AC Conductivity Studies Of Sodium-Boro-Vanadate Glasses Prepared By Microwave Method

Asha Rajiv, M. Sudhakar Reddy, Jayagopal Uchil
Department of Physics, School of Graduate Studies,
Jain University, Bangalore 560027, India.

C. Narayana Reddy
Department of Physics, Maharani's Science College for Women,
Bangalore University, Bangalore, 56000,India.

***Abstract*— Frequency and temperature dependent conductivity measurements have been carried out in the frequency range 10 Hz to 10 MHz and temperature range of 323K to 403K respectively on the sodium-boro-vanandate glass prepared by a novel microwae method. Impedance plots of the investigated glasses show good semicircles with spikes, indicating single conductivity mechanism operating in these glasses, where in the intersection of the semicircle on Z' - axis gives bulk resistance. Resistance of the sample decreases with increasing temperature, indicating that conductivity is a thermally activated process. The transport mechanism is governed by the concentrationof Na^+ ion motion in the macromolecular structure. The behavior of ac conductivities in the investigated glasses exhibited change of slope to higher values as the frequency increased and the flat portion at lower frequencies increased to higher values of conductivity at higher temperatures. The conductivity has been examined using Almond- West type of power law.**

Keywords- Microwave method, Impedance plot, Almond-West type of power law

I. INTRODUCTION

Migration of ions through disordered materials has attracted researchers for many years because of its importance in technological applications and in understanding the nature of conduction mechanism. Many monovalent (Li^+, Na^+, Ag^+, etc.) and divalent (Pb^{2+}, Zn^{2+}, Sr^{2+}, etc.) ion conducting glasses find applications in electrochemical devices such as solid state batteries, electronic and electro-optic devices. Apart from their applications, studies on these glasses help one to understand how the structure of the host glass in which the ions present and influences their mobility. Glasses with a low concentration of Transition metal ions (TMI) and a high concentration of alkali or silver oxide are well known as super ionic conductors [1-3]. On the other hand glasses with high concentration of TMI and low concentration of alkali oxide, a 'cross over' from predominantly ionic to electronic conductivity takes place [4-5]. Li_2O, Na_2O, Ag_2O glasses with archetypal glass-forming oxides such as B_2O_3, SiO_2, TeO_2 etc. exhibit high ionic conductivity due to Li^+, Na^+, Ag^+ ion exhibit high ionic transport [6-9]. In glasses containing two glass formers such as B_2O_3 and V_2O_5, the coordination number and connectivities of both borate and vanadate species can vary in a complex manner as a consequence of modification when a modifier oxide is added to the glass. The purpose of the present work is to analyze the conducting mechanism in a ternary glass system prepared by a novel energy efficient microwave method.

Ever increasing demand for high–quality and inexpensive products has led to enormous developments in material science and technology. There is a need for new methods to synthesize tailor making of materials to meet societal demand and new technologies to shape them. Microwave processing of materials is a relatively new technology undergoing rapid developments due to potential advantages it offers such as reduced processing times, energy efficient and products with enhanced properties. Though microwave synthesis is quite faster, simpler and energy efficient, the exact nature of microwave interaction with reactants during synthesis of materials is unclear and speculative. However, the energy transfer from microwaves to the reactants is believed to occur either through resonance or relaxation, which results in fast heating. Microwave preparations of solid materials reported in the literature is limited. There is a fundamental difference between microwave and conventional heating. In conventional heating, heat transfer mechanisms like conduction, convention and radiation are responsible for heat transfer to the material. In these processes thermal energy is delivered to the surface of the material which first gets heated. The only requirement is that at least one of the components used for making glass must be microwave susceptor. Many ionic materials are microwave susceptors because of the ionic current which cause the coupling to microwaves. Therefore, rapid heating occurs with the use of microwaves when highly ionic components are present in the glass composition.

II. EXPERIMENTAL

Glasses were prepared by microwave heating technique using the general formula: $xNaBO_2 - (100-2x)\ V_2O_5$ (where x = 45,42.5,40,38.5 and 35 mol%) using analar grade sodium carbonate (Na_2CO_3), orthoboric acid (H_3BO_3), and vanadium pentoxide(V_2O_5) as starting materials and with one of the ingredients as a microwave susceptor. An appropriate quantity of weighed chemicals were mixed and thoroughly ground to homogenize the mixture and kept in a silica crucible inside a domestic microwave oven operating at 2.45 GHz and at a tunable power level up to a maximum of 850W. Within 6–8 min of microwave exposure a good homogeneous melt was obtained (which is only a fraction of the time required in conventional glass preparation methods), which was immediately quenched between copper blocks. The silica crucible was found to remain clean and unaffected during the short duration of melting. The glass was annealed in a muffle furnace for 1 hour at 200^0 C to remove thermal strains that could have developed during quenching. The samples were preserved under anhydrous Calcium chloride atmosphere ($CaCl_2$).

