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Raman and AC Conductivity studies of ZnO doped CaO-TeO_2-B_2O_3 glasses

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Abstract
Glass series of different ZnO content with composition xZnO.10CaO.30TeO$_2$.(60-x)B$_2$O$_3$; (x=0 to 20 mol % with a of 5 mol %) was fabricated by conventional melt quenching method. The non-crystalline nature of the produced glasses were verified by X-ray diffraction analysis. The Raman spectra confirmed different vibration modes of constituents of glass matrix and also the structural changes with varying ZnO content. To study transport properties, AC conductivity measurements were carried out on the glass system in the frequency range 5Hz-35MHz. The conductivity have been studied in two regions as frequency dependent and frequency independent. It is also purely a function of temperature. The conductivity results were good at high temperature and frequency. For all studied glasses, the conductivity enhanced by almost three orders in both regions. The highest conductivity was observed for high ZnO containing BTCZ-4 sample. It was also observed that the ionic conductivity plays significant role. The samples connected with high frequency and high temperature were shown the best results. The highest value of AC conductivity of the glass network is of the order 10^{-3} $\Omega^{-1}cm^{-1}$.Cole-Cole Impedance plots were exhibited semi-circular behavior with decreasing radius.

Keywords: *Raman studies, Structural studies, AC conductivity, Cole-Cole plots*

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I. Introduction

Glassy materials made up of oxides have gained prominence due to transparent nature, high viscosity and chemical durability as well as many different peculiar and interesting properties. A lot of industrial applications are made possible, especially in the area of optics as well as opto-electronics. Glasses made up of borate oxide, in particular, have high thermal stability and good solubility, making them promising materials for a large number of technological applications [**1-3**]. The crystals and glassy materials containing borates, the boron atom is generally co-ordinated with either three or four oxygen atoms, that forms [BO_3] pyramidal or [BO_4] tetrahedral structural units which are fundamental. These [BO_3] and [BO_4] units can randomly form either the supposed superstructure or B_xO_y structural groups like diborate, tetraborate, pentaborate, boroxal-ring. Glasses incorporated with ZnO and TeO_2 are of particular attention various areas of optical and electronics based materials [**4-6**]. Structural characteristics of the glasses containing ZnO, depends on the nature of other glass former oxides present in the network. In the recent days, there is a focus on the ZnO containing glasses owing to their manifold uses as antibacterial and bio sensors, photo-transistors, transparent electrodes, solar cells as well as diodes.

AC conductivity measurements provide useful information concerns various dielectric relaxation phenomena related to the electrical or dielectric polarization process [**7-8**]. The characteristic hopping lengths and hopping rates of carriers between localized states can be determined with high frequency measurements; on the other side low frequency data is more sensitive to slower relaxation process like the reorientation of dipoles etc.

Chemistry and physics both employ Raman spectroscopy to determine the structural properties of substances. The wave number and intensity of an element's inelastic scattered light are measured in a Raman spectrum. The Raman scattered light has distinct wavelengths from the incident light because molecular vibrations have different energy. It has to do with the electron cloud around the molecule's ability to be polarised. The majority of photons are elastically scattered when light is scattered from a molecule or an amorphous material. Changes in a substance's vibrational, rotational, or electrical energy result in Raman

scattering. When a light source's energy does not change, a phenomenon known as Rayleigh scattering takes place. If the substance is not elastic, the process is referred to as Raman scattering.
The present article focused on the influence of ZnO on the Raman and conductivity of calcium-borotellurite glass system. Raman spectroscopy are also done to get the information of the structure of the neighbourhood structure of CaO-TeO_2-B_2O_3 based glasses. In this paper we have discussed the behaviour of ZnO in these glasses i.e., in the presence of two glass forming oxides namely classical glass former B_2O_3 and conditional glass former TeO_2 interestingly.

