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Microhardness and Electron Paramagnetic Resonance Studies of Manganese Doped Lithium Borate Glasses

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Abstract

Microhardness and Electron Paramagnetic Resonance (EPR) measurements are performed on 20 L_{i2} O-(80-x) B_2O_3 -xMnO glasses (where x = 0,10 to 20 in steps of 2 mol%) have been investigated to find out the role played by Mn^{2+} on the structure of these glass. These glass samples have been prepared using a conventional melt – quenching method. Microhardness studies revealed that the hardness of the glasses increases with an increase in applied load. Meyer's index number / workhardening exponent 'n' was calculated and found that the material belongs to hard material category. The EPR spectra of all the investigated sample exhibit resonance signals that are characteristic for the Mn^{2+} ions. The shapes of the spectra are also changed with the increasing of manganese ion content. The resonance line centered at $g_{eff} \approx 2.0$ has not hyperfine structure and is attributed to coupled Mn^{2+} ion by dipolar or / and super exchange interactions.

Keywords: Microhardness, EPR, Meyer's index number and dipolar interactions.

Introduction

B₂O₃ is one of the most important glass formers incorporated into various kinds of glass systems as a flux material, in order to attain materials with specific physical and chemical properties suitable for high technological applications. Microhardness is an important parameter often used to define the mechanical properties of a material on a microscopic scale. Hardness of the material is an important solid-state phenomenon. The hardness of a material is defined as the resistance it offers to the motion of dislocations deformation, or damage under an applied stress¹. Generally, the apparent hardness of the materials varies with applied load. This phenomenon, known as the indentation size effect (ISE), usually involves a decrease in the microhardness with increasing applied load²⁻⁵. The decrease of microhardness with increasing applied load has been reported by various researchers^{6,7}. In contrast to the ISE, a reverse type of indentation size effect (reverse ISE), where the microhardness increases with increasing applied load, is also known^{8,9}.

Electron paramagnetic resonance (EPR) studies are important and useful technique in understanding the microscopic properties in glasses¹⁰. Among all the transition metal ions, manganese (Mn) ion is particularly interesting because it exists in different valence states in different glass matrices¹¹⁻¹³. With the composition of the glass, the local environment of the transition metal (TM) ion incorporated into the glass network can be changed, leading to the local ligand field in homogeneities. Most Mn²⁺ complexes are octahedral and have a high spin arrangement with five unpaired electrons¹¹. In recent years, the interest in inorganic glasses containing transition metal ions has grown because these glasses have properties of

technological importance in electronic, tunable solid state lasers and fiber optic communication systems¹⁴. Manganese ions have been frequently used as paramagnetic probes for exploring the structure and properties of vitreous systems¹⁵.

Thus, the present work has been carried out to investigate the effect of manganese ion doped with the lithium borate glasses with various spectroscopic techniques such as microhardness and EPR will give valuable information on these systems.

Material and Methods

The glass samples of the formula $20Li_2O$ - (80-x) B_2O_3 -xMnO (LBM) (where x = 0, 10 to 20 in steps 2 mol %) have been prepared by using the conventional melt-quenching technique. Required quantities of analytical grade of Li_2Co_3 , $BaCo_3$, H_3Bo_3 and MnCo₃ were obtained from E-merck, Germany and Sd-Fine chemicals, India. The proper compositions were mixed together by grinding the mixture repeatedly to obtain a fine powder. The mixture is melted in platinum crucible at about 1223 K and the same temperature was maintained for about 45 minutes to homogenize the melt. Then the glass samples were annealed at 573K for two hours to avoid the mechanical strains developed during the quenching process.

Microhardness measurements were carried out using Zwick 3212 hardness tester fitted with a Vicker's diamond pyramidal indenter. All the indentation measurements were carried out on the freshly polished glass samples at room temperature. The indentation was made by varying the load from 0.3 to 1 kg and the time of indentation was 10 sec each. The indented impressions were approximately square. Further, the glass

surfaces were indented at different sites with fixed load of 25g using MH-6/MH3 [®] Series Digital Microhardness tester with a diamond indenter pyramid.

