EPR STUDIES OF ALKALI AND ALKALINE EARTH BORATE GLASSES

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Abstract: The alkali and alkaline earth borate (20-x)CaO-xSrO-(20-y)Na_2O-60B_2O_3-y(CSNB) (5≤x≤15) glasses doped with 0.1mol% of manganese ions were prepared by the melt quench technique. The structural and Optical analysis of glasses is carried out by X - ray diffraction (XRD), Electron Paramagnetic Resonance (EPR) Optical absorption Spectra and FTIR(Fourier transform Infrared Spectroscopy) techniques. The EPR spectra of all the glass samples exhibit three resonance signals which are characteristic of the Mn^{2+} ions. A six line hyperfine structure has also been observed at $g \approx 2.0$, $g \approx 3.1$ and $g \approx 4.05$. The distribution of the Mn^{2+} ions on several structural units of vitreous matrix revealed by EPR spectra depends on the MnO content in CSNB glasses.

Keywords: Alkaline and Alkaline Earth Borate Glasses, EPR, FT-IR, Optical Absorption.

Introduction: Alkali borate glasses are particularly interesting model systems as they exhibit a variety of structural changes with alkali content. Many physical properties of Oxide glasses show non-linear behavior exhibiting a minimum or maximum, as a function of alkali content. A host of borate rich glasses containing alkaline earth Oxides along CaO, PbO, ZnO as glass modifiers are Optimistic materials for their probable applications in the fields of Optical communications (Optical fibers), laser hosts, optical filters, γ-ray absorbers, photonic devices etc., [1-5].

Alkali borate glasses are an important class of solid materials for various technological applications such as solid materials for various technological applications such as solid electrolytes, insulation materials, textile fiber glass etc. [6].The alkali [M^+] or the alkaline earth [M^{2+}] cations act as network modifiers in the glass structure, breaking bridiging oxygen bonds to form non-bridging oxygens (NBO) [7,8] and extend their scope of applications to radiation dosimetry, vaccum ultra violet(VUV) optics, phosphors,solar energy converters, etc[9-12].

Borate glass is well known best choice as optical materials for its high transparency low melting point and high thermal stability [9]. The addition of modifier oxides such as alkali, and alkaline earth, and transition oxides to borate glasses suggests that there will be local configurational changes in the glass network, in addition to an increase in the number of free carriers [13]. Addition of alkali modifiers, CaO, SrO, Na_2O to the borate glasses brings drastic changes in the structural units. The structure of glassy alkali borate is a complex three-dimensional network of boron and oxygen composed of larger strucutal units. Stronsium tetra borate glass is an ideal host matrix for ferroelectric crystalline and non linear optical glasses. Strontium borate glasses have been studied by means of EPR [14] and also by ^{11} B nuclear magnetic resonance [14,16],infrared spectroscopy and hardness measurements [16]. SrO, CaO are modifier Oxides which enters the glass net work by breaking up the random network. Normally the oxygens of such Oxide break the local symmetry while the cations (Ca^{2+}, Sr^{2+}ions) occupy the interstitial positions in the glass System. [17]The study of optical absorption of transition metal (TM) ion doped glasses is an attractive area of research both from the fundamental and technological view point [18-22]

Manganese ions have been very frequently used as paramagnetic probes for exploring the structure and the properties of vitreous systems. The EPR is very sensitive to change in paramagnetic ions vicinity and may offer valuable information about the structural units evolution, the strengths of bonding the valence state and the distribution mode of the manganese ions in the network of oxide glasses [18-24]. The structure of glasses has been studied by X-ray diffraction , infrared and nuclear magnetic resonance spectroscopies.

The present study is intended to have a comprehensive understanding of the influence of manganese ions on the structure of CSNB glasses. The modifiers, CaO, SrO, Na_2O oxides are expected to increase the thermal stability and chemical durability of borate glasses. In the present study, preparation and characterization of $(20\text{-}x)CaO\text{-}xSrO\text{-}(20\text{-}y)Na_2O\text{-}60B_2O_3\text{-}y$ (CSNB) glasses were done by using EPR, Optical and IR studies.