II. Material And Methods

Preparation of glasses

ZnO doped glasses with chemical compositions x ZnO-10CaO-30TeO_2-(60-x) B_2O_3- where x values lies from 0 to 20 mol% with 5 variation were synthesized by rapid melt-quench route. AR grade B_2O_3, ZnO (Sigma), B_2O_3 (AR grade) were taken for preparation of the glass samples. About 15 grams of oxides powder are taken in a crucible made of porcelain, and melted at 1000-1050 ^oC for 1hr. The powder melted and formed liquid. The liquid in the crucible was agitated/swirled frequently for 1 hr to form a homogeneous liquid melt. The crucible with melt was emptied on a steel plate which is at 200^oC and hard-pressed using another steel disc which is also at 200^oC which resulted in the formation of glasses. The prepared glassy samples were annealed at around 200 ^oC for 24 hours for removal of thermal stress and strain and also to avoid cracking of glass samples. The glass samples thus obtained were good transparency and light chocolate colour. The glass formation was confirmed with the transparency and uniformity.

Raman spectra

The micro Raman spectrum of the obtained glasses was recorded on LABRAM HR-800 model spectrometer at the room temperature in the range of 200-2000 cm^{-1} with spectral resolution 2cm^{-1}. LASER was used for excitation of the atoms.

AC conductivity analysis:

The glasses were prepared in the button shape of dimensions 2mm thickness and 10mm diameter for the AC conductivity measurement. After measuring the cross-section area (A) of the glasses, they were coated with silver paste. It enhances the accessibility between the sample and electrodes of the measuring device. The data was recorded in the frequency range 5Hz-35MHz on the LCR meter. The range of temperature was room temperature to 350^oC with 50^oC variation. Determination of AC conductivity was done by the following [**9-11**]

$$\sigma_{ac} = \omega\varepsilon^{/}\varepsilon_0 tan\delta \qquad (1)$$

where $\varepsilon^{/}$ and ε_0 are the dielectric permittivity in material and vacuum, respectively. tan δ- represents the dielectric loss.

The plot of Cole-Cole impedance was drawn by the following;

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

$$Z'' = \frac{\omega C}{(G^2 + \omega^2 C^2)} \qquad (3)$$

Where $Z^{/}$ and $Z^{//}$ are the real and imaginary complex impedance, respectively.

III. Results and Discussion

Raman spectra of BTCZ glass samples Series

In the BTCZ glass series, Zn-O molar percentage rises 0 to 20 with a 5 variation, whereas B_2O_3 concentration decreases from 60 to 40 molar ratio and TeO_3 concentration remains the same. **Figure 1**illustrates the Raman spectra of the synthesized glass series of (60-x) B_2O_3-30TeO_2-10CaO-xZnO (where x=0, 5, 10, 15, & 20). Three broad, high-intensity peaks were mostly seen in this series of Raman spectra about 458 cm^{-1}, 625 cm^{-1}, and 755 cm^{-1}. A few weaker peaks were also seen around 220 cm^{-1}, 650 cm^{-1},1150 cm^{-1}, 1138 cm^{-1}, and 1350 cm^{-1}.

