

Influence of molybdenum ions on optical absorption, ESR and IR OF A_2O (A=LI, NA, K)-NAF- B_2O_3 glass system

R. VIJAY, B. TILAK^a, P. RAMESH BABU, D. KRISHNA RAO

Department of Physics, Acharya Nagarjuna University, Nagarjuna Nagar, Andhra Pradesh, India

^a*Department of Materials Science, Addis Ababa University, Addis Ababa, Ethiopia*

A $20A_2O$ (A=Li, Na, K)- $20NaF$ - $(60-x)B_2O_3$: $xMoO_3$ glass system with $x=0$ and 0.5 mol % was prepared by conventional melt quenching technique and investigated by optical absorption, ESR, and IR spectroscopies. The optical absorption spectra of 0.5 mol% exhibited a predominant broad band in the region $600-800$ nm, which can be attributed the presence of MoO_3 ion and also the excitation of Mo^{5+} ($4d^1$) ion in the glasses. It is observed that LNBMO absorption band is more dominant when compared to the KNBMo, NNBMo. The optical band gap (E_o) has been evaluated using Urbach plots. IR studies reveal that the stretching relaxation of B-O bond, trigonal BO₃, and BO₄, the bending vibrations of B-O-B linkages in the borate network at different wave numbers. ESR results show that there is a co-existence of Mo^{5+} ions with Mo^{6+} ion the glass matrix. The hyperfine structure is nearly smeared out and a relatively broad line with an isotropic g values characterizes the spectra.

(Received May 2, 2012; accepted July 19, 2012)

Keywords: Molybdenum ions, Optical absorption, ESR and IR

1. Introduction

Electron Spin Resonance (ESR) spectroscopy is an experimental technique to obtain information on some of the structural and dynamic phenomenon of material and to identify the site symmetry around the transition metal(TM) ions in glasses. Glasses doped with transition metal ions have attracted a great deal of attention because of their potential applications in the development of new tunable solid state lasers, solar energy converters. It has been well established [1-5] that alkaline borate glasses can be used as solid electrolytes in solid state batteries.

Many investigations on MoO_3 containing glasses had been done due to their catalytic properties. The molybdenum ions are characterized by high activity and selectivity in a series of oxidation reactions in the glass matrices [6, 7]. Interesting studies are available on the environment of molybdenum ion in different inorganic glasses [8-13]. Mo-O bond in molybdenum hexavalent oxide is identified as significantly covalent. The Mo ion exist a stable valence state viz., MoV and MoVI in the glass network. Molybdenum ions act both as network formers as well as network modifiers depending upon their concentration and nature of the host network. According to author knowledge on literature survey a certain physical properties of lithium oxy borate glasses are available on $20A_2O$ (A=Li, Na, K)- $20NaF$ - $(60-x)B_2O_3$: $xMoO_3$ glasses, but there is no systematic or detailed study on spectroscopic properties.

In the present study, we report a detailed investigation of spectroscopic properties of these glasses,

i.e., optical absorption, infrared and ESR spectra of both molybdenum ions (for $x=0$ mol% and 0.5 mol%) doped glass systems, $20A_2O$ (A=Li, Na, K)- $20NaF$ - $(60-x)B_2O_3$: $xMoO_3$ for $x=0$ mol% and 0.5 mol%, is expected to throw some light on the possible use of these glasses in solid state ionic devices.

2. Experimental

The composition $20A_2O$ (A=Li, Na, K)- $20NaF$ - $(60-x)B_2O_3$: $xMoO_3$ (for $x=0$ mol% and 0.5 mol%) were prepared by the conventional melt quenching technique. The following compositions were studied

LNB : $20Li_2O-20NaF-60B_2O_3$
 NNB : $20Na_2O-20NaF-60B_2O_3$
 KNB : $20K_2O-20NaF-60B_2O_3$
 LNBMo : $20Li_2O-20NaF-59.5B_2O_3: 0.5MoO_3$
 NNBMo : $20Na_2O-20NaF-59.5B_2O_3: 0.5MoO_3$
 KNBMo : $20K_2O-20NaF-59.5B_2O_3: 0.5MoO_3$

