Conductivity Spectra of a New Lithium ion Conductor: Micro-structure, Hopping Frequency and Conductivity-scaling

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Abstract—*A glass-ceramic sample, $0.1Li_2O$-$(0.9)(0.05ZnO$-$0.475MoO_3$-$0.475SeO_2)$ have been prepared using melt quenching route. The study of XRD patterns reveals the dispersal of dissimilar types of nanocrystallites superposing over the amorphous glass-ceramic matrices. The ionic conductivity dependency on frequency and temperature has been established, which follows Jonscher's universal power-law and Almond-West formalism. The variation of activation energy values corresponding to AC conductivity (E_{AC}) with composition has been studied. The frequency independent conductivity (plateau region) in low-frequency zone is caused by sub diffusive motion of Li^+ ions. Moreover, in the high-frequency dispersive region, the conductivity is because of correlated and pseudo-three-dimensional motion of Li^+ ions in percolating networks. The master curve in scaling analysis signifies temperature independency of conductivity relaxation process.*

Keywords: *Glass-ceramics; Composite materials; X-ray diffraction; Ionic conductivity; Li^+ ion migration.*
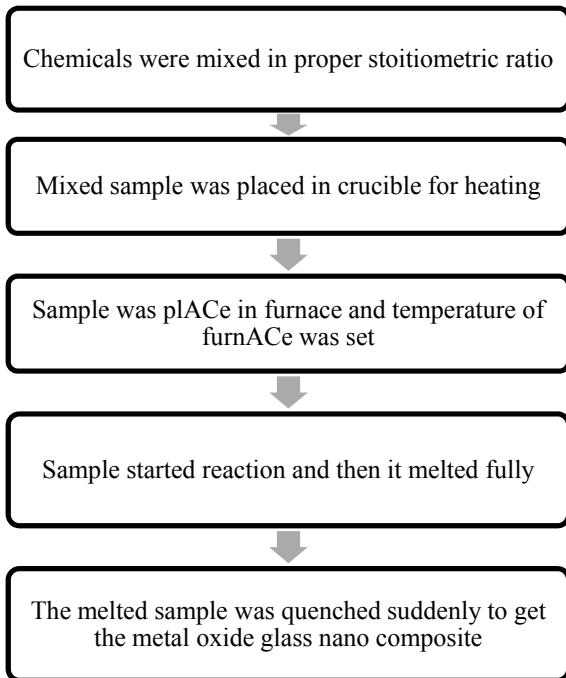
INTRODUCTION:

Physical properties of Nano phased materials are presently of great scientific interest. Improved electrical properties of Nano phased materials, compared to the bulk counter parts are main reason of it. Comparing the electrical and mechanical properties of the conventional materials so far available efforts will be made towards the evolution of a better material suitable for engineering practice. The objective of the present work is to prepare a lithium based glassy systems by conversional melt quenching route and to study its structural and electrical properties like ionic conduction, activation energy, temperature scaling etc. In recent era, lithium is one of the key components of rechargeable batteries, which in hence is the most useful part of most of the human needs today such as electric vehicles, smart phones le computers etc. with the promise of renewable energy storage [1,2].Lithium is indispensable to every glass-ceramic, because of its

responsibility for the products' zero expansion, ensuring their use in high temperature ranges without voltage breakage [3]. After incorporation of suitable metal ions (like molybdenum) to the glassy system, the chemical inertness, thermal stability and also electrical properties can further be improved [4].

EXPERIMENTAL SETUP AND PRECEDURE:

A glass ceramic, xLi_2O-$(1-x)$ $(0.05ZnO$-$0.475MoO_3$-$0.475SeO_2)$ with x=0.1was prepared using familiar melt quenching technique with high purity (≥99%) precursors Li_2O, ZnO, $MoO_3$and SeO_2. These chemicals were mixed maintaining proper stoichiometric ratio in alumina crucible. It was melted in a high-temperature electric muffle furnace in the temperature range 600 K-700 K depending on the concentration of $Li_2O(x)$. To ensure homogeneous mixing, the melts were equilibrated by stirring. The homogeneous melts then were instantly quenched at room temperature (300 K) by pouring it in between two aluminum plates. As a consequence, glassy ceramic was formed of thickness ~ 1 mm. The glass-ceramic flakes were then gently crushed into fine powder for X-ray diffraction, through which the (XRD) patterns were recorded using a Seifert (model 3000P) X-ray diffract meter. The XRD-peaks confirmed the size and distribution of different nano crystallites, grown in the glassy.