Vicker's microhardness value $(H_v)^{16}$ has been calculated using $H_v = 1.8544 \text{ P/d}^2 \dots$ (1)

where 'P' is the applied load, 'd' is the mean diagonal length of the indentation impression and 1.8544 is a constant, a geometrical factor / Vicker's conversion factor for the diamond pyramid.

According to Meyer's law¹⁷, the relation connecting the applied load is given by $P_{n} = e^{i\theta_{n}}$ (2)

$$\mathbf{P} = \mathbf{ad}^{\mathbf{n}} \tag{2}$$

where 'n' is the Meyer's index number or workhardening exponent and 'a' is a constant for a given material. The value of workhardening exponent (n) was estimated from the plot of log P versus log d by the least square fit method. The 'n' value is useful to determine whether the material is hard or soft.

EPR spectra were recorded at room temperature on an EPR spectrometer (JEOL – JES – TE 100 EPR) operating in the X – band frequencies with a field modulation of 100 KHz. The microwave frequency was kept at 9.345 GHz and the magnetic field was scanned from 0 to 600 mT. A powder glass specimen of 100 mg was taken in a quartz tube for EPR measurements.

The samples were encapsulated in order to avoid moisture effect prior to measurements. The 2, 2 - diphenyl -1 - picrylhydrazyl (DPPH) with g = 2.0036 was used as a standard field marker.

The EPR spectra were obtained by varying the magnetic field at constant frequency. Absorption of energy associated with the spin transition occurs at the resonant condition: $hv = g\beta B$ (3)

where, 'h' is Planck's constant (6.626 X 10^{-34} J^{s-1}), B is applied magnetic field, 'v' is the microwave frequency, β is a constant, the Bohr magnetron(β =eh/4 π mc=9.723X10⁻¹²JG⁻¹). The factor g, the gyromagnetic ratio / spectroscopic splitting factor, has a value of 2.0023 for a free electron but varies significantly for paramagnetic ions in the solid state. The value of g depends on the particular paramagnetic ion, its oxidation state and coordination number.

Results and Discussion

The experimental values of microhardness (H_v) and Meyer's index number (n) with various applied load for the LB and LBM glass series at room temperature are shown in table 1.

Further, the measured values of microhardness and average microhardness with various distances for the LB and LBM glasses with a fixed load (25 g) are shown in table 2.

 Table-1

 Values of microhardness (H_v) and Meyer's index number / workhardening exponent (n) for various glass compositions with different applied load at room temperature

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Close Semulas	Glass		Microhardness I	Meyer's index number/				
Glass Samples	Composition in		Load / kg	workhardening exponent				
ladel	mol %	0.3	0.5	1	(n)			
$Li_2O - B_2O_3$								
LB	20 - 80	204	206	210	2.041			
$Li_2O - B_2O_3$ -MnO								
LBM1	20 - 70 - 10	255	289	453	3.835			
LBM2	20 - 68 - 12	275	402	533	5.241			
LBM3	20 - 66 - 14	441	736	788	3.050			
LBM4	20 - 64 - 16	543	715	858	3.231			
LBM5	20 - 62 - 18	710	802	865	2.390			
LBM6	20 - 60 - 20	639	740	792	2.441			

Table-2

Values of microhardness (H_v) with various distance for different glass compositions at room temperature

	Ν	/licrohardness H _v /N	Microhardness Average H _v /MPa					
Glass Samples label		Distance d/µm						
_	0	100	200					
$Li_2O - B_2O_3$								
LB	312.1	352.1	304.1	322.8				
Li ₂ O - B ₂ O ₃ -MnO								
LBM 4	752.4	822.7	793.3	789.5				

For all the glass systems there is an increase in microhardness value (table 1) with increasing the applied load from 0.3 to 1kg. Above the load of 1kg significant crack initiation and glass chipping occurs and hardness tests could not be carried out. Further from the above table it was observed that the microhardness values are increases with increasing the mol % of MnO content with all the applied load. It is seen that microhardness increases with the increase of MnO content for LBM glasses, indicating the formation of rigid structure¹⁸. The increasing value of microhardness makes the glass harder and vice versa. In all the studied glass systems the increase of the microhardness with increasing load is in agreement with the reverse indentation size effect (reverse ISE)¹⁹.