The starting materials used for the preparation of glasses were analytical grade reagents (99.9 % pure) of Li_2CO_3 , Na_2CO_3 , K_2CO_3 , NaF, H_3BO_3 and MoO_3 . Each batch of compositions was taken in agate mortar and was mixed thoroughly for several hours for homogeneity. Each batch of the mixed composition taken in a platinum crucible and was melted at temperature 900 °C for 2 hours till a bubble free liquid was formed. These glass samples

were subsequently annealed at 250 °C in another furnace. Further, the resultant melt was poured on a rectangular brass mould (containing smooth polished inner surface) at room temperature. The dimensions (i.e., 1 cm × 1 cm × 0.2 cm) of the glasses are used to facilitate measurements. These glass samples were polished to give parallel and shiny surfaces. Samples of uniform were employed for optical absorption, ESR and IR measurements. Optical absorption spectra of the glasses were recorded at room temperature in the wavelength range 200–1200nm up to a resolution of 0.5nm using JASCO V-670 UV–Vis–NIR spectrophotometer. ESR spectra were recorded at room temperature using E11Z Varian X-band ($\nu = 9.5$ GHz) ESR spectrometer of 100 kHz field modulation. Infrared transmission spectra for the studied glasses were recorded using a PERKIN-ELMER spectrum BX FT IR system Spectrophotometer. Infrared Spectrophotometer in the frequency range 200-2000 cm^{-1} by KBr pellet method.

3. Results and discussion

Physical parameters

The physical properties provide an insight into the atomic arrangements in a glass network. The concentration of ions is an important parameter, which affects the laser gain of the host material. The Number of ions (N_i) per cubic centimeter can be evaluated. Physical parameters such as total molybdenum (calculated as Mo^{6+} ions) ion concentration N_i , mean Mo^{6+} ion separation R_i , has been evaluated by using the equation [14-18].

The transition metal ion concentration (N_i) could be obtained from

$$N_i(\text{ions} / \text{cm}^3) = \frac{N_A M(\text{mol}\%)d}{\bar{M}} \quad (1)$$

Where d is the density of the glass, N_A is the Avagadro's number, M is the mole fraction of the oxides, \bar{M} is the average molecular weight or molar mass of the glass

From the N_i values obtained, inter – ionic distance (r_i) of transition metal ions could be evaluated

$$\text{Inter –Ionic distance } r_i(\text{\AA}^o) = \left[\frac{1}{N_i} \right]^{\frac{1}{3}} \quad (2)$$

The density, d of the glass samples was determined using Archimedes principle. The density of the glass samples is observed to increase with the due addition of alkali oxides in the order Li_2O , Na_2O and K_2O to $\text{NaF-B}_2\text{O}_3$: MoO_3 glass network. This states that the K_2O mixed $\text{NaF-B}_2\text{O}_3$: MoO_3 glasses are more rigid than the other glasses. Thus, we expect that the cross-link density and oxygen coordination is high for the glass samples KNB (among MoO_3 free glasses) and KNBMo (among MoO_3 doped glasses). Physical parameters of the studied glasses, i.e., density d , Concentration of Mo^{6+} ions N_i and Inter ionic distance r_i are tabulated in Table 1.

Table 1.