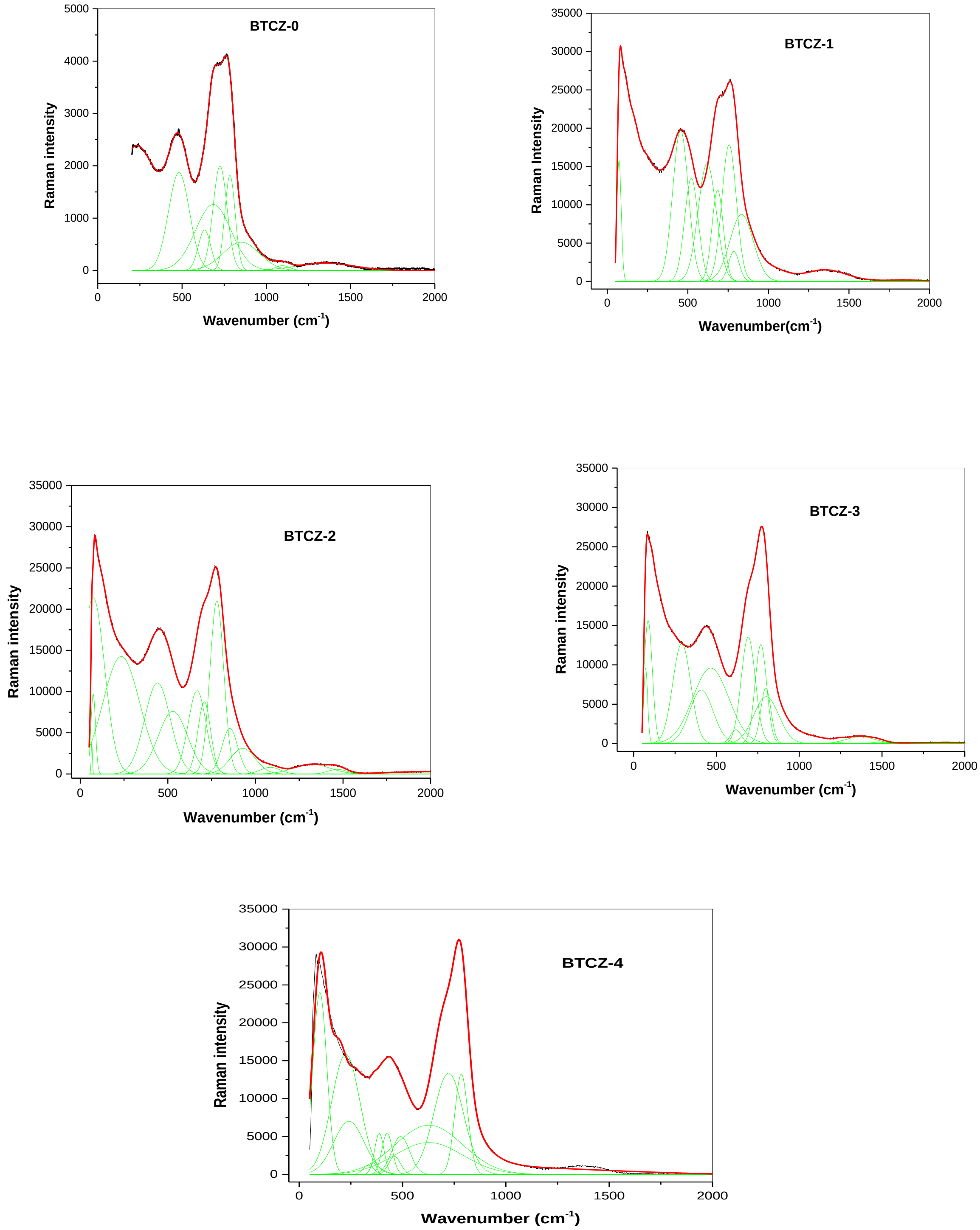

Fig.1Deconvoluated Raman spectra of BTCZ glass system

Te-O-Te bond linkage bending vibrations have a broad peak in the 458 cm^{-1} range. Another peak was detected between 625 and 755 cm^{-1}, which may have been caused by the Te-O bond in the TeO$_4$ structural unit [12-14]. The vibrations of the Te-O linkage in the TeO$_3$ structural unit are responsible for a large, high intensity peak in the 763 cm^{-1} regions.