According to Onitsch²⁰, workhardening exponent 'n' is greater than 2 when the hardness increases with the increasing load. Since the values of n (table 1) for LB and LBM glasses were greater than 2, the hardness of the material was found to increase with increase of load conforming the prediction of Onitsch. From the table 1 and 2 the magnitude of H_v value is in order: LBM > LB. From the above magnitude it can be concluded that LBM glass possess higher rigidity than the LB glass. It is well known that the magnitude of microhardness related to bond energies²¹.

The electron paramagnetic resonance (EPR) is a very powerful technique for investigating paramagnetic centers in oxide glasses containing transitional metal oxides and it is useful for identifying the local environmental of a paramagnetic imparing and mapping the crystal field²². The EPR absorption spectral of all the glass samples of LBM at room temperature have been recorded are shown in figure 1.



EPR spectra for various mol% of Mn²⁺ ions in lithium borate glass at room temperature

No EPR resonance was detected in the spectra of MnO free samples indicating the absence of paramagnetic impurities in the prepared glasses (not shown in the figure). Recorded EPR spectra show the resonance lines due to Mn^{2+} (3d⁵, ${}^{6}S_{5/2}$) paramagnetic ions for all investigated concentration. As it can be observed in the figure 1 the structure of the spectra at g ≈ 2.0 strongly depends on the MnO content of the samples. Generally, the glasses with doping of MnO show the EPR spectra which consists mainly of intense resonance line centered at $g_{eff} \approx 2.0$ and $g_{eff} \approx 4.3$ values, their relative intensity depends on the manganese content of the samples. The absorption line at $g_{eff} \approx$ 2.0 was attributed to isolated Mn^{2+} ions in octahedral symmetry sites, slightly tetragonally distorted, to the Mn^{2+} ions participating at dipolar interactions or/ and to super exchange coupled pairs of these ions^{23,15}. The resonance line at $g_{eff} = 4.3$ is due to magnetically isolated Mn^{2+} ions, in distorted sites of octahedral symmetry^{24,25}. The g-values (table 3) are decreasing gradually with increase in the content of MnO which indicates that the Mn^{2+} ions that might be responsible for the EPR lines broadening participated in dipolar interaction.

The increasing ionic bonding nature between Mn^{2+} ions and O^{2-} ions generating the octahedral symmetric ligand field was evidenced from the fall of g-parameter with the content of $MnO^{26,27}$. The g_{eff} values are expected to lie very near the free ion value of 2.0023. However a 'g' values (table 3) very much greater than 2.0023 often occurs, and these large 'g' values arise when certain symmetry elements are present. From the figure 1 it was concluded that the presence resonance signal at $g \approx 2.0$ which is due to Mn^{2+} ion in an environment close to the octahedral symmetry and the absence of resonance signal at $g \approx 4.3$ which is due to non-existence of isolated Mn^{2+} ions in cubic symmetric sites slightly tetragonally or rhombically distorted²⁸.

Table-3 The values of g and Ag factor in LBM glasses at room temperature

temperature							
Glass samples label	g	$\Delta \mathbf{g}$					
LBM 1	2.4453	- 0.4430					
LBM 2	2.4337	- 0.4314					
LBM 3	2.4230	- 0.4207					
LBM 4	2.4140	- 0.4117					
LBM 5	2.0327	- 0.0304					
LBM 6	2.0132	- 0.0109					

Further, from the table 3 it was observed that the values of Δg shows negative shift. It was also noted²⁹ 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 the free electron value (2.0023), then the bonding is ionic and conversely, if the shift is positive, then bonding is more covalent in nature. In the present study, from the measured negative shift in the g-value, with respect to free electron 2.0023, it is apparent that the Mn²⁺ ion is in ionic environment³⁰. Further, the negative deviation with increase in the content of MnO indicating the increasing concentration of the octahedrally positioned Mn²⁺ ions.

