhler). The dielectric response on these rectangular glass bars was measured over a frequency range of 20 Hz to 1 MHz by using automated LCR meter (Agilent 4284A precision LCR) in the frequency range of 20–10^6 Hz over temperature range of 30 °C to 450 °C. All the measurements were performed in air at the heating rate 5 °C/min with temperature stability ± 1 °C. The rectangular glass bars were silver pasted to have a better electrode connectivity during measurements. The refractivities of the samples were measured with an Abbe refractometer (Atago DR-A1 or RX-5000α-Bev) and the uncertainties were <2 × 10^{-4} or 4 × 10^{-5} RI unit, respectively. Ferroelectric hysteresis loop measurements were performed using TF Analyzer 2000 (aixACCT Systems). The values of remnant polarization (P_r) and coercive field (E_c) were determined from hysteresis loop.

3. Results and discussion

3.1. X-ray diffraction

X-ray diffraction patterns of all the glasses are shown in Fig. 1. The absence of any peak and presence of a broad hump in the range of 20–30° in diffraction pattern clearly shows the amorphous nature of glasses with the long range structural disorder.
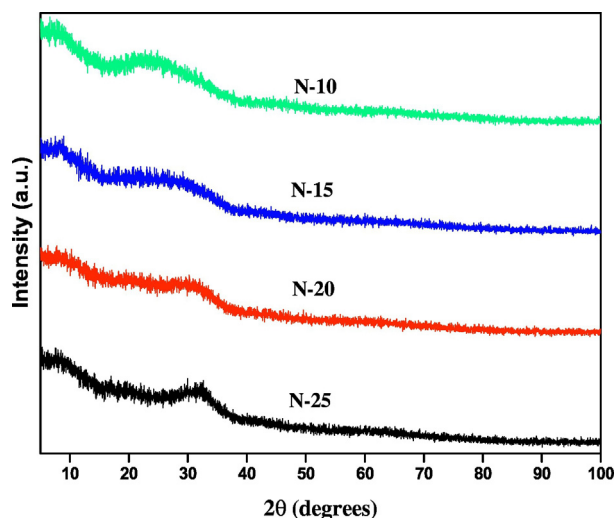

Fig. 1. X-ray diffraction pattern of (60-X) SiO_2–15 CaO-10 Al_2O_3–5 TiO_2 - (10 + X) Na_2O (where X = 0, 5, 10, and 15 mol%).

3.2. Dielectric properties

3.2.1. Dielectric constant (real part)

The variation of real part of dielectric constant at certain different temperatures for all the samples are shown in Fig. 2. These curves do not exhibit any peak which clearly indicates that polarization in these systems is dominated by hopping mechanism [17]. At a particular temperature, the value of ε' decreases with increasing frequency and attains a constant limiting value at high frequencies which is a commonly observed phenomenon in ionic materials [18]. This variation indicates that two dispersion mechanism are present in a single material: one dominates at low frequency and other at high frequency (above 10^3 Hz). The high value of dielectric permittivity at low frequency region can be explained on the basis of external interfacial Maxwell-Wagner model [19]. According to this model, the dispersion at low frequencies is mainly due to the interfacial polarization as the blocking electrodes do not permit the mobile ions to transfer into external circuits, as a result, mobile ions pile up near the electrodes and give a large bulk polarization at low frequencies in the materials. The high frequency behaviour resembles the Debye behaviour and in this region ε' varies as w^{m-1}. In the low frequency region, the ions jumps in the applied field direction and pile up at the high energy barrier sites. It happens due to increase of capacitance in the applied field direction. At high frequencies, the periodic reversal of the field takes place so rapidly that there is no excess ion jumps in the field direction. The capacitive effect disappears at high frequencies, which reduces the contribution of the charge carriers to the dielectric constant.

With the rise in temperature, the dispersion at the low frequency side also increases for all the samples. After 250 °C, the dielectric permittivity of the present glasses increases abruptly even at high frequencies. The increasing temperature brings structural changes in the glass matrix and reduces the rigidity of the glasses but at the same time the mobility of the ions increases which enhances dielectric permittivity [20].

The effect of Na_2O content on the dielectric behaviour of the present samples can be clearly seen in terms of the maximum dielectric constant value for N-25 sample which has highest concentration of Na_2O among all the present studied samples. At 30 °C, as the sodium content in the glasses decreases, the dielectric constant values also show a decreasing trend. According to Anderson and Stuart model, the dielectric constant is a measure of the looseness of the structure of glass network [21]. It also measure the ease with which a modifier cation can migrate through glass network. As such silica do not exhibit any dielectric properties but inclusion of the modifier ions (like Na, Ca or Al) reduces the network rigidity by creating the non-bridging oxygen (NBOs) in the glass network. These NBOs are responsible for the migration of the ions and polarization in the glass network. With the increase in the concentration of the Na_2O, the concentration of the NBOs also increase in the system and hence the dielectric constant. As the temperature increases (at 100 and 250 °C), the low frequency dielectric constant do not follow any trend with respect to change in composition of the glasses. This variation can be attributed to the electrode contacts and interfacial polarization. The high frequency dielectric constant is more or less same for all the glass compositions.

3.2.2. Dielectric losses

The variation of Tan δ with frequency at 30 and 250 °C are shown in Fig. 3. At 30 °C, no peak has been observed in all the samples. The values of Tan δ decreases with the increase in frequency. This can be due to the presence of interfacial polarization or hopping of ions at low frequencies. These phenomenon mainly enhances the conductivity and hence the dielectric losses in the present studied samples. Around 250 °C, the relaxation peaks can be seen in all the samples at low frequency region. These peaks can be due to the interfacial polarization as no other relaxation mechanism is dominant in this frequency range. As the temperature increases, the values of Tan δ also increases due to the increase