INTERNATIONAL JOURNAL FOR INNOVATIVE RESEARCH IN MULTIDISCIPLINARY FIELD ISSN: 2455-0620 Volume - 6, Issue - 1, Jan – 2020
Monthly, Peer-Reviewed, Refereed, Indexed Journal with IC Value: 86.87 Impact Factor: 6.497
Received Date: 03/01/2020 Acceptance Date: 16/01/2020 Publication Date: 31/01/2020

AC conductivity and dielectrics studies in potassium, strontium doped boro-phosphate glasses

[1] Anand Thipperudra, [2] N.Nagaraja*, [3] M. Prashanth Kumar. [4] B. Arun kumar
[1] Asst. Prof., [2] Professor, [3] Professor, [4] Asst. Prof.
[1, 2, 3] Department of Physics,
[1, 2,] R.Y.M. Engineering College Ballari, Karnataka, India.
[3] Government first grade college Kalaburagi. [4] Government first grade college Shahapura.
Email – [1] anand.tippeswamy@gmail.com, [2] nagphysics@gmail.com,

Abstract: *A composition of alkali and alkaline doped borophosphate glasses, of the composition 20(B_2O_3) + 30(P_2O_5) + x (SrO) + (50-x) (K_2O) where x = 10, 20, 30, 40 and 50 were prepared by the standard melt quenching method at 1200K. The amorphous nature was confirmed by XRD studies and dc and ac components of the conductivity were determined. And investigated for dielectric properties in the frequency range from 100Hz to 1MHz and temperature range from 300K to 573K. The conductivity was derived from the dielectric spectrum. The dielectric constant and loss were observed to be decreased with increase in frequency and that has been ascribed to the decrease in ionic contribution with increase in frequency. It is for the first time that the alkali and alkaline doped borophosphate glasses have been investigated for dielectric properties and conductivity over wide temperature and frequency ranges and the data have been subjected to a thorough analysis.*

Key Words: *Boro-Phosphate glasses, SrO, K_2O, ionic conductivity, NBO's.*

1. INTRODUCTION:

The glassy state announce that "it is an amorphous solid completely lacking in long range periodic atomic structure and exhibiting a region of glass transformation behaviour" [1]. The glasses are amorphous materials and in which no long range lattice symmetry can be observed. Structurally glasses are unstructured and chemically insulators, glasses are typically brittle and optically transparent. Glass is now recognized as one of the major scientific material in the branch of materials science due to its wide range of applications. Experimental studies on phosphate and borate glasses have been limited by their hygroscopic nature [2]. However, addition of borate to the Phosphate glasses, and TMI elements was found to increase glass transition temperature and also improve the conductivity and chemical durability of the glasses [3]. Borophosphate glasses doped with alkali, alkaline earth and TM ion materials was found wide applications in scientific, technical and domestic such as, electrolytes in solid state batteries, electrochemical cells, fast ion conductors, switches in electronic circuits, reference electrodes, Fuel cells, super-capacitors and electro-chromic displays etc. [4]. Electrical studies in oxide glasses containing transition metal ion (TMI) and alkali ions are investigated owing to interest in their conduction mechanisms and their other properties. The studies in pure borate and phosphate glasses have limitations due to their hygroscopic nature despite the fact they posses low melting temperatures and can be easily prepared. However, addition of few boron atoms into phosphate glass network lead to enhanced chemical durability and improved thermal properties [5-8]. Ionic conduction in Ag_2S doped silver phosphate glasses have been studied for frequencies up to 60 GHz and temperature up to 413K. Conductivity obeyed power law type variation with progressive increase with frequency [9, 10]. The Ionic conductivity in glasses arises mainly from the dynamics of mobile ion hopping from one ionic site to next ionic site which exhibit ionic conductivity and is generally assumed that cations move into equivalent sites [11]. In 1833 Michael Faraday was first discovered Ionic conduction in solid state materials, who detected high ionic conductivity in Ag_2S and PbF_2 at higher temperatures [12]. Goodman (1975) suggested that there is a natural tendency for foreign alkali cations to plate out onto the surfaces of the clusters which blocks the preferred pathways and the diversion of the current onto clusters [13]. The ionic conductivity in oxide glass systems doped with alkali and alkaline earth ions is due to migration of ions from one ionic site to another ionic site by hopping. However the amorphous structure and non-equilibrium nature of oxide glass systems often hinder the fundamental understanding of their ionic transport mechanism [14]. Generally the fast ion conducting glasses are formed by three components; glass network former, metal oxides acting as a glass network modifier and dopant cations. The glass network formers are oxide materials of covalent nature, the assembly of oxygen tetrahedral or trigonals for example B_2O_3 and P_2O_5 etc [15]. In ion conducting glasses the electronic contribution to the total conductivity is usually very weak, which is the consequence of periodic potential fluctuations imposed by the disordered structure [16]. For increasing the ionic conductivity of glasses, different approaches were adopted. The addition of metal salts (halides,