The peak of the 220 cm^{-}1wavenumber region is the linkage of the Zn-O atoms in the structural unit of ZnO$_4$. A second small peak that was seen in the 1150 cm^{-1}wavenumber range was caused by the bending vibrations of the B-O-B connection [15-17]. The B-O stretching vibrations in BO$_3$ units from borate groups have a peak at about 1373 cm^{-1}.In this series of glass samples 220-236 cm^{-1}, 458-462 cm^{-1}, 625-696 cm^{-1}, 755-763 cm^{-1}, 1150-1180 cm^{-1}and 1373-1351 cm^{-1} wavenumber region peaks were observed. Wave number region peak at 220-236 cm^{-1} is related to the Zn-O linkage of ZnO$_4$ structural unit. Te-O-Te bond bending vibrations have a broad, high intensity peak at 458–462 cm^{-1}. Peaks in the 625-696 cm^{-1}range are associated with the Te-O bond linkage in the TeO$_4$ structural unit. Around 755-763 cm^{-1}, a second broad, high-intensity peak was seen; this peak corresponds to the Te-O bond connection in the TeO$_3$ structural unit. The B-O bond linkage is represented in the 1150-1180 cm^{-1}wavenumber region peak. Furthermore, the peak of the wavenumber region between 1373 and 1351 cm^{-1} corresponds to the BO$_2$-O triangular bond coupling in the BO$_4$ structural unit [18-20].

Table.1. Band assignments of Raman spectra of BTCZ glass system

Characteristic bands	Assignment
220-236 cm^{-1}	Ca-O linkage of cationic structural unit.
458-462cm^{-1}	Te-O-Te bond bending vibrations.
625-696 cm^{-1}	Te-O bond linkage in TeO$_4$ structural unit
755-763 cm^{-1}	Te-O bond linkage in TeO$_3$ structural unit
1150-1180 cm^{-1}	B-O bond linkage BO$_3$ structural unit
1373-1351 cm^{-1}	BO$_2$-O triangular bond linkage in BO$_4$ structural unit.

3.2 AC conductivity

Figure 2 depicts the variation of frequency dependent AC conductivity of the BTCZ system at different temperatures.It was found to increase with applied frequency and temperature supplied to the sample. It was also found to be the highest value at 350^{o}C for all the glass samples in the order of 10-4 Ω^{-1}cm^{-1}. σ_{ac} almost frequency independent in the low frequency domain and strongly dependent in the high frequency domain. The low frequency region also considered as the dc conductivity region in which the conductivity varied from 10-8 Ω^{-1}cm^{-1}to 10-6 Ω^{-1}cm^{-1}. The conductivity values obtained from Cole-Cole plots is the same as the σ_{ac} in the low frequency domain [21-23]. High ZnO containing glasses were shown the higher order conductivity. BTCZ-0 sample was shown the highest impedance than the Zinc containing BTCZ-4 sample was shown the lowest impedance and highest conductivity over the remaining samples in the glass system.