Conclusion

The effect of MnO content with doping of lithium borate glasses have been investigated using microhardness and EPR measurements at room temperature. The Microhardness studies revealed the anisotropic nature of the material and it further confirms that the glasses belong to hard materials. The EPR spectrum of LBM glasses show the resonance signals at $g \approx 2.0$ which is due to Mn^{2+} ion in an environment close to the octahedral symmetry. Further, negative shift in the g – values reveals the Mn^{2+} ion is in ionic environment.

References

- Mukerji S. and Kar T., Microhardness Study of the Nonlinear Optical Crystal L- Arginine Hydro Chloride Monohydrate, *Metall. Mater. Trans.*, A31, 3087- 3089 (2000)
- Gong J., Pan X., Miao H. and Zhao Z., Effect of Metallic Binder Content on the Microhardness of TiCN – Based Cements, *Mater. Sci. Eng.*, A, 359, 391-395 (2003)
- Sangwal K., On the Reverse Indentation Size Effects and Microhardness Measurement of Solids, *Mater. Chem. Phys.*, 63, 145-152 (2000)
- Mukerji S. and Kar T., Vicker's Microhardness Studies of L-Arginine Hydrobromide Monohydrate Crystals (LAHBr), Cryst. Res. Technol., 34, 1323-1328 (1999)
- Guille J. and Sieskind M., Vicker's Hardness Anisotropy of RFeO 3 (R=Yb, Dy) Single Crystals, J. Mater. Sci., 26, 899-903 (1991)
- Charles J.B. and Gnanam F.D., Vicker's Micromechanical Indentation of NaSb₂F₇ and Na₃Sb₄F₁₅ Single Crystals, *J. Mater. Sci. Lett.*, 9, 165 -166 (1990)
- Irusan T., Arivouli D. and Ramasamy P., Microhardness Studies on Ammonium Acid Urate Crystals, *J. Mater. Sci. Lett.*, 12, 405 -406 (1993)
- Banerjee R. and Feltham P., Theory and Application of Microindentation in Studies of Glide and Cracking in Single Crystals of Elemental of Semiconductors, *J. Mater, Sci.*, 27, 1626 - 1632 (1992)
- Manimaran M., Kalkura S.N. and Ramasamy P., Crystallization of ZnSnAs₂, by Physical Vapor Transport, *J. Mater, Sci. Lett.*, 14, 1366-1368 (1995)
- Muralidhara R.S., Kesavulu C.R., Rao J. L., Anavekar R.V. and Chakradhar R.P.S., EPR and Optical Absorption Studies of Fe³⁺ Ions in Sodium Borophosphate Glasses, J. Phys. Chem. Solids, 71, 1651-1655 (2010)
- 11. Lee J.D., Concise Inorganic Chemistry, Blackwell Scientific, Oxford, (1996)
- Van Die A., Leenaers A.C.H.I., Blasse G. and Van Der Weg W.F., Germanate Glasses as Hosts for Luminescence of Mn²⁺ and Cr³⁺, *J. Non-Cryst. Solids*, 99, 32-44 (1988)
- Margaryan A., Choi J.H. and Shi F.G., Spectroscopic Properties of Yb³⁺ in Heavy Metal Contained Fluorophosphates Glasses, *Appl. Phys. B*, 78, 409-413 (2004)