The amorphous nature of the glass samples were confirmed using powder X-ray Diffraction (XRD) (Model: Rigaku DMAX-IC employing Cr-Kαradiation). Glass transition temperature (T_g) of the samples were recorded using Differential Scanning Colorimeter (Perkin Elmer DSC-2). Electrical conductivity measurements were carried out as a function of frequency and temperature by employing a Hewlett- Packard HP 4192 A impedance gain phase analyzer from 10Hz -10MHz in the temperature range 323 K-403 K. A home built cell assembly (having two terminal capacitor configuration and spring loaded silver electrodes) was used for the measurements. The temperature was controlled using Heaton (Bangalore 560090, India). Temperature controller and temperature of ±1 K was achieved in the entire range of measurements. The temperature of the sample was measured using Pt-Rh Thermocouple positioned very close to the sample. Annealed and polished glass pieces having a thickness of about 0.1 cm and diameter of about 1 cm were coated with silver paint on both sides to serve as electrode were used for measurements.

III. RESULTS AND DISCUSSION

Compositions and 'r' values of sample are listed in Table 1. The XRD pattern of 0.66 mole fraction of Na_2O is as shown in Fig.1 and all the investigated glasses show a similar hump in the low 2θ region which is the characteristic feature of amorphous structure.

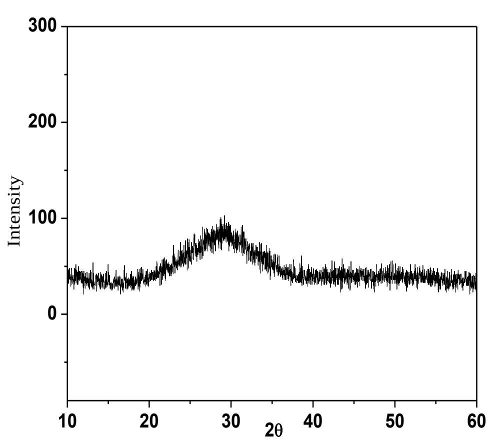

Fig :1 XRD spectra of r= 0.66 sample

This indicates the absence of long range periodicity of the three dimensional network.

The conduction mechanism can be well understood using complex impedance spectroscopy. In Na_2O rich glasses, cole –cole plot exhibits one semicircle with a spur. The conductance (G) and the capacitance (C) were directly measured from impedance bridge, the real and imaginary parts of impedance Z' and Z" are computed using the relation

$$Z^* = Z' + j\,Z''$$

$$Z' = \frac{G}{G^2 + \omega^2 C^2}$$

$$Z'' = \frac{\omega C}{G^2 + \omega^2 C^2}$$

Typical impedance plots are shown in Fig.2, which were used in dc conductivity determination. Values of Z' corresponding to the intersection of low frequency side of the high frequency arc were used for the purpose in the formula

$$\sigma_{dc} = \frac{d}{RA}$$

where 'd' is the thickness of the sample, 'R' is the bulk resistance of the samples and 'A' is the conducting area of cross section of samples. Variation of dc conductivity for various compositions as a function of 1000/T are shown in Fig. 3. As can be seen from Fig .3, the conductivity follows Arrhenius behavior. The calculated Arrhenius activation barriers, E_{dc} for various compositions lie in the range 0.696 to 0.503 eV. The variation of E_{dc} as a function of mole fraction of modifier oxide is shown in Fig. 4. E_{dc} decreases linearly in the range of Na_2O concentration employed here. The variation of log (σ_{dc}) can be attributed to the variations in the nature of the anionic environment on the transport of Na^+ ions. As the concentration of modifier oxide increases the boro-vanadate network gets depolymerized, resulting in the formation of structural motifs. The modification of the network is in accordance with the Sanderson's electronegativity principle. Unmodified glasses have a structural dimensionality of two, since both $[BO_{3/2}]^0$ and $[VOO_{3/2}]^0$ are only three connected and the structure is similar to that of the B_2O_3 glass except that as a result of substitution of B by V = O. It has been shown in our earlier communications that as a result of modification by alkali oxide, four connected B_4 and V_4 units are formed initially and they increase the dimensionality of the glass structure. These changes in the structure promote medium range order. Hence the formation of clusters in which there is an increased positional ordering. This results in increase of conductivity with increasing concentration of Na_2O, due to well-connected paths in the cluster regions.

Ac conductivities have been measured from 10 Hz to 10 MHz. A typical plot of log (σ) verses log (f) at different temperatures is shown in Figure 5. All the samples exhibited high frequency dispersion and essentially flat frequency insensitive conductivities at low frequencies. The dispersion region rises to high frequencies at high temperatures. The σ(0) values increase with temperature and they compare well with the dc conductivity values seen in Fig.3. These conductivities have been fitted to Almond-West type power law expression [10-11]

$\sigma(\omega) = \sigma(0) + A\omega^{s}$, where $\sigma(0)$ is the low frequency (d.c conductivity) constant. It is the frequency independent part in log (σ) verses log (f). 's' is the power law exponent with a magnitude $0 < s \leq 1$ and A is a constant. s-values obtained from non-linear fits lie in the range of 0.6 to 0.7 and the value of s marginally decreases with temperature. Also the highest value of s observed in these glasses are slightly greater than 0.7.