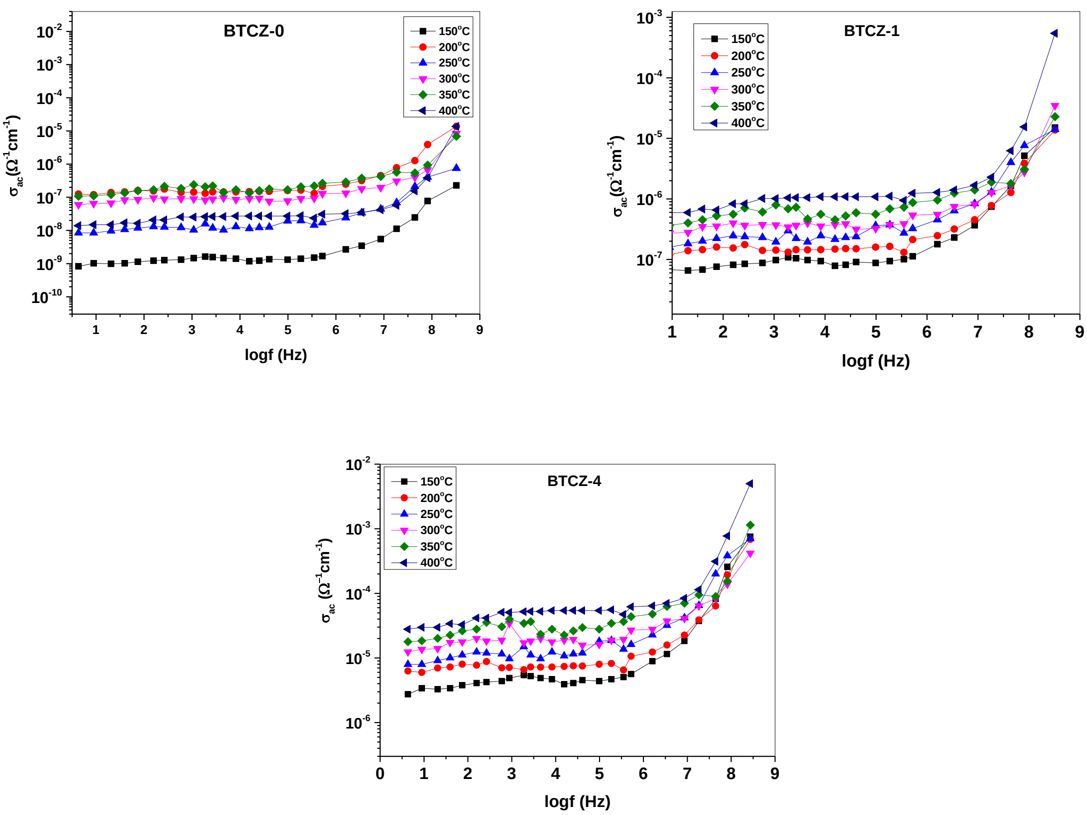

Fig.2Variation of AC conductivity of BTCZ glass system with logf

Cole-Cole plots

Figure 3shows the Cole-Cole impedance plots of BTCZ-0, BTCZ-1 & BTCZ-4 samples. At low temperatures, the impedance Cole-Cole plots did not give good results due to the in homogeneities in the glass samples. At 100^{o}C, all the glass samples show single semicircle in the impedance plots which may be due to bulk effects. At high temperatures, the impedance plots of high ZnO containing glasses also shown single semicircle only [24-28]. The radius of the semicircle is decreasing with increase of temperature and modifier content for all the glass samples containing high ZnO content. Appearance of semicircle below the real axis indicates that the sample-electrode system in which the relaxation time distributes continuously and it is not single valued. The electrode-sample interface dispersion is more pronounced in the low frequency region, and in the high frequency region the depressed semicircle may be due to the dispersive behavior of the glass bulk resistance or the sample bulk resistance.