Glass sample	Density d (g/cm^3)	Avg.Mol. weight(\bar{M})	Conc.of Mo^{6+} ions N_i ($10^{20}/\text{cm}^3$)	Inter ionic distance $r_i(\text{\AA}^o)$
LNB	2.4534	56.15	-	-
NNB	2.5026	62.57	-	-
KNB	2.5129	69.01	-	-
LNBMo	2.4649	56.52	131.27	4.25
NNBMo	2.5141	62.94	120.24	4.37
KNBMo	2.5243	69.38	109.51	4.50

Optical absorption spectra

Fig. 1 shows the optical absorption spectra of glasses in the wave length region of 200-1200 nm. A single broad peak has been observed in MoO_3 doped compositions (LNBMo, NNBMo and KNBMo) in the range of 600-

800nm (Insert Fig. 1), which can be attribute the presence of MoO_3 ion and also the excitation of Mo^{5+} ($4d^1$) ion in the glasses. In fact, for this ion, two optical excitations were predicted starting from $b_2(d_{xy})$ ground state to (d_{xz-yz}) and ($d_{x^2-y^2}$) with $\delta=15000 \text{ cm}^{-1}$ and $\Delta=23000 \text{ cm}^{-1}$ [19].

Perhaps, due to inter charge transition transfer ($\text{Mo}^{5+} \leftrightarrow \text{Mo}^{6+}$) in the glass network, the resolution of these transitions could not be observed. The highest intensity of this band observed in the spectrum of glass LNBMo points out that the presence of the highest concentration of Mo^{5+} ions in this glass. Such Mo^{5+} ions may form $\text{Mo}^{5+}\text{O}^{3-}$ molecular orbital states and are expected to participate in the depolymerisation of the glass network [20, 21] creating more bonding defects and non-bridging oxygen's (NBO's). The higher the concentration of such modifiers, the higher is the concentration of NBO's in the glass matrix.

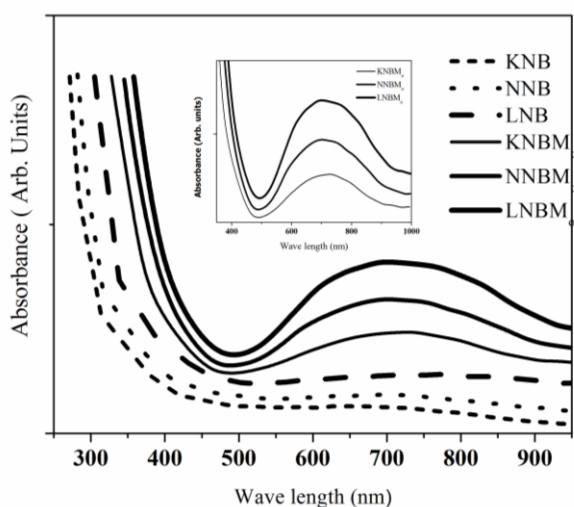


Fig. 1. Optical absorption spectra $20\text{A}_2\text{O}$ (A=Li, Na, K)- 20NaF - $(60-x)\text{B}_2\text{O}_3$: $x\text{MoO}_3$ for $x=0$ and 0.5 mol%.

This leads to an increase in the degree of localization of electrons there by increasing the donor centers in the glass matrix. The presence of larger concentration of these donor centers decreases the optical band gap and shifts the absorption edge towards higher wavelength side (Table 2). This optical absorption spectra (Fig. 1) of MoO_3 free A_2O (A=Li, Na, K)- NaF - B_2O_3 glasses exhibited lower cut-off wavelength than that of MoO_3 doped A_2O (A=Li, Na, K)- NaF - B_2O_3 glasses. It seems to comprise lower optical band gap for the MoO_3 doped glasses (particularly, for the Li_2O mixed glasses).

From the observed absorption edges, we have evaluated the optical band gaps (E_0) of these glasses by drawing Urbach plot between $(\alpha\hbar\omega)^{1/2}$ and $\hbar\omega$ as per the equation [22]

$$\alpha(\omega)\hbar\omega = C(\hbar\omega - E_0)^2. \quad (3)$$

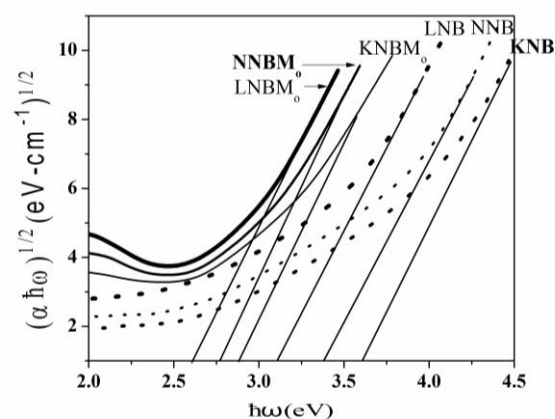


Fig. 2. Urbach plots for $20\text{A}_2\text{O}$ (A=Li, Na, K)- 20NaF - $(60-x)\text{B}_2\text{O}_3$: $x\text{MoO}_3$ for $x=0$ and 0.5 mol%.