Preparation algorithm[5,6]:

Chemicals were mixed in proper stoitiometric ratio

Mixed sample was placed in crucible for heating

Sample was plACe in furnace and temperature of furnACe was set

Sample started reaction and then it melted fully

The melted sample was quenched suddenly to get the metal oxide glass nano composite

RESULT AND DISCUSSION:

Analysis of frequency dependency of ionic conductivity at different temperatures of the present work under investigation reveals: hopping frequency of Li ion, DC conductivity, temperature dependent conductivity and thermally activated nature of mobile ions [7-10].Fig1. Exhibits frequency dependent conductivity plot for the test sample.
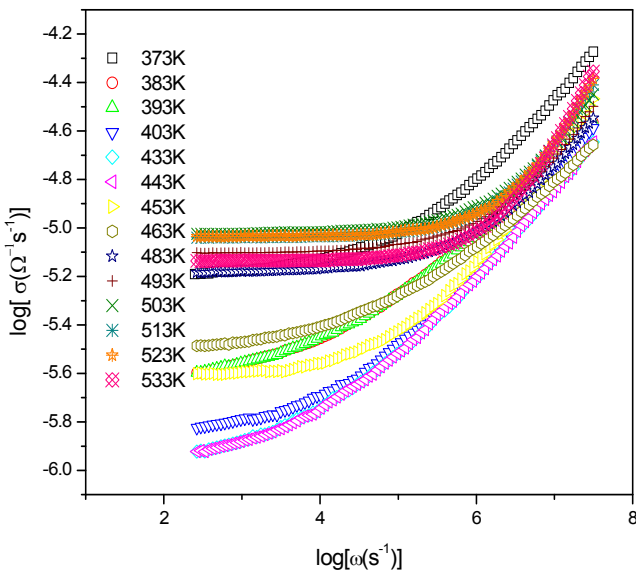
The prime observations in Fig.1 are as follow: (i) the high frequency dispersive region corresponding to AC conductivity caused by correlated and pseudo-three-dimensional motion of Li^+ ions in percolating networks and (ii) the low frequency plateau region corresponding to DC conductivity caused by sub diffusive motion of Li^+ ions[11]. The characteristics of conductivity at both the conductivity regions can be analyzed using Almond-West formalism relation [12,13].

$$\sigma(\omega) = \sigma_{dc}[1 + (\frac{\omega}{\omega_H})^n] \qquad (1)$$

Here,σ_{DC} is the frequency-independent conductivity (DC conductivity),ω_H is hopping/ crossover frequency, which indicates the beginning of the conductivity relaxation process, and is the frequency exponent. It is significantly noted that at ion migration (hopping) frequency, the conductivity spectra show dispersion [11], which are with rise in the temperature shifted towards higher frequencies. Here, the possible reason for the resultant graph may be due to enhancement of kinetic energy and vibration frequency of Li ions .It is also observed from the analysis of Fig. 1 consisting of both DC as well as AC conductivity and onset ion migration frequency are thermally activated with different values of activation energy which is shown in Fig 2 and Fig. 3. This can be described by Arrhenius relation[14,15,16] given as

$$\sigma_{dc} = \sigma_0 \, exp(^{-E_\sigma}/_{k_B T}) \qquad (2)$$

Where $\sigma_0$is the pre-exponential factor, $E_\sigma$is the activation energy corresponding to DC conductivity, k_B is the Boltzmann constant and T is the absolute temperature. The values E_σ, estimated from the least square straight-line fits using Eq. (2)

Fig. 1:Temperature and frequency dependent conductivity of 0.1Li2O-(0.9)(0.05ZnO-0.475MoO3-0.475SeO2)
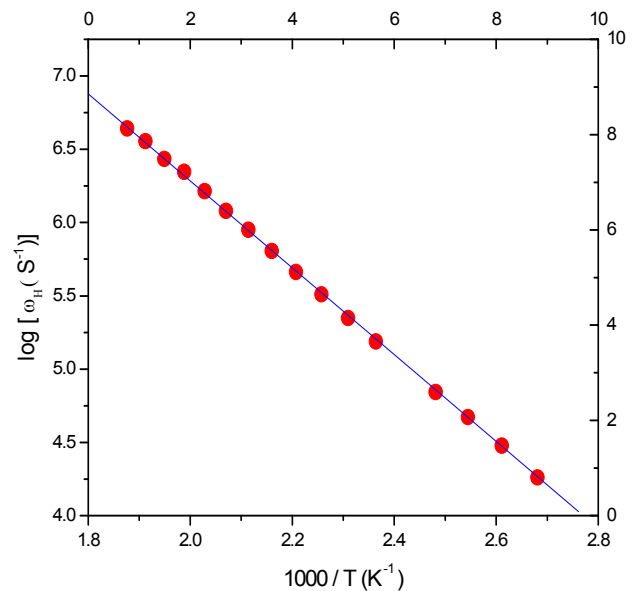