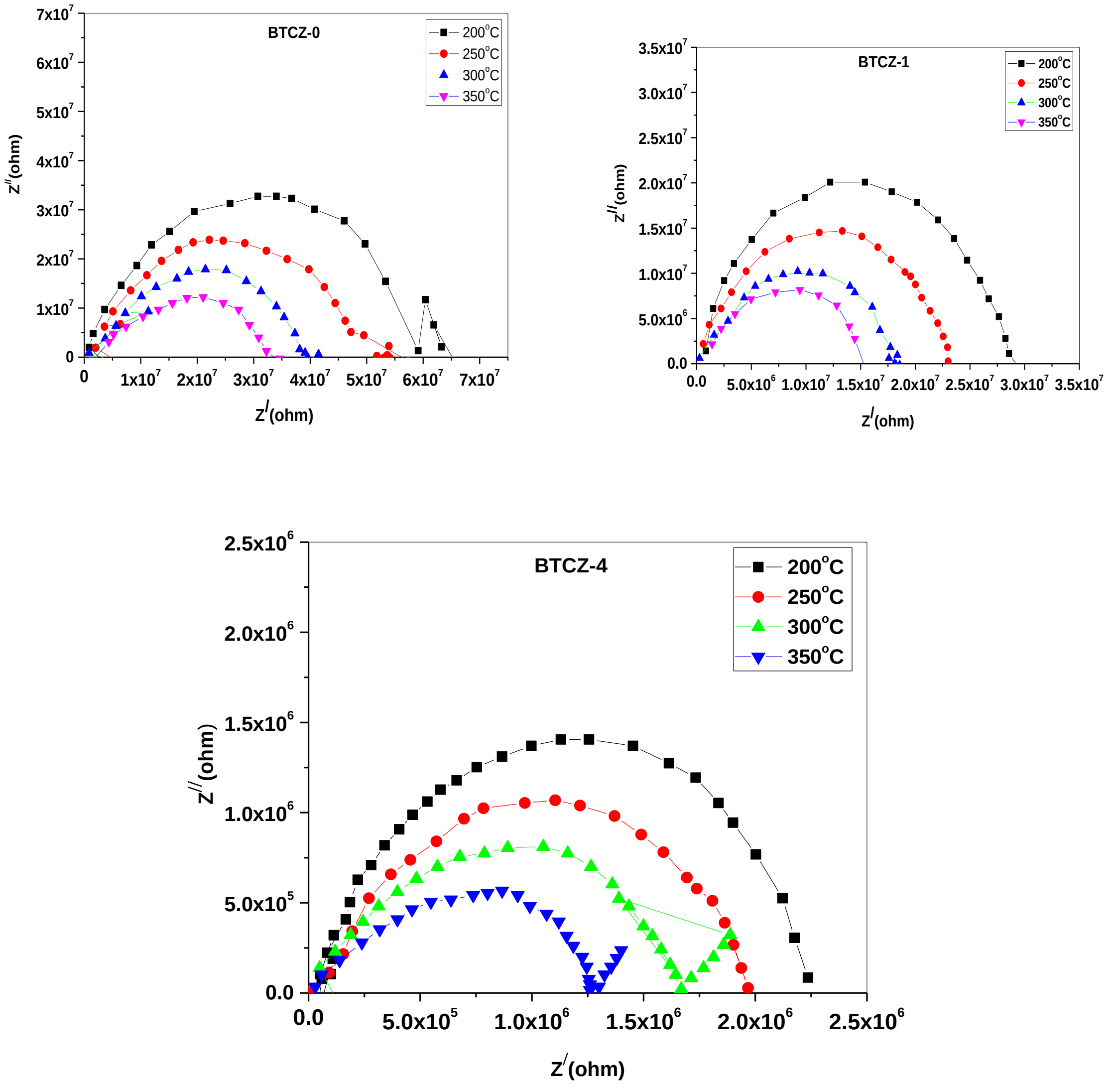

Fig.3. Cole-Cole plots of BTCZ glass system

IV. Conclusion

The selected glass composition was prepared by melt quench route. The Raman spectra of the studied glasses conforms the clear variations in the glass structure with different mole percentages of network modifier ZnO. It also showed the Te-O-Te bond linkage bending vibrations, Te-O linkage in the TeO$_3$, structural linkage of the Zn-O atoms in the structural unit of ZnO$_4$, B-O stretching vibrations in BO$_3$ units were presented in the glass matrix along with metal oxide bonds in the low-frequency domain. AC conductivity was enhanced with increasing temperature, frequency and also dopant content. The Cole-Cole impedance behavior was confirmed with the semicircles presented in the plots. The decrease in radius of the semicircle confirmed the increase of conductivity and decrement in bulk resistance with increasing temperature.