Table: 1 Sample composition and " r " values

Composition			Mole fraction of Na_2O
Na_2O	B_2O_3	V_2O_5	$r = [Na_2O]/[B_2O_3+V_2O_5]$
35	35	30	0.54
37.5	37.5	25	0.60
40	40	20	0.67
42.5	42.5	15	0.74
45	45	10	0.82

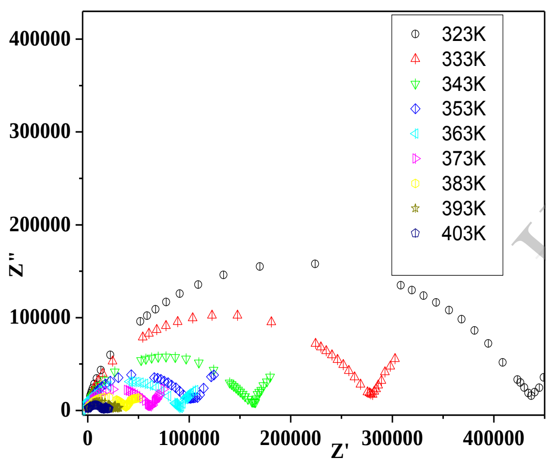

Fig : 2 Complex impedance plots of r= 0.66 sample

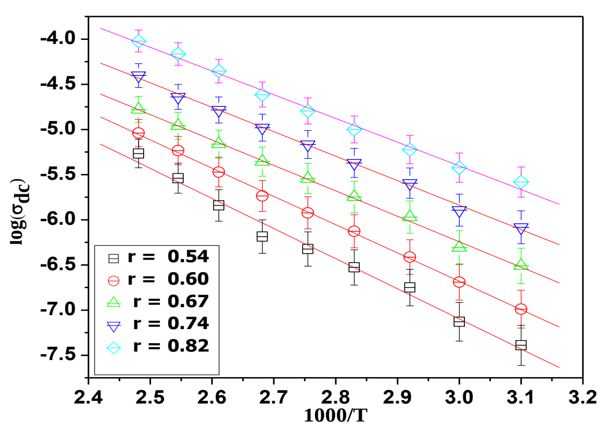

Fig :3 Graphs of log (σ_{dc}) versus 1000/T

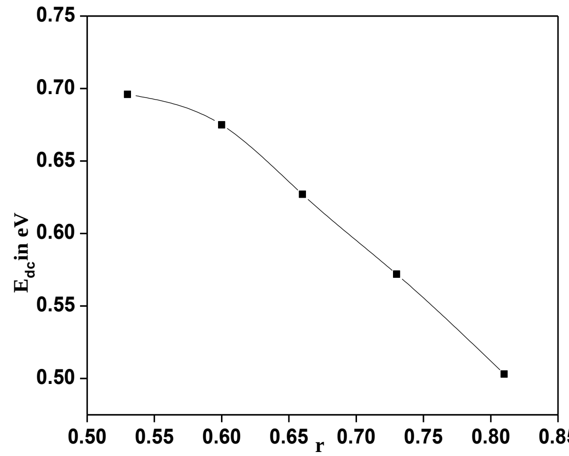

Fig: 4 Variation of activation energy with "r" values

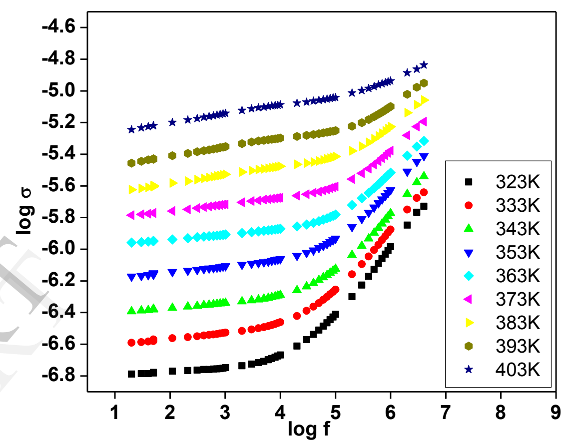

Fig: 5 AC conductivity graphs of r = 0.66 sample

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IV. CONCLUSIONS

Frequency response of sodium-boro-vanadate glasses are studied using an energy efficient time saving microwave method. The ion transport in these glasses show composition, frequency and temperature dependent trends and it is due to the migration of Na^+ ions in modified boro-vanadate network. The dependence of conductivity with temperature follows Arrhenius behavior. Conductivity increases while activation energies calculated from least square fit decreases with increasing Na_2O concentration. A.C conductivity behavior has also been studied and the d-c conductivity extracted from log σ verses log f plots are comparable with the dc conductivity calculated from cole-cole plots.

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