Fig. 2 depicts the Urbach plots of all these glasses in which a considerable part of each curve is observed to be linear. From the extrapolation of the linear portion of these curves, the values of optical band gap (E_0) are determined in Table 2.

Table 2.

Glass sample	Cut-off wavelength (nm)	Optical band gap (E_0) (eV)
LNB	305	3.15
NNB	282	3.42
KNB	271	3.75
LNBMo	358	2.55
NNBMo	345	2.66
KNBMo	328	2.81

ESR spectra

The ESR spectra for the samples LNBMo, NNBMo and KNBMo of glass system are shown in the Fig. 3. From the spectral analysis, $g_{||}$, g_{\perp} , Half width are calculated and presented in Table 3.

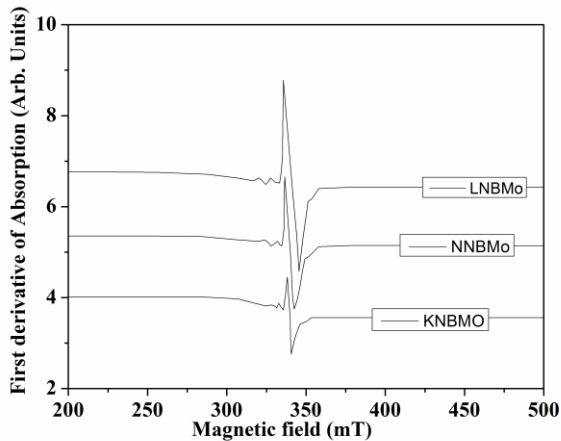


Fig. 3. ESR spectra for LNBMo, NNBMo and KNBMo of glass system.

The ESR spectra (Fig. 3) of MoO_3 doped glasses consist of a main central line surrounded by less intense satellites. The central line arises from even molybdenum isotopes ($I=0$) whereas satellite lines correspond to the hyper fine structure from odd ^{95}Mo and ^{97}Mo ($I=5/2$) isotopes [23]. Thus the existence of molybdenum ions in Mo^{5+} state in these glasses is confirmed by ESR spectra. A considerable intensity has been observed in the spectra of LNBMo, NNBMo and KNBMo glasses, suggesting that there is an existence of $\text{Mo}^{5+}\text{O}_3^-$ complexes [24, 25]. The structural disorder arising from the site-to-site fluctuations of the local surroundings of the paramagnetic Mo^{5+} ions can be accounted for the two components of the g values. The intensity (\mathfrak{I}) of the EPR signal is assumed to be proportional to the product of the peak-to-peak height (I) and the square of its width (ΔB) [26]

$$\mathfrak{I} \approx I(\Delta B)^2 \quad (4)$$

The dependence of this factor, for the central line with the due addition of alkali oxides Li_2O , Na_2O and K_2O to $\text{NaF-B}_2\text{O}_3: \text{MoO}_3$ glass network is shown in Fig. 4.

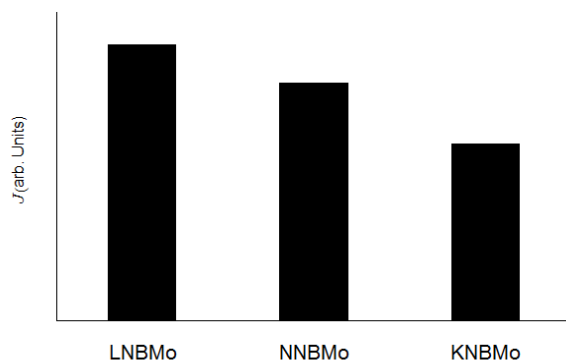


Fig. 4. Variation of intensity of ESR signal for LNBMo, NNBMo and KNBMo glass system.