sulphates) to alkali glasses is found to increase the ionic conductivity [17-19]. The host glass system contains BO_4, PO_4, BPO_4 tetrahedra and BO_3 triangles to which no bridging oxygens are attached. Incorporation increases number of NBOs and ion expands the glass network increasing the ion mobility. Different ionic transport models were proposed to explain the ionic conductivity of glass systems [20-21]. Ionic conductivity in glasses arises mainly from the dynamics of ion hopping. A diffusive model contributes to the D.C. ionic conductivity. In ion transport theories it is generally assumed that the cations move into equivalent sites which are equivalent NBO environments [22].

2. EXPERIMENTAL TECHNIQUE

By following melt-quenching technique the glasses were prepared by using analytical grade relevant chemicals. The chemicals in appropriate weight ratios were melted in a silica crucible placed at high temperature electric furnace at 1500 K. The melt was quenched to room temperature. The random pieces of the glasses were collected, annealed and their glassy nature was confirmed by XRD studies. The glasses were cut to the required size (3 mm X 2 mm X 2 mm) and coated with silver paint on either sides of the surface. The measurements of capacitance, C and dissipation factor, tan δ, were carried out in a computer controlled impedance analyser (Wayne Kerr, 6520B) for the frequency range from 100 Hz to 1 MHz and temperature from 300 to 600 K [23].

3. DISCUSSION AND RESULT:

Electrical conductivity

The measured total conductivity in terms of frequency is generally expressed as

$$\sigma_{Total} = \sigma_{dc} + \sigma_{ac} \quad (1)$$
$$= \sigma_{dc} + Aw^{S}$$

Where σ_{dc} is the frequency-independent component, A is a temperature dependent constant, s is the frequency exponent and ($\sigma_{ac} = Aw^{S)}$ represents ac or dissipative contribution to the total conductivity, which depends on frequency, temperature and composition of the sample [24].

DC conductivity

The conductivity values at 500 K were in the range of $3.13x10^{-6}$ $(ohm\text{-}m)^{-11}$ to $3.75x10^{-08}$ $(ohm\text{-}m)^{-1}$ and DC activation energy W_{dc} values were determined and are in the range of 0.63 eV to 1.01 eV. The data are comparable with that of reported values for similar kind of glasses in literature [25, 26]. The high temperature activation energy decreases and conductivity increases up to x = 30 mole fractions of K_2O. For further increase in K_2O ion concentration, the activation energy increases and conductivity decreases. The variation of activation energy and conductivity as a function of '*x'* mole fractions of K_2O is shown in fig. (2). Because of addition of two different cation species in to the glass matrix, among two, the species of one type ions such as K_2O ions dominating to contribute to the conductivity. That is due to mobility or diffusion of K_2O ion species in the glass matrix greater than alkaline earth K_2O ions, Because of less mobility of K_2O ion it contribute less to the conductivity in the present series of glasses. In the oxide glasses doped with alkali and alkaline earth ions, the alkali ions contribute more and the alkaline earth ions less to the conductivity [27, 28]. Hence in the present studies initially the conductivity increases up to 30 mole fraction of K_2O where within this composition range both SrO and K_2O ions contributing to the conductivity. Above the 30 mole fraction of the SrO ions where in the composition region the K_2O ion concentration decreases hence the conductivity decreases. This is because of less mobile SrO and more mobile K_2O ions and the ratio of mobile ion concentration go on reducing by the addition of SrO. This nonlinear variation of activation energy and dc conductivity in studied composition range of present series glasses is attributed as mixed cation effect is taking place [29, 30].