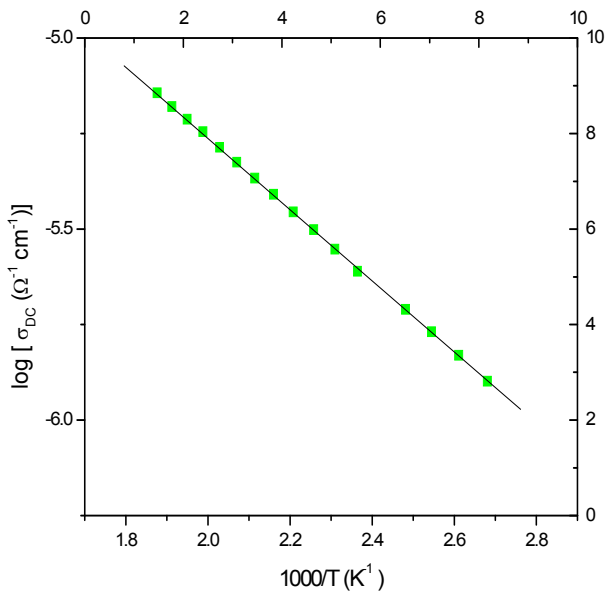**Fig. 2: Temperature dependency of Hopping Frequency**

Fig. 3: Temperature dependency of DC conductivity

In the present study, we used "Ghosh and Pan" scaling approach [17] is adopted successfully. according to linear response theory, in thermal equilibrium we can relate electrical conductivity to the time-dependent displacement of the mobile Li^+ ions and ion dynamics which is represented by a non-random forward and backward hopping process. From this we can predict that, long-time regime requires random walker of ions [18]. The temperature-scaling for conductivity spectra for present glass-ceramic composition using "Ghosh and Pan" scaling approach [17] are shown in Fig. 4.which ensures the conductivity remains unchanged with respect to temperature.
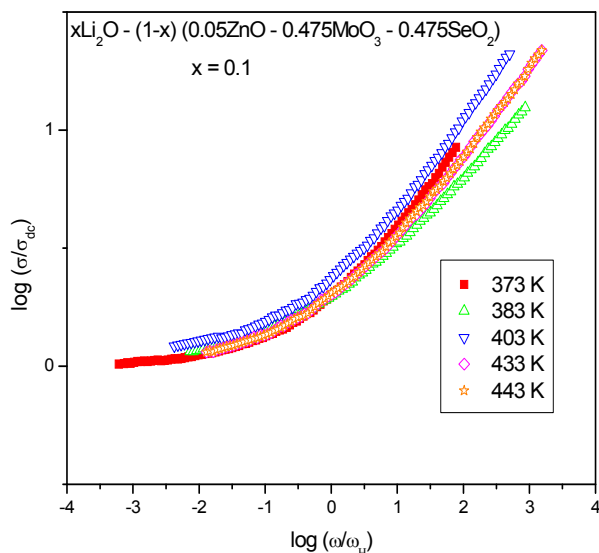

Fig. 4: Temperature Scaling of Conductivity Spectra

X-ray diffraction patterns of the tested glass-ceramic sample has been presented in Fig. 5. The significant long-range order or crystallinity is proven by the presence of many sharp peaks that has been disclosed from Fig. 5. Thus, it can be asserted that the present work composition is mixed-phased (polycrystalline) in nature. With the help of data found by literature survey, the dispersed nano phases within the amorphous matrices have been recognized from different Bragg's angle (2Θ) peaks. A few unidentified peaks, probably owing to impurities or mixed phases, have also been observed with lower intensity. The sizes of nano crystallites have been estimated using Debye-Scherer relation [19,20].

$$d_c = \frac{0.891\lambda}{\beta \cos\theta} \tag{3}$$

Here, β is the full width at half maximum (FWHM), θ is the Bragg's diffraction angle and λ is the wavelength (1.54 Å) of the Cu-Ka-X-ray radiation.
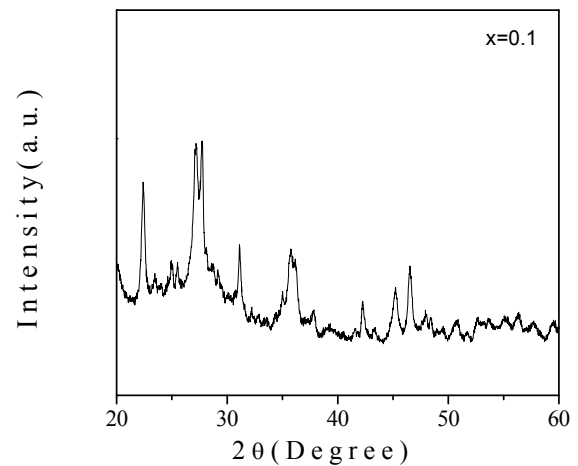

Fig. 5: XRD diffraction pattern of sample

CONCLUSION:

A Li_2O-doped glass-ceramic has been prepared using the conventional melt quenching route. The XRD patterns confirm the presence of nano crystallites of different type and size over the amorphous glass-ceramic matrices. The study of DC ionic conductivity spectra shows the present work obey the Arrhenius law. The temperature dependence of AC conductivity is well fitted to Jonscher's universal power-law and Almond-West formalism. "Ghosh and Pan" scaling approach is used to explore the effect of temperature on the AC ion conduction mechanism and it is found that the ion conduction relaxation mechanism is independent of temperature. Therefore, further investigations on such glass-nano composites might enlighten the way for the development of solid electrolytes having high conductivity and stability for application of solid-state lithium ion batteries.