From the Fig. 4 it is observed that the intensity of the ESR signal is high in LNBMo glass and it may be attributed to the presence of higher concentration of Mo^{5+} ions in the glass network (as it is also evidenced from optical absorption studies).

Table 3. Data on ESR spectra of $\text{A}_2\text{O}(\text{A}=\text{Li, Na, K})-\text{NaF}-\text{B}_2\text{O}_3: \text{MoO}_3$ glasses.

Glass	g_{\parallel}	g_{\perp}	Half-width $\Delta B_{1/2}$ (mT)
LNBMo	1.8556	1.9261	6.5
NNBMo	1.8599	1.9289	4.6
KNBMo	1.8694	1.9306	3.3

Infrared spectra

Fig. 5 shows the infrared transmission spectra of pure $\text{A}_2\text{O}(\text{A}=\text{Li, Na, K})-\text{NaF}-\text{B}_2\text{O}_3$ glasses exhibit three groups of bands: (i) in the region $1250-1550 \text{ cm}^{-1}$, due to the stretching relaxation of the B-O-B bond of the trigonal BO_3 units (ii) in the region $900-1050 \text{ cm}^{-1}$ attributed to the BO_4 units and (iii) a band is located at about 710 cm^{-1} due to the bending vibrations of B-O linkages in the borate network [27, 28].

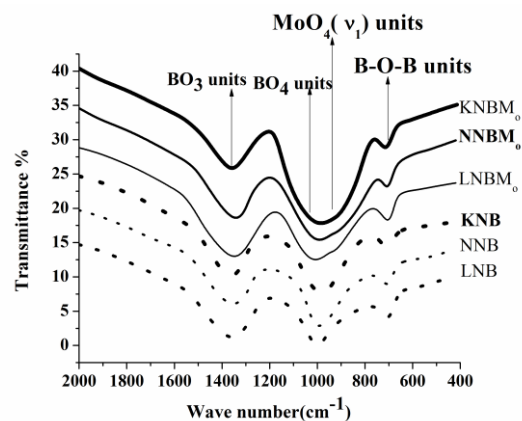


Fig. 5. Infrared spectra for $20\text{A}_2\text{O}(\text{A}=\text{Li, Na, K})-20\text{NaF}-(60-x)\text{B}_2\text{O}_3: x\text{MoO}_3$ for $x=0$ and $0.5 \text{ mol}\%$.

The infrared transmission spectra of MoO_3 doped $\text{A}_2\text{O}(\text{A}=\text{Li, Na, K})-\text{NaF}-\text{B}_2\text{O}_3$ glasses exhibited another feeble band at around 900 cm^{-1} in addition to the before

mentioned bands. This band is attributed to ν_1 vibrational modes of MoO_4^{2-} tetrahedral units/isolated Mo-O units

[29, 30]. Positions of various bands was summarized and presented in Table 4.

Table 4.

Glass sample	BO ₃ units	BO ₄ units	B-O-B units	MoO ₄ (ν_1) units
LNB	1345	1012	704	-
NNB	1353	1006	704	-
KNB	1356	994	710	-
LNBM ₀	1332	1029	700	914
NNBM ₀	1339	1022	706	906
KNBM ₀	1342	1015	711	896