AC conductivity

The σ_{dc} values were subtracted from the total conductivity and obtained pure ac component, as per the expression given in Eq. (1). The ac conductivity of the present glasses was observed to be increasing with temperature in the same fashion as that of dc conductivity. The ac conductivity increased with increase in frequency. As an example, plots of ln ($\sigma_{Total}T$) versus reciprocal temperature at different frequencies for all the BPSK glasses are depicted in Fig.(3).

The ac activation energy, Wac, was determined from the slopes of the linear fits. The Wac values thus obtained at three different frequencies for BPSK5 glass are recorded in Table1. From the table, it can be noted that the ac activation energy decreases with frequency in all the present glasses. The compositional dependence of ac conductivity (at 500K and 100 kHz) and activation energy for the present glasses is shown in Fig.(1). similar kind of analysis has been carried out on the ac conductivity data of all the glasses. The observed trend of change of W_{dc} with composition is found to be the same as that.

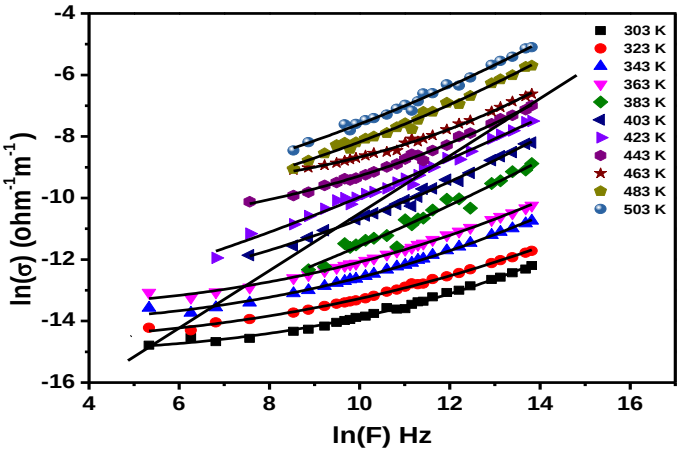

Fig.1. The plots of total conductivity, ln (σ), versus ln (F) for BPSK30 glasses.

Table.1. Variation of dc activation, W_{dc} and ac activation energy, W_{ac} at different frequencies for BPSK glasses.

Glass	W_{dc} (eV)		W_{ac} (eV)	
		10 KHz	50 KHz	100 KHz
BPSK10	0.521	0.527	0.521	0.526
BPSK20	0.486	0.482	0.489	0.499
BPSK30	0.221	0.255	0.298	0.308
BPSK40	0.483	0.481	0.483	0.474
BPSK50	0.182	0.184	0.182	0.188

