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Physical and Structural Characterization of Manganese Ions Doped SrO-Li_2O-CaO-B_2O_3 (SLCB) Glasses

M. Ratna Raju[1], M. Subba Rao[2], Dr. Sandhya Cole[2*]

[1]Department of Physics, Andhra Christian College, Guntur-522 001, A.P, India
ratnaraju.mikkili@gmail.com.
[2*]Department of Physics, Acharya Nagarjuna University, Guntur-522 510, A.P, India

[*]sandhya.cole@gmail.com

Abstract: ***The physical and structural characterization of 0.1 mol% MnO doped x SrO+ (20-x) Li_2O+ (10-y) CaO+70B_2O_3+y, (5≤x≤15) mol% glass systems (SLCB) are synthesized and studied. Various physical parameters are evaluated for the glasses under study. The glassy nature of all the SLCB glasses is confirmed from X-ray diffractograms (XRD). The various assignments are given in the Fourier Transform Infrared spectra (FT-IR).***

Keywords: XRD, FT-IR Spectra

1. Introduction

In comparison, among the other oxide glass forming systems, Borate glasses provide an ideal case to demonstrate the effectiveness of UV-visible, infrared spectroscopy in glass science. Borate is one of the most important glass forming oxides and has been incorporated into various kinds of glass systems to obtain required physical and chemical properties. Borate glasses (B_2O_3) are easily melted and are good hosts for transition metals ions. Hence when glasses are doped with transition metal ions, they will become suitable for many practical applications. The properties of glasses have been established in terms of the stereo chemical environment that they provide and the oxidation number that they favor for the transition metal ions [1]. These properties can change according to the alkali oxide or modifiers content [2]. With the earlier elements in the first transition series it is found that increasing the alkali oxide content, tends to favor upper oxidation state, for example chromium favors the +3 state in low alkali borate glasses and the +6 state in the high alkali content [3]. Even when there is no change in oxidation number, there can be a change in stereochemistry or coordination as in the case of cobalt (II) which transforms from octahedral to tetrahedral as the alkali oxide content is increased [4]. Another advantage of borate glasses is when compared with other network forming elements boron has the smallest mass and thus the main vibrational modes associated with the glass network appear well above 500 cm^{-1} in the mid-infrared region [5]. These network modes are well separated from the metal ion site and vibrational modes active in the far-infrared region, i.e., below 600 cm^{-1} [6–8]. Borates have the ability to change the boron coordination with oxygen between three and four to certain limit and this provides a range of anionic environments that can coordinate the modifying metal ions. Recently, the interest in borate glasses has been renewed in views of the fast conductive properties exhibited by some of these glasses containing transition metal ions [9, 10]. This glass system is important in laser and infrared detection applications [11]. Borate glasses containing transition metal oxides are very useful materials for the radiation dosimetry applications in view of the fact that their effective atomic number is very close to that of human tissue [12].

2. Experimental

2.1 Synthesis of xSrO+ (20-x) Li_2O+ (10-y) CaO+70B_2O_3 + MnO glasses

The starting materials SrCO3, Li_2CO_3, CaO, H_3BO_3 and MnO, used in the preparation of the glasses are of analar grade (AR). The batch compositions of the glasses studied in the present work are listed in **Table 1**.

Table 1: Composition of the glasses studied in the present work and their corresponding codes

Glass System	Glass Code	Glass chemical Composition
$SLCB_0$	M_0	10 SrO+10 Li_2O+10 CaO+70 B_2O_3+ ---
$SLCB_1$	M_1	5 SrO+15 Li_2O+9.9 CaO+70 B_2O_3+0.1 MnO
$SLCB_2$	M_2	10 SrO+10 Li_2O+9.9 CaO+70 B_2O_3+0.1 MnO
$SLCB_3$	M_3	15 SrO+5 Li_2O+9.9 CaO+70 B_2O_3+0.1 MnO

The chemicals are weighed accurately, mixed thoroughly and ground to fine powder. The batches are melted in air in an electrical furnace at 950^0C for 20 min. The melts are then poured onto the surface of a polished brass plate and pressed with another brass plate. The formed glasses are annealed at 400^0C for about 1 h to make the glasses free from the structural stress and cooled to room temperature. Translucent glasses are obtained.

2.2 Measurements

Using the Archimedes principle with xylene (99.99% pure) as inert buoyant liquid, the density (ρ) of the prepared glass samples are determined with a precision of ±0.001g/cm^3. For recording the x-ray diffractograms of glass samples prepared

are taken in powder form and done using XRD-6100 (Shimadzu) diffractometer with Copper K_α radiation. The infrared spectra were recorded in the wave number range 400-2000 cm^{-1} using IR Affinity-1s (Shimadzu) spectrometer using KBr pellet technique at room temperature.