It is observed from the infrared transmission spectra of these glasses, BO₄ units increase on expense of BO₃ units due to the addition of alkali oxides in the order Li₂O, Na₂O and K₂O respectively to NaF-B₂O₃: MoO₃ glass network for x= 0 and 0.5 mol%; further, for x=0.5 mol%, ν_1 vibrational modes of MoO_4^{2-} tetrahedral units are supposed to merge with BO₄ units [31]. Hence, there is a possibility for the formation of a single boron-oxygen-molybdenum framework in the glass network. The atomic radius and molecular weight of Li⁺ ions are relatively low in the first group [32]; thus, the mobility of Li⁺ ions is high (comparing with Na⁺ and K⁺ ions). Hence the Li⁺ ions are expected to break the bonds B-O-B and B-O-Mo etc., which causes the creation of larger number of NBOs in the glass matrix [33]; whereas the molybdenum ions in the Mo⁵⁺ state occupy the network modifying positions and depolymerize the glass matrix [34]. As a result, highest disorder in the glass samples LNB and LNBMo takes place. However, replacing Li₂O by Na₂O and K₂O in the glass system NaF-B₂O₃: MoO₃, as the mobility of Na⁺ and K⁺ ions is low (comparing with Li⁺ ions) they create lower number of NBOs in the glass matrix where as the molybdenum ions in the Mo⁶⁺ state occupy the network forming positions with tetrahedral MoO_4^{2-} units and polymerize the glass matrix. Such structural units may alter with BO₄ structural units and increase the rigidity of the glass network. As a result, lowest disorder in the glass samples KNB and KNBMo takes place.

4. Conclusions

The Optical absorption, ESR and IR studies have been carried out for 20A₂O(A=Li, Na, K)- 20NaF- (60-x)B₂O₃: xMoO₃, for x= 0 and 0.5 mol% glass system, which has been prepared by melt quenching method. From Optical absorption, the MoO₃ doped 20A₂O(A=Li, Na, K)- 20NaF- (60-x)B₂O₃ glasses show a broad absorption band in the region 600-800 nm This broad absorption band is attributed to the excitation of Mo⁵⁺ (4d¹) ion. It is observed that LNBMo absorption band is more dominant when compared to the KNBMo, NNBMo. It is predicted that there are two optical excitations from b₂ (d_{xy}) ground state to (d_{xz-yz}) and (d_{x²-y²) with $\delta=15000$ cm⁻¹ and $\Delta=23000$ cm⁻¹ respectively due to the inter charge transition transfer (Mo⁵⁺ \leftrightarrow Mo⁶⁺) in the glass network, the resolution of these transitions could not be observed. ESR spectra reveal that there is a co-existence of Mo⁵⁺ ions with Mo⁶⁺ ion the glass matrix. IR spectra exhibit a feeble band attributed to ν_1 vibrational modes of MoO_4^{2-} tetrahedral units/isolated Mo-O units at around 900 cm⁻¹ to spectra of glasses without MoO₃ doping.}

References

- [1] M. D. Ingram, Physics and Chemistry of Glasses, **28**, 215 (1987).
- [2] M. Dawy, A. H. Salama, Materials Chemistry and Physics, **71**(2), 137 (2001).