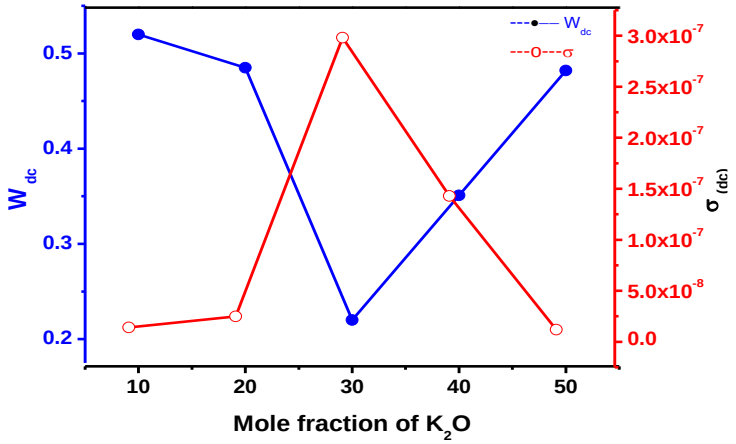

Fig.2. Plot of DC Conductivity, DC activation energy with mole fraction of K_2O

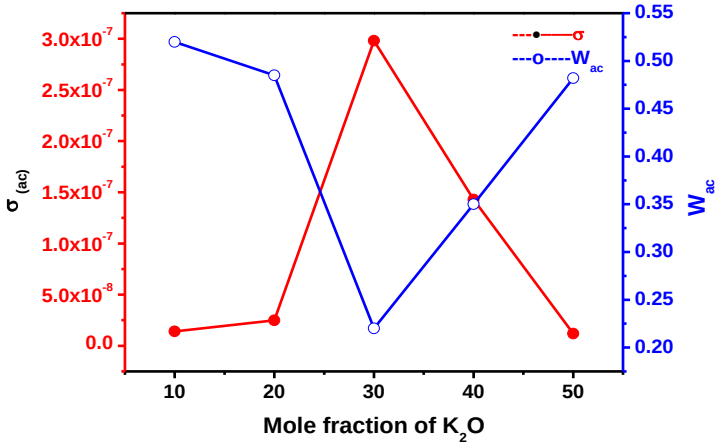

Fig.3. Plot of AC Conductivity, AC activation energy with mole fraction of K_2O

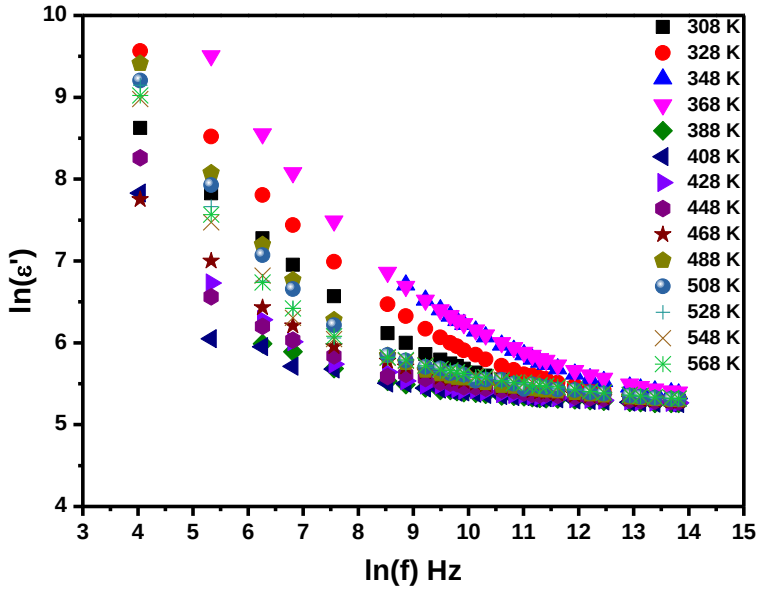

Fig.4. Plots of ln (ε′) versus ln (F) for BPSK30 glass at different temperatures.