REFFERENCES:

[1] K. Takada, Progress in solid electrolytes toward realizing solid state lithium batteries, J. Power Sources Vol 394, p. 74-85, 2018.

[2] H. Pan, S. Zhang, J. Chen, M. Gao, Y. Liu, T. Zhu, Y. Jiang, Li- and Mn-rich layered oxide cathode materials for lithium-ion batteries: a review from fundamentals to research progress and applications, Mol. Syst. Des. Eng. Vol 3, p. 748-803, 2018.

[3] E. Zanotto, A bright future for glass ceramics, Am. Ceram. Soc. Bull. Vol 89, p. 19-27, 2010.

[4]. M.C. Rao, K. Ravindranadh, A. Kasturi, M.S. Shekhawat, Structural Stoichiometry and Phase Transitions of MoO3 Thin Films for Solid State Microbatteries,Res. J. Recent Sci., Vol 2p. 67-73, April2 (2013).

[5]. T. Som and B. Karmakar, "Surface plasmon resonance in nano-gold antimony glass–ceramic dichroic nanocomposites: One-step synthesis and enhanced fluorescence application",Appl. Surf. Sci., Vol. 255, p. 9447, 2009.

[6]. T. Som and B. Karmakar, "Plasmon tuning of nano-Au in dichroic devitrified antimony glass nanocomposites by refractive index control", Chem.Phys. Lett., Vol. 479, p. 100, 2009.

[7] S.R. Elliott, Frequency-dependent conductivity in ionic glasses: a possiblemodel, Solid State Ionics Vol27 ,P.131-149,1988.

[8] D.P. Almond, A.R. West, Mobile ion concentrations in solid electrolytes froman analysis of A.C. conductivity, Solid State Ionics Vol.9, p. 277-282, 1983.

[9] K. Funke, R.D. Banhatti, Ionic motion in materials with disordered structures,Solid State Ionics Vol. 177, p. 1551-1557, 2006

[10] K.L. Ngai, A.K. Rajagopal, S. Teitler, Slowing down of relaxation in a complex system by constraint dynamics, J. Chem. Phys. Vol. 88, p. 5086-5094 ,1988.

[11] D.P. Almond, A.R. West, Anomalous conductivity refactors in fast ion conductors, Nature Vol.306, p. 456-457,1983.

[12] D.P. Almond, G.K. Duncan, A.R. West, The determination of hopping rates and carrier concentrations in ionic conductors by a new analysis of AC conductivity, Solid State Ionics vol. 8, p.159-164 ,1983.

[14] S.B. Aziz, T.J. Woo, M.F.Z. Kadir, H.M. Ahmed, A conceptual review on polymer electrolytes and ion transport models, J. Sci.: Advanced Materials and Devices Vol. 3, p. 1-17, 2018.

[15] M.D. Ingram, Ionic conductivity in glass, Phys. Chem. Glasses vol. 28, p. 215-234, 1987.

[16] A.S. Das, D. Biswas, M. Roy, D. Roy, S. Bhattacharya, Effect of V2O5concentration on the structural and optical properties and DC electrical conductivity of ternary semiconducting glassy Nanocomposites, J. Phys. Chem. Solid. Vol. 124, p. 44-53, 2019.

[17] A. Ghosh, A. Pan, Scaling of the conductivity spectra in ionic glasses: dependence on the structure, Phys. Rev. Lett. 84 (2000) 2188-2190.

[18]A.S. Das, M. Roy, D. Biswas, R. Kundu, A. Acharya, D. Roy, S. Bhattacharya, A.C. conductivity of transition metal oxide doped glassy nanocomposite systems: temperature and frequency dependency, Mater. Res. Express vol. 5, p. 1-10, 2018.

[19] B.D. Cullity, Elements of X-Ray Diffraction, Addison-Wesley, Philippines, Chap. 9 ,p. 1-284, 1978.

[20] H.M. Xiong, X. Zhao, J.S. Chen, New polymer - inorganic Nanocomposites: PEOZnO and PEOZnOLiClO4 films, J. Phys. Chem. B Vol. 105, p. 10169-10174, 2001.