3. Results and Discussion

3.1 Physical Parameters

Using conventional formulae [13], density (ρ) of the synthesized glass samples, total molecular weight M of glass samples, various physical parameters such as transition metal ion concentration (Manganese ion), mean separation (r_i), polaron radius (r_p) and Optical basicity (Λ_{th}) values are determined.

3.11 Optical Basicity

The optical basicity of an oxide glasses can be conveniently measured in terms of the ability of the glass to donate a negative charge to an acidic probe ion [14-17]. Duffer and Ingram [18] reported that the optical basicity can be predicted from the composition of the glass and the basicity moderating parameters of various cations present. The theoretical values of optical basicity (Λ_{th}) of the SLCB glasses can be estimated using the formula,

$$(\Lambda_{th}) = \frac{\sum_{i=1}^{n} Zi\, ri}{2\gamma i} \quad (1)$$

where 'n' is the total number of cations present. Z_i is the 'is the oxidation number of the i^{th} cation to the number of oxides present and 'γ_i' is the basicity moderating parameter of the i^{th} cation. The basicity moderating parameter 'γ_i' can be calculated from the following equation

$$\gamma_i = 1.36(x_i - 0.26) \quad (2)$$

where x_i is the Pauling electro negativity of the cation [19]. The theoretical optical basicity values computed for the glasses in the present study are given in **Table 2**.

Table 2: Physical parameters of Manganese ions doped in SLCB glasses

Physical Parameters (Units)	Glass System			
	$SLCB_0$	$SLCB_1$	$SLCB_2$	$SLCB_3$
Average molecular weight(M)(g/mol)	67.69	64.01	67.70	71.39
Density (gr/cc)	2.65	2.79	2.67	2.54
Transition metal ion (N_i) Concentration (10^{+19}ions/cc) (±0.005)	…..	2.63	2.37	2.14
Inter ionic distance (r_i)(A^0)(±0.005)	…..	33.61	34.78	35.97
Polaron radius (r_p)(A^0)(±0.005)	…..	13.54	14.01	14.49
Optical basicity (Λ_{th})	0.43	0.43	0.43	0.43

It is observed that for the Λ_{th} values gradually increases from $SLCB_1$ to $SLCB_3$.

3.2 X-ray Diffraction Study (XRD)

The X-ray diffraction spectra have not shown any sharp peaks, indicating that the samples prepared are amorphous in nature are shown in **Figure 1**.

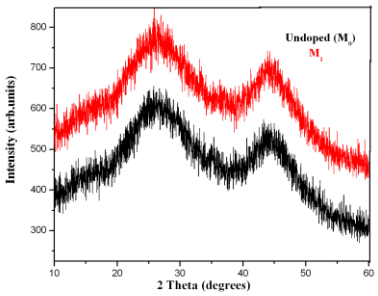

Figure 1: Powder X-ray diffraction patterns of undoped and Manganese ions doped SLCB glasses

3.6 FT-IR Studies

The FT-IR transmission spectrum is shown in Figure 2.

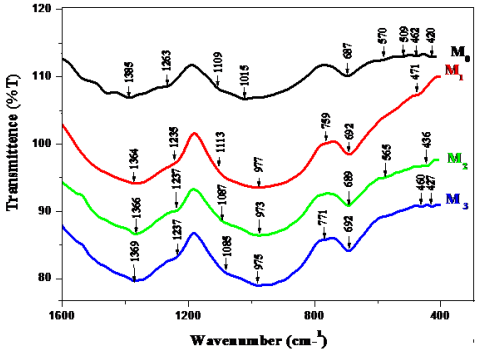

Figure 2: FT-IR spectra of Manganese ions doped SLCB glasses

The assignments of various absorption bands are given in **Table 3.**

The IR spectra have been divided into three spectral regions. The first group of band is reported to occur from 1200-

1600cm^{-1} which arise due to the asymmetric stretching vibrations triangular BO_3 units. The second group of bands region is from 800-1200cm^{-1} which was assigned to the stretching vibrations of tetrahedral BO_4 units. The third group observed around 700 cm^{-1} and was attributed to bending of B-O-B linkages in the networks. The band at 900 cm^{-1} was a characteristic of glass with high boric acid content i.e. due to boroxil rings [20].

Table 3: Assignments of absorption bands in the FTIR spectra of Manganese ions doped in SLCB glasses

M_0	M_1	M_2	M_3	Assignment
420	-	436	427	Ca-O stretching mode of BO_3 units.
462	471	-	460	Ca-O_6 stretching mode of BO_3 units.
509	-	-	-	Ca-O stretching mode of Borate units.
570	-	565	-	Ca-O stretching mode of Borate units.
687	692	689	692	B-O-B bending vibrations.
-	977	973	975	Boroxil ring vibrations.
1015	-	-	-	B-O-B stretching vibrations of BO_4 units.
1109	1113	1087	1085	Pyro-borate units, meta borate units.
1263	1235	1237	1237	Stretching vibrations B-O bonds in BO_3 units from pyro-ortho borate group's
1385	1364	1366	1369	Stretching vibrations of B (III)-O-B (IV) units.