Recently, the authors reported the EPR, Optical and IR spectra of VO^{2+} ions in CSNB glasses [25]. In continuation of these studies on correlating the EPR and Optical absorption spectra's extensive work have been carried out to get information about the spin-Hamiltonian parameters, bonding parameters etc. In the present work, the authors have carried out EPR, IR and Opticalabsorption studies of Calcium strontium sodium borate glasses (CSNB) doped with 0.1mol% of manganese ions.

2. Experimental: Glasses of the system $(20\text{-}x)CaO\text{-}xSrO\text{-}(20\text{-}y)Na_2O\text{-}60B_2O_3\text{-}y$(CSNB) have been prepared in the composition range ($5 \leq x \leq 15$) by using reagent grade CaO(99.9%), $SrCO_3$(99.9%), Na_2CO_3(99.9%), B_2O_3(99.9%) and MnO (99.9%). All the chemicals were weighed accurately using an electrical balance, ground to fine powder and mixed thoroughly. The batches were melted at 970°C - 980°C in porcelain crucibles by placing them in an electrical furnace. The melts were then poured onto a polished brass plate and pressed quickly with another plate. The glasses so formed are annealed at 300°C for about 1 hr. The glasses thus obtained were transparent with the thickness of 1.5mm. The codes of the samples prepared along with their compositions are given in Table 1. Care was taken to obtain glasses of uniform thickness for recording the optical absorption spectra. XRD, density, molar volume, were done to characterize the sample. The amorphous nature of the glass samples is checked by using powder x-ray diffraction recorded with an x-ray diffractometer using copper $K_\alpha$radiation.

Table 1: Summary of the Data on Glass Composition of CSNB Glasses

Glass code	CaO	SrO	Na_2O	B_2O_3	MnO
Mn_0	15	5	20	60	-
Mn_5	5	15	19.9	60	0.1
Mn_{10}	10	10	19.9	60	0.1
Mn_{15}	15	5	19.9	60	0.1

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The room temperature electron paramagnetic resonance spectra of calcium strontium sodium borate glasses containing different wt% of 0.1 Mn^{2+} ions were recorded on an EPR spectrometer. Operating in the X-band frequencies (9.305GHz) with a modulation frequency of 100KHz. A Powdered glass specimen of 100mg was taken in a quartz tube for EPR measurements. Optical absorption spectra of all the glass samples were recorded at room temperature on a UV-VIS-JASCO-V670 spectrometer in the wavelength region 200-900nm. Polished glass samples of thickness 1 mm were used for optical measurements. Infrared transmission spectra of all the glass samples in KBr matricesses were recorded in the range 400-4000cm^{-1} using a JASCO FT-IR 5300 spectrometer.

Results and Discussion:

3.1 XRD: The X-ray powder diffraction data for all glasses was obtained from Central Instrumentation Lab, HCU, Hyderabad, India. The Philips Pw1710 X-ray powder diffractomer was used. The results were recorded using a PM8208A chart recorder and an A100 (Digital) printer with VT125 terminal simultaneously. Details of the Operating conditions were as mentioned generater setting 35KV, 20mA; radiation: Cuk⍰ (angle range:0.500S and divergence slit:10).X-ray diffraction technique was used to check for possible crystallinity of the sample after quenching and annealing. All samples were found to be completely amorphous in nature.

3.2 EPR Studies: No EPR signal was detected in the spectra of undoped glasses. When 0.1mol% of manganese ions were introduced to CSNB glasses Table. 2 The EPR spectra of all the investigated samples exhibit resonance signals due to $Mn^{2+}(3d^5, 6s_{5/2})$ ions entering the matrix as paramagnetic species. The resonance signal at g=2.02 shows a six line hyperfine structure (hfs) which is due tothe interaction of electron spin of manganese ions with its own nuclear spin I=5/2, the ability to observe the ^{55}Mn hfs has two tangible benefits, (1) it generally allows unambiguous assignments of positions of complex resonance lines to manganese and (2) The magnitude of hyperfine splitting constant provides a measure of the covalent bonding between Mn^{2+} ions and its surrounding ligands [29,30]. Their relative intensities vary with glass structure and composition.