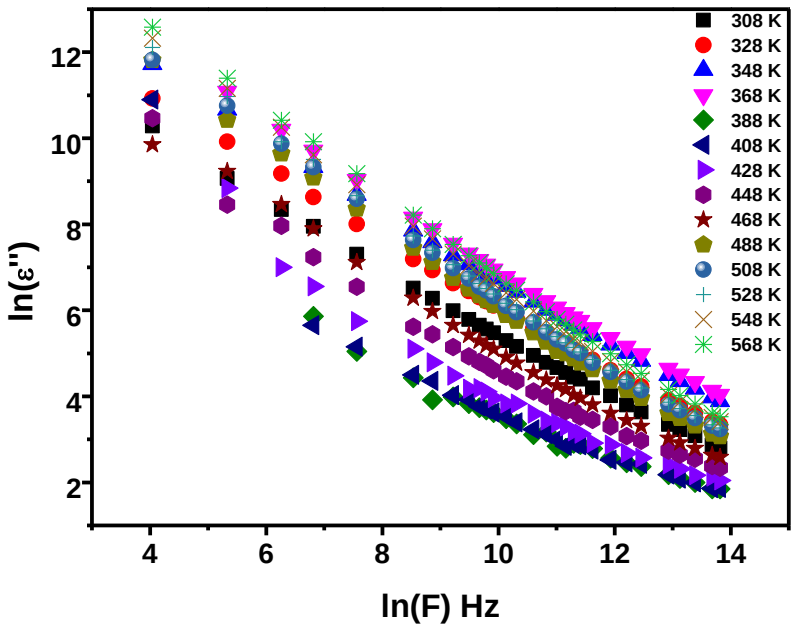

Fig. 5. Plots of ln (ε″) versus ln (F) for BPSK30 glass at different temperatures

The plots of dielectric constant, ε' and dielectric loss, ε'', versus frequency, ln (F), for BPSK3 glass at different temperatures is shown in Figs.(4) & (5). From the figures it can be noted that both dielectric constant and loss decreases with increase in frequencies and increases with increase in temperature. This is due to the fact that alkali ions cannot follow field variation at higher frequency and hence there cannot be much contribution to ε', from ions at those frequencies irrespective of the ionic concentration. These results are consistent with the reported literature for similar glass systems [31].

The typical plots of *ln (ε′)* at 488K versus *ln* (*F*) for BPSK glasses for different temperature are shown in Fig. 4 & 5 It can be noticed that dielectric constant, ε′, decreased with increase in frequency.

Dielectric properties

The increase in dielectric constant of the sample with increase in temperature is usually associated with the decrease in bond energies that is, as the temperature increases two effects on the dipolar polarization may occur: (i) It weakens the inter molecular forces and hence enhances the orientational vibration. (ii) It increases the thermal agitation

and hence strongly disturbs the orientational vibrations. The dielectric constant becomes larger at low frequencies and at high temperatures, which is normal in oxide glasses and this cannot be taken as an indication for spontaneous polarization [32]. This could be due to the fact that as the frequency increases, the polarizability contribution from ionic and orientation sources decreases and finally disappears due to their inertia. Dependence of dielectric constant, ε′, and dielectric loss, ε″ with mole fraction of K_2O for all BPSK glass samples is shown in fig. (6). Here at mole fraction x=20 both dielectric constant, ε′, and dielectric loss, ε″ showing similar nature of decrement and as the concentration of mole fraction increases and again it decreases, it shows non-linear variation with the concentration K_2O.