References

[1]. J. Zhong, P.J. Bray, J. Non-Cryst. Solids. 111 (1989) 67-76.
[2]. G. Ferlat, A.P. Seitsonen, M. Lazzeri, F. Mauri, Nat. Mater.11 (2012) 925–929.
[3]. B.N. Meera, J. Ramakrishna, J. Non-Cryst.Solids. 159 (1993) 1-21.
[4]. A.C. Wright, N.M. Vedishcheva, Phys. Chem. Glasses Eur. J. Glass Sci. Technol. B 54 (4) (2013) 147–156.
[5]. C.E. Stone, A.C. Wright, R.N. Sinclair, S.A. Feller, M. Affatigato, D.L. Hogan, N.D. Nelson, Y.B. Dimitrov, E.M. Gattet, D. Ehrt, Phys. Chem. Glass. 41(2000) 409-412.
[6]. A. Pan, A. Ghosh, J. Non-Cryst. Solids. 271 (2000) 157-161.
[7]. L. Srinivasa Rao , M. Srinivasa Reddy , D. Krishna Rao , N. Veeraiah ,Solid State Sciences 11 (2009) 578–587
[8]. S. Bale, S. Rahman, Materials Research Bulletin 47 (2012) 1153–1157.
[9]. F. A. Abdel-Wahab,J Mater Sci (2014) 49:720–728 DOI 10.1007/s10853-013-7753-3
[10]. Da-Wei Fu, Hong-Ling Cai, Yuanming Liu, Qiong Ye, Wen Zhang, Yi Zhang, Xue-Yuan Chen, Gianluca Giovannetti, Massimo Capone, Jiangyu Li, Ren-Gen Xiong,Science, 2013,339,425-428.
[11]. Da-Wei Fu, Wen Zhang, Hong-Ling Cai, Yi Zhang, Jia-Zhen Ge, Ren-Gen Xiong, Songping Huang, J. Am. Chem. Soc., 2011, 133, 12780-12786.
[12]. EI Kamitsos, MA Karakassides, GD Chryssikos,Phy. Chem. of glass. 28 (5)(1987) 203-209.
[13]. Kamistos E.I., Patsis A.P., Karakassides M.A. and Chryssikos G.D., J. Non-Cryst. Solids. 126(1990) 52-67.
[14]. Toderas M., Filip S, Ardelean I., J. Opt.elec. and Adv. Mater.8 (2006)1121.
[15]. Chandkiram Gautham, Avadesh Kumar Yadav, Arbindh Kumar Singh, ISRN Ceramics. 428497(2012).
[16]. P. Gayathri Pavani, K. Sadhana,V.Chandra Mouli, Physica B. 406 (2011)1242–1247.
[17]. E.I. Kamitsos and G.D. Chryssikos, J. Mol. Struct. 247 (1991) 1-16.
[18]. M. Anand Pandarinath, G. Upender, K. Narasimha Rao, D. Suresh Babu, Journal of Non-Crystalline Solids 433 (2016) 60–67
[19]. E. I. Kamitsos,M. A. Karakassides,G. D. Chryssikos,J. Phys. Chem. 1987, 91, 5, 1073-1079
[20]. Swapna, G. Upender, M. Prasad. J. Taibah Univ. Sci. 11 (2016) 583–592.
[21]. Pallati Naresh, A. Padmaja, K. Siva Kumar, Materialia. 9(2020)100575.https://doi.org/10.1016/j.mtla.2019.100575
[22]. P. Naresh, B. Kavitha, H. K. Inamdar, D. Srinivasu, N. Narsimlu, Ch. Srinivas, V. Sathe, K. Siva Kumar, J.Non.Cryst.Solids.514(2019)35-45.
[23]. P. Naresh, B. Kavitha, D. Srinivasu, N. Narsimlu, Ch. Srinivas, Uday Deshpande, K. Siva Kumar, AIP conf. proceedings, 1953 (2018) 090079.
[24]. Hajeebaba K. Inamdar, Narsappa Reddy, S.Abdul Khader, Pallati Naresh, M.V.N. Ambika Prasad, G.S. Durga Prasad, Composite. Communications. 14 (2019) 21-28.
[25]. D. Ravi Kumar, Ch Abraham Lincoln, G. Vijaya Charan, Gugulothu Thara, D. Ravinder, M. Veeraswamy, Pallati Naresh,Materials Chemistry and Physics,278(2022)125648
[26]. Pallati Naresh, N. Narsimlu, Ch. Srinivas, Md. Shareefuddin, K. Siva Kumar, J. Non. Cryst. Solids.549 (2020) 120361.
[27]. Pallati Naresh, A. Padmaja, K. Siva Kumar,Materialia. 9(2020)100575.
[28]. B. Srinivas, Ashok Bhogi, Pallati Naresh, Abdul Hameed, M. Narasimha Chary, Md. Shareefuddin ,Journal of Non-Crystalline Solids, 575(2022)121218

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