In case of d^5 transition metal ions, it is known that axial distortion of octahedral symmetry gives rise to three Kramer's doublets 1±5/2>, 1±3/2> and 1±1/2 [31]. Applications of Zeeman field lifts the spin degeneracy of the Kramer's doublets, As the crystal field splitting is normally much greater than the Zeeman field, the resonances observed are due to transitions with in the Zeeman field split Kramer's doublets. The resonances at g=2.98 and 4.64 can be attributed to the rhombic surroundings of the Mn^{2+} ions. The resonance at g=2.0 is due to the Mn^{2+} ions in an environment close to octahedral symmetry and is known to arise from the transition between the energy levels of the lower doublet, while the resonances at g= 2.98 and 4.64 are from the transition between the energy levels of middle Kramer's doublet.

Table.2 gives some typical values of the hfs (A) and g-values for 0.1mol% of Mn^{2+} ions in CSNB glasses at room temperature. It is apparent from different average values of A measured from peak to peak, A_{pp} and trough to trough, A_{tt}, that the individual lines are strain broadened, leading to an asymmetry in the absorption [32]. The first derivative spectrum as a consequence, shows larger values of A, when measured trough to trough, rather than peak to peak.

Table.2: Summary of the data on EPR Spectrum of manganese ions doped in CSNB Glasses

Glass code	g	Δg	$A_{pp}(10^{-4}T)$	$A_{tt}(10^{-4}T)$	$A((10^{-4}T)$
Mn_5	2.048	-0.0457	88	96	92
Mn_{10}	2.058	-0.0557	83	86	84.5
Mn_{15}	2.052	-0.0497	88	96	92

An overall average was calculated from

$$\mathbf{A_{avg} = [\ (\Delta_{opp} + \Delta_{ott}\ )/5 + (\ \Delta_{Mpp} + \Delta_{Mtt})/3 + (\ \Delta_{IPP} + \Delta_{Itt})/6]\ (1)}$$

Where Δ_{opp} and Δ_{ott} represent the differences between the first and sixth peak positions, measured peak to peak and trough to trough respectively. Δ_{Mppand} Δ_{Mtt} represents difference in positions between second and fifth peaks andΔ_{IPP} and Δ_{Itt} between second and third peaks. It is interesting to note that, in all of the glass samples, $\Delta_{opp}/ 5 \sim \Delta_{ott}/ 3 \sim \Delta_{IPP}$ and $\Delta_{ott} / 5 \sim \Delta_{Mtt} / 3 \sim \Delta_{Itt}$. This indicates that the g-value in each case is well behaved [32].

The Mn^{2+} signals are similar in all the glasses studied so far, the major difference appearing in the magnitude of the hyperfine splitting. Van wieringen [29] has noted that the strength of the hyperfine splitting depends on the matrix into which the ion is dissolved and is mainly determined by the electro negativity of the neighbors. This means a qualitative measure of the covalence of the bonding in the matrix which can be determined from the value of A, The smaller the splitting, the more covalent the bonding of the anion. It was also noted [29] that the g-value for the hyperfine splitting was indicative of the nature of bonding in the glass. If the g-value shows a negative shift with respect to 2.0023, then the bonding is ionic and conversely, if the shift is positive, then the bonding is more covalent in nature. In the present work, from the measured negative shift in the g-value, with respect to 2.0023, it is apparent that the Mn^{2+} ion is in an ionic environment [29]. The composition dependence of the g_{eff}= 2.0 absorption line intensity is presented in fig 1. In the concentration range 5≤x≤15 mol% 0.1mol% of MnO and by varying of CaO and SrO content in the samples determine an increasing of this line-intensity. Generally the signal intensity is proportional to the number of EPR active species involved in the resonance absorption, so the increasing of the g_{eff}= 2.0 line intensity reflect an increase of the Mn^{2+} ions concentration involved in other structural vicinities. Also from analyze of the line-intensity by varying CaO and SrO content Fig.1 result that in our glasses, at 0.1mol% MnO and by varying CaO and SrO content not favorized rising of the Mn^{2+} ions number which participate at the $g_{ef\,f}$= 2.0 over x = 5CaO% and x = 15 CaO% content in the samples determine an decreasing of line-intensity, due to the decreasing of Mn^{2+} ions number and probably, appearance in studied glasses of the Mn^{3+} ions have been frequently reported as progressively involved when 0.1mol% of MnO content[30-32].