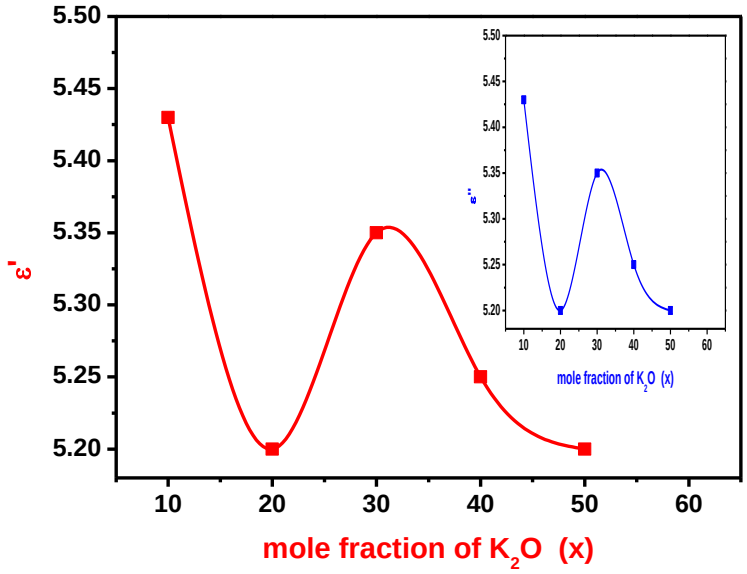

Fig. 6. Compositional dependence of dielectric constant, ε′, and dielectric loss, ε″ (inset), versus mole fraction (x) at a frequency of 1 MHz and temperature of 573 K for all 5 samples of Borophosphate glasses.

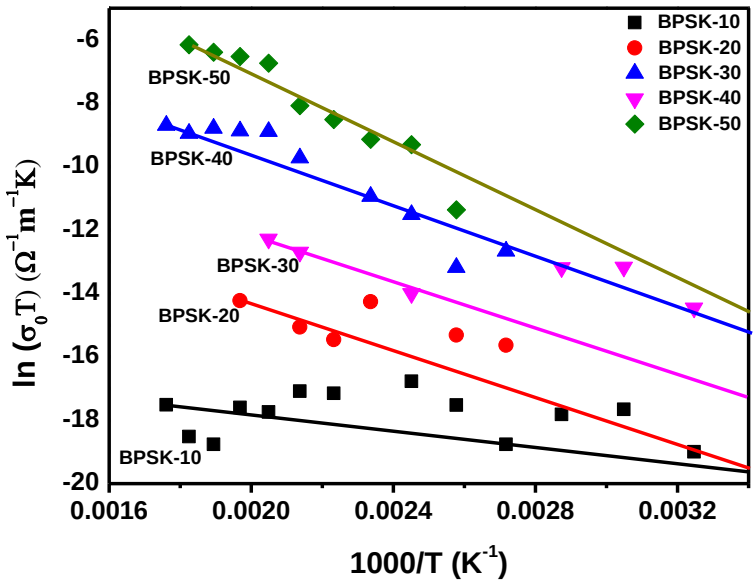

Fig.7. Plot of ln (σ_0T) versus 1000/T all 5 samples of Borophosphate glasses.

4. CONCLUSIONS :

A novel set Alkali and alkaline doped borophosphate glasses were synthesized by melt quenching technique and their noncrystalline nature has been confirmed. And investigated for dielectric properties over a wide range of frequency and temperature. The dielectric spectra in terms of frequency, temperature and composition have been discussed. Dielectric constant and dielectric loss decreased with increase in frequency and that has been attributed to the decrease in ionic contribution to the total polarization with increase of frequency. Further plan was there to investigate impedance studies, imaginary part of modulus. It has been observed that of ac conductivity and activation

energy occurring for K_2O mole fractions For the first time that the borophosphate glasses in the present compositions have been investigated for frequency dependent dielectric properties and conductivity and dielectric studies.

REFERENCES:

1. T. Sujatha, T. Sankarappa, International Journal of Engineering Sciences, 2(7) July 2013, Pages: 302-309.
2. J. M. Delaye, D. Ghaleb, J. Non-Cyst. Solids 195 (1996) 239.
3. J. M. Delaye, D. Ghaleb, Phys. Rev. B 61 (2000) 14481.
4. W. Li, S. H. Garofalini, Solid State Ionics 166 (2004) 365.
5. Takebe, H, Harada, T, Kawabata, M. 2006, Effect of B2O3 addition on the thermal properties and density of barium phosphate glasses. J. Non-Cryst. Solids 352 (March 2006) 709 - 713.
6. Ducel, J.F and Videau, J.J. 1992, Physical and chemical characterizations of sodium borophospahte glasses. Material Letters 13 (January 1992) 271-274.
7. Benson K. Money and Hariharn, K. 2008, Glass formation and electrical conductivity studies of melt quenched and mechanically milled $50Li_2O$:(50-x) P2O5:xB2O3. Solid State Ionics 179 (December 2008) 1273-1277.
8. Kyungseok Han, Chawon Hwang, et.al, 2012, Effects of Substituting B2O3 for P2O5 on the structures and properties of V2O5-P2O5 glass systems. *Electronic Materials Letters*, 8, 6 (December 2012) 655-658.
9. Cutroni, M. Madanici, A, Mustarelli, P, Tomasi, C, Federico, M. 2002, Ionic conduction and dynamical regimes in silver phosphate glasses. J. Non-Cryst. Solids 307-310 (2002) 963-970.
10. Cutroni, M, Mandanici, A, Piccolo, A, Fanggao, C, Saunders, G.A. and Mustarelli, P, 1996, Frequency and temperature dependence of a.c. conductivity of vitreous silver phosphate electrolytes. Solid State Ionics 90 (April 1996) 167-172.
11. P.Balaya and C.S.Sunandana, J.Non.Cryst.Solids 175 (1994) 51.
12. K. Ngai, G. Greaves, and C. Moynihan, Phys. Rev. Lett. 80, 1018 (1998).
13. Proceedings of the International Conferences on Solid State Ionics, Solid State Ionics, Vols. 9/10 (1983); 18/19 (1986); 28-30 (1988); 40141 (1990); 53-56 (1992); 86-88 (1996).
14. Takahashi T in Super Ionic Conductors ed. Mahan G.D and Roth W L (Plenum Press. New York. (1976) 379.
15. M. Malki, M. Micoulaut, F. Chaimbault, and Y. Vaills, Phys. Rev. Lett. 96 (2006).
16. K. Ngai and A. Rizos, Phys. Rev. Lett. 76, 1296 (1996).
17. S.I.Smedley and C.A.Angell, Solid State Commun. 27 (1978) 21.
18. D.P.Button, R.P.Tandon, H.L.Tuller and D.R.Uhlmann, Solid State Ionics 5 (1981) 655.
19. S.Rokade, K.Singh and V.K.Deshpande, Solid State Ionics 18/19 (1986) 374.
20. O.L.Anderson, D.A.Stuart, J.Am.Ceram.Soc., 37 (1954) 573.
21. D.Ravine, J.L.Souquet, Phys.Chem.Glasses, 18 (1977) 27.
22. P.Balaya and C.S.Sunandana, J.Non.Cryst.Solids 175 (1994) 5.
23. Thombare, M.D. (2014). Study of Physical Properties of Lithium Borophosphate Glasses, Int. J. Res. Pure and Appl. Phy., 4(2), 9–15.
24. M. Prashant Kumar, T. Sankarappa, Solid State Ionics 178 (2008) 1719.
25. Ghosh, A, 1992, Correlated-barrier hopping in semiconducting tellurium molybdate glass. Phys. Rev. B 45, 19 (November 1992), 11318-11320.
26. A. Ghosh, Phys. Rev. B 47 (1993) 537.
27. A.A. Bahgat, Y.M. Abou-Zeid, Phys. Chem. Glasses 42 (2001) 01.
28. H.El. Mkami, B. Deroide, R. Backov, J.V. Zanchetta, J. Phys. Chem. Solids 61 (2000) 819.
29. A F. Wright et al. (eds.), Glass ... Current Issues© Martinus Nijhoff Publishers, Dordrecht 1985, 440.
30. Vladimir Belostotsky, Journal of Non-Crystalline Solids. 353 (2007) 1078.
31. L.D. Raistrick, J.R. Macdonald, D.R. Franceschetti, in: J.R. Macdonald (Ed.), Impedance Spectroscopy, Wiley, New York, 1987 (Chapter 2).
32. M. Cutroni, A. Mandanici, A. Piccolo, C. Fanggao, G.A. Saunders, P. Mustarelli.