- [3] Md. Jamal, G. Venugopal, Md. Shareefuddin, M. Narasimha charyod, *Materials Letters*, **39**(1), 28 (1999).
- [4] Md. Jamal, Md. Shareefuddin, M. Narasimha charyod, *Journal of Power sources*, **58**(2), 217 (1996).
- [5] Md. Shareefuddin, Md. Jamal, M. Narasimha Chary, *Materials Letters*, **24**(5), 291 (1995).
- [6] S. M. D. Nery, W. M. Pontuschka, S. Isotani, C. G. Rouse, *Phys. Rev. B*, **49**, 3760 (1994).
- [7] Bjorn O. Mysen, *Journal of Non-Crystalline Solids*, **95-96**(1), 247 (1987).
- [8] M. Srinivasa Reddy, V. L. N. Sridhar Raja, N. Veeraiah, *EPJ Appl. Phys.*, **37**(2), 203 (2007).
- [9] P. Syam Prasad, B. V. Raghavaiah, R. Balaji Rao, C. Laxmi Kanth, N. Veeraiah, *Solid State Commun.*, **132**(3-4), 235 (2004).
- [10] G. D. Khattak, M. A. Salim, A. S. AlHarthi, David J. Thompson, L. E. Wegner, *J. Non-Cryst. Solids*, **212**(2-3), 180 (1997).
- [11] K. S. Sidhu, S. Singh, S. S. Sekhon, S. Chandra, A. Kumar, *Phys. Chem. Glasses*, **32**(6), 255 (1991).
- [12] A. A Bahgat, M. M. El-Samanoudy, Al. Sabry, *Journal of physics and chemistry in solids*, **60**(12), 1921 (1999).
- [13] Manisha Pal, K Hirota, Y. Tsujigami, H. Sakata, *Journal of Physics D: Applied Physics*, **34**(4), 459 (2001).
- [14] B. R. Judd, *Phys. Rev.* **127**, 750 (1962).
- [15] W. T. Carnall, P. R. Fields, K. Rajnak, *J. Chem. Phys.*, **49**(10), 4424 (1968).
- [16] F. Auzel, ed. *Spectroscopy of Solid-State Laser – Type Materials*, London: Plenum Press, 293 (1987).
- [17] C. Guery, J. L. Adam, J. Lucas, *Journal of Luminescence*, **42**(4), 181 (1988).
- [18] M. J. Weber, R. A. Saroyan, R. C. Ropp, *Journal of Non-Crystalline Solids*, **44**(1), 137 (1981).
- [19] A. Goldstein, V. Chiriach, D. Becherescu, *Journal of Non-Crystalline Solids*, **92**(2), 271 (1987).
- [20] W. Grunert, W. Morke, R. Feldhaus, K. Anders, *Journal of catalysis*, **117**(2), 485 (1989).
- [21] M. Jamnicky, P. Znasik, D. Tunega, M. D. Ingram, *Journal of Non-Crystalline Solids*, **185**(1-2), 151 (1995).
- [22] G. Srinivasarao, N. Veeraiah, *Journal of Physics and Chemistry of solids*, **63**, 705 (2002).
- [23] P. Syam Prasad, M. Srinivasa Reddy, V. Ravi Kumar, N. Veeraiah, *Philosophical Magazine*, **87**(36), 5763 (2007).
- [24] O. Cozar, D. A. Magdas, I. Ardelean, *Journal of Non-Crystalline Solids*, **354**(10-11), 1032 (2008).
- [25] M. V. N. Padma Rao, L. Srinivasa Rao, M. Srinivasa Reddy, V. Ravi Kumar, N. Veeraiah, *Croat. Chem. Acta*, **82**(4), 747 (2009).
- [26] I. Bratu, I. Ardelean, A. Barbu, V. Mih, D. Maniu, G. Botezan, *Journal of Molecular Structure*, **482**, 689 (1999).
- [27] F. A. Khalifa, H. A. El Batal, A. Azooz, *Indian Journal of Pure and Applied Physics*, **36**(6), 314 (1998).
- [28] M. R. Reddy, S. B. Raju, N. Veeraiah, *Journal of Physics and Chemistry of Solids*, **61**(10), 1567 (2000).
- [29] G. Govindaraj, N. Baskaran, K. Shahi, P. Monoravi, *Solid State Ionics*, **76**(1-2), 47 (1995).
- [30] N. Machida, H. Eckert, *Solid State Ionics*, **107**(3-4), 255 (1998).
- [31] L. Srinivasa Rao, M. Srinivasa Reddy, M. Rami Reddy, N. Veeraiah, *Journal of Alloys and Compounds*, **464**(1-2), 472 (2008).
- [32] J. D. Lee, *Concise of Inorganic Chemistry* (Fifth Edition), Blackwell Science (2005).
- [33] Fatma H. ElBatal, *Indian Journal of Pure & Applied Physics*, **47**, 471 (2009).
- [34] L. Srinivasa Rao, M. Srinivasa Reddy, D. Krishna Rao, N. Veeraiah, *Solid State Sciences*, **11**(2), 578 (2009).

*Corresponding author: ranguvijay111@gmail.com