- Kreidl N.J., Recent Applications of Glass Science, J. Non-Cryst. Solids, 123, 337-384 (1990)
- **15.** Ardelean I., Simone Cora, Raluca ciceo Lucacal, and Octavia Hulpus, EPR and FTIR Spectroscopic Studies of B₂O₃ Bi₂O₃ MnO Glasses, *Solid State Sci.***7**, 1438-1442 **(2005)**
- Chenthamarai S., Jayaraman D., Subramanian C. and Ramasamy P., Mechanical and Optical Studies on Pure and Nitro Doped 4hydroxyacetophenone, *Materials Lett.*, 47, 247-251 (2001)
- Bull S.J., Page T.F. and Yoffe E.H., An Explanation of the Indentation Size Effect in Ceramics, *Phil. Mag. Lett.*, **596**, 281-288 (**1989**)
- Sinouh H., Bih L., Axrour M., El Bouari A., Benmakhtar S., Manoun B., Belhorma B., Baudin T., Berthat P., Haumont R. and Solas D., Elabotation and Structural Characterization of Glasses Inside the Ternary SrO-TiO2-P2O5 System, J. Phys. & Chem. Solids, 73, 961-968 (2012)
- Hemalatha P., Veeravazhuthi V. and Mangalaraj D., Vicker's Microhardness Study of Nonlinear Optical Single Crystals of Doped and Undoped S. BenzylIsothiouronium chloride, *J. Mat.* Engg. & Perform, 18, 106-108 (2009)
- 20. Onitsch E.M., Strain Rate Dependence of the Hardness of Glass and Meyer's Law, *Mickroskopie*, 2, 131-151 (1944)
- 21. Yamane M. and Mackenzie J.D., Vicker's Hardness of Glass, J. Non-Cryst. Solids, 15, 153 164 (1974)
- 22. Chinna Babu J. and Chandra mouli V., Spectroscopic and dc Conductivity Studies of Cu²⁺ Spin Probe in 10Li₂O x Nb₂O₅-(89-x) TeO₂ Glass System, *Ind. J. Pure & appl. Phys.*, 47, 241-247 (2009)
- Griscom D.L., Electron Spin Resonance in Glasses, J. Non-Cryst. Solids, 40, 211-272 (1980)
- 24. Cerny V., Petrova B. and Frumar M., EPR Spectra of Mn^{2+} Doped $Cdx_2 - Pby_2 - Kl$ (x,y = Cl, Br) Glasses, J. Non-Cryst .Solids, 125, 17-24 (1990)
- Petrova B., Frumar M., Cernoskova E. and Cerny V., New Chalcohalide Glasses from the System GeS₂ – Ga₂S₃ – MnCl₂, J. Non-Cryst. Solids., 161, 316 - 319 (1993)
- **26.** Peteanu M., Ardelean I., Filip S., Alexandru D. and Ram, EPR of Mn^{2+} Ions in $70TeO_2 25B_2O_3 5$ PbO Glasses, *J. Phys*, **41**, 593 601 (**1996**)
- Ardelean I. and Filip S., Structural and Magnetic Investigations of Transition Metal Ions in TeO₂ Based Glasses, *J.Optoelectron. Adv. Mater.*, 5, 157-169 (2003)
- Dana Toloman, Biris A.R., Adriara Popa, Oana Raita, Giurgiuand L.M. and Ardelean I., Raman and EPR Studies of Calcium Phosphate Glasses Doped with Manganese Ions, *J. phys.*, Conference series, 182, 012032 (2009)
- 29. Van Wieringen J.S, Paramagnetic Resonance of Divalent Manganese Incorporated in Various Lattices, *Discuss Faraday* Soc., 19, 118-126 (1955)
- 30. Sreekanth Chakradhar R.P., Ramesh K.P., Rao J.L. and Ramakrishna J., Mixed Alkali Effect in Borate Glasses – EPR and Optical Absorption Studies in xNa₂O- (30-x) K₂O-70B₂O₃ Glasses Doped with Mn²⁺, J. Phys. & Phem. solids, 64, 641-650 (2003)