The FT-IR spectrum of the undoped glass system contains three major broad bands with some shoulders in the wavenumber range of 400cm^{-1}- 460cm^{-1}, 500cm$^{-1,}$ 600cm^{-1}. These bands are the characteristics band vibrations of the calcium–oxygen. When Li_2O is incorporated in the glass, some of borons become tetrahedrally coordinated. The spectrum of fused B_2O_3 consists of a completely continuous triangle like coordinated network and also contains some BO_4 tetrahedral coordination. The band which lies in the region 800 cm^{-1} – 1200 cm^{-1} splits into two broad bands whose intensity increases with increase in mol% of SrO and decrease of mol% of Li_2O content. In the undoped glass with x=5 mol% SrO and 15 mol% Li_2O a shift in vibrational band at 1385 cm^{-1} is noticed with feeble increase in intensity. When x=10 mol% SrO and Li_2O, Li_2O causes a shift in the vibrational band from 1364 cm^{-1} to 1366 cm^{-1} with a noticeable increase in intensity of these peaks. Another band at 1235 cm^{-1} with x=10 mol% SrO and x=10 mol% Li_2O is assigned to stretching vibrations of B–O bonds in BO_3 units from pyro-ortho borate groups. The bands 1109cm^{-1},1113cm^{-1},1087cm^{-1} and 1085cm^{-1} are assigned B–O stretching vibrations of tetrahedral BO_4 units in tri-borate, tetra borate and penta borate groups [21]. The bands at 977cm^{-1},973cm^{-1}, and 975cm^{-1} are assigned to Boroxil ring vibrations. The bands 687cm^{-1},682cm^{-1},689cm-^{1} and 692cm^{-1} corresponds to B-O-B bending [22]. The bands 570cm^{-1},565cm^{-1},509cm^{-1} are due to stretching vibrations of CaO stretching mode of Borate units [23]. The absorption bands 462cm^{-1},471cm^{-1},460cm^{-1} and 420cm^{-1},436cm^{-1},427cm^{-1} corresponds to Ca-O_6 stretching mode of BO_3 units [24]. It is observed that on increasing of SrO content, the frequency bands shifts from higher to lower wavenumber, which suggests the formation of non bridging oxygen (NBO'S) i.e. conversion of BO_3 to BO_4 structural units. The formation of NBO'S indicates that the addition of Lithium oxide (Li_2O) in SLCB glasses act as a modifier.

4. Conclusion

From the physical and optical characterization of 0.1 mol% of Manganese ions doped xSrO + (20x) Li_2O + (10-y) CaO + 70B_2O_3 + y glasses with ($5 \leq x \leq 15$mol%) the following conclusions are drawn.

i. The density values are found to decrease with increase of SrO mol% or with decrease of Li_2O mol%. The density of undoped glass and the glass doped with Manganese oxide with 10 mol% of SrO and Li_2O are observed to be nearly equal.
ii. Powder XRD diffractograms confirm the glassy nature of the glasses under investigation.
iii. when x=5mol% of SrO and x=10 mol% Li_2O from the FT-IR spectra, the glass matrix is stable.

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Author Profile

Dr. Sandhya Cole, M.Sc., M. Phil, Ph.D., She is working as Assistant professor in the department of Physics since 2006, Acharya Nagarjuna University, Nagarjuna Nagar, Guntur, A.P., India. Her research fields are Solid state Spectroscopy, Nanotechnology, Material Science, and Glass Materials. She is a life member of several scientific bodies like Indian Association of Physics Teachers, Indian Physics Association and associated fellow of A.P. Akademy of sciences, A.P, 2014. She has successfully completed UGC major research project. She also received best research paper award in sciences-2014. At present 15 research scholars including one CSIR-UGC (SRF) fellow and two BSR research fellows are working for their research degree under her guidance.

Mr. M. Ratna Raju is working as lecturer in Physics, Andhra Christian College, Guntur, A.P, India. He is having 19 years of teaching experience. He is currently associated with research for his Ph.D., work under UGC (FIP) program under the guidance of Dr. Sandhya Cole.

M. Subba Rao had received his M.Sc., degree in Physics with specialization in condensed Matter physics from Department of Physics, Acharya Nagarjuna University, Nagarjuna Nagar, Andhra Pradesh, India. He is currently Ph.D., Student in the field of Solid State Spectroscopy and Nanomaterials. He is CSIR-UGC (SRF) Fellow and he had attended International and national Conferences, workshops and International Symposium. Under the guidance of Dr. Sandhya Cole.