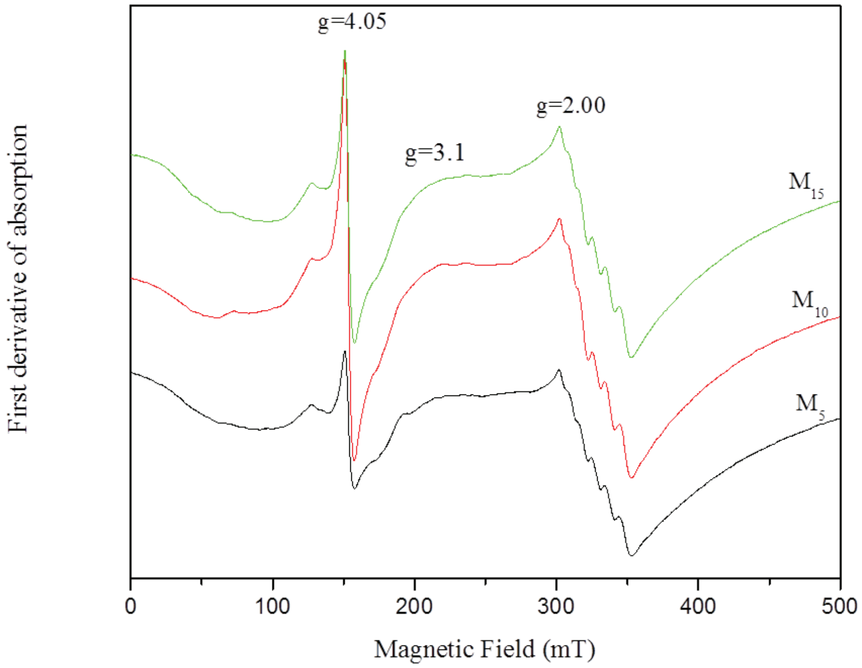

Fig 1: EPR Spectrum of Manganese Ions Doped in CSNB Glass Systems

The line-width of g_{eff} = 2.0 lines depends also on the MnO concentration, indicating an increase of this EPR characteristic parameter in whole concentration range. This fact shows that a little part of the Mn^{2+} ions participate, besides dipolar, at the super-exchange interactions which determine relative narrowing of this resonance line. By varying CaO and SrO concentration in the studied glasses determine decreasing of the effective values of the line width. These data evidenced that the number of manganese ions which participate at super exchange magnetic interactions increases by varying CaO and SrOcontent.

Conclusions: The EPR ,Optical absorption and IR studies on the network structure of quaternary CSNB glasses doped with transition metal ions Mn^{2+} have revealed the following conclusions.

1. The TM ions Mn^{2+} doped quaternary CSNB glasses have been prepared. The amorphous state of the prepared glasses was confirmed by X-ray diffraction spectra.
2. The distribution of Mn^{2+}ions on several structural units of the vitreous matrix depends on the 0.1 mol % MnO concentration range($5 \le x \le 15$). The Mn^{2+}ions were identified in sites of Octahedral symmetry slightly tetragonally distorted. They give rise to intense absorption line centered at $g \approx 2.02$ showing well resolved hyperfine structure up to x=10CaO and 10SrO content. There are also the strongly distorted versions of these sites, subject to strong crystal field effects. Mn^{2+}ions in tetragonal sites give resonance lines at $g_{eff} \approx 4.3$ and $g_{eff} \approx 3.3$ Their intensity is small enough to indicate a relatively 0.1mol% concentration of Mn^{2+}ions involved in such structural units.

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