

## Mössbauer and infrared studies of manganese doped iron borate glasses

Roshan Lal\*, N D Sharma,\* H K Sharma\*\* & Kailash Chandra\*\*\*

\*Department of Physics, Kurukshetra University, Kurukshetra 136 119

\*\*Department of Chemistry, Kurukshetra University, Kurukshetra 136 119

\*\*\*I I C, Indian Institute of Technology, Roorkee 247 677

Received 21 May 2003, revised 15 September 2003, accepted 20 October 2003

The infrared absorption spectra of Manganese-doped Iron borate glasses ( $X=0,10,15,20\&30$  mol% MnO) have been investigated to find out the role played by Manganese on the structure of these glasses. MnO was gradually introduced to replace  $\text{Fe}_2\text{O}_3$  in the series of manganese doped iron borate glasses containing 60%  $\text{B}_2\text{O}_3$ . The structural changes induced were consistent with  $\text{Mn}_2\text{O}_3$  formulation and were inferred by monitoring the I.R. spectra of these glasses in the range 200-4000  $\text{cm}^{-1}$  by KBr Technique. The similar ionic radii of  $\text{Fe}^{3+}$  and  $\text{Mn}^{3+}$  cause no structural changes in either series as observed from infrared spectroscopy, which show that the  $\text{Fe}^{3+}$  ions concentration at B-site is replaced by  $\text{Mn}^{3+}$  ions. Mössbauer Technique was applied to study the effect of manganese doping at the Fe site for all the samples.

**Keywords:** Mössbauer study, Infrared spectra, iron borate glasses, glasses

### 1 Introduction

Infrared spectroscopy has been extensively employed over the years to investigate the structure of glasses. Borate glasses have been the subject of numerous infrared studies due to their structural peculiarities. Recently, the study of oxide glasses has received considerable attention due to their structural characteristics. In borate glasses,  $\text{B}_2\text{O}_3$  is a basic glass former because of its higher bond strength, lower cation size, smaller heat of fusion and trivalency of boron. In borate glasses  $\text{B}^{3+}$  ions are triangularly coordinated by oxygen, form glasses readily. In  $\text{B}_2\text{O}_3$  the units are triangles, which are corner bonded in a random configuration<sup>1</sup>. The main structural units of borate glasses are  $\text{BO}_3$  groups and they form a planar triangular structure. This structure further gets modified into three-dimensional network. The structure of borate glasses is different than other glasses such as phosphate, silicate, etc. The structure of borate glasses heavily depends upon the cooling rate of the melt through the range of the glass transition temperature<sup>2</sup>. MnO ( $\text{MnO}/\text{Mn}_2\text{O}_3$ ) can enter the glass network both as a network former and also as a network modifier and due to this the glass formed is expected to be different from the alkali borate glasses. In the present work the structure of  $\text{XMnO} \cdot (40-X) \text{Fe}_2\text{O}_3 \cdot 60 \text{B}_2\text{O}_3$  glasses is discussed

with the help of infrared spectra. To elucidate the conduction mechanism in the present glass system, one has to know the structure. Since infrared spectroscopy is the most advantageous tool for the study of amorphous materials, we have used it to determine the structure of borate glasses containing various amounts of MnO( $\text{MnO}/\text{Mn}_2\text{O}_3$ ) and  $\text{Fe}_2\text{O}_3$ . Here we have replaced iron oxide concentration at B-site by manganese oxide to study the effect of +3 charge state on iron. The room temperature Mössbauer study of these glasses is also reported.

### 2 Experimental Details

#### 2.1 Sample preparation

Manganese doped iron-borate glasses were prepared from reagent grade powders of  $\text{MnCO}_3$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{H}_3\text{BO}_3$ , which were thoroughly mixed, in appropriate proportions. Manganese oxide was introduced as  $\text{MnCO}_3$ ,  $\text{B}_2\text{O}_3$  was introduced as orthoboric acid while the hematite was in the form of  $\text{Fe}_2\text{O}_3$ . The batch materials were dry mixed and melted in platinum crucibles placed in a electrically heated muffle furnace at  $1080\pm 20^\circ\text{C}$  for about 30min, until a bubble free liquid was formed. The molten glass was equilibrated at the melting temperature until a clear and homogeneous melt was obtained. The melt was cast onto a stainless steel plate and annealed at

about 450 °C in a muffle furnace which was left to cool down to room temperature at a rate of 30°C/hr. The glasses obtained were subsequently annealed to release strain. The general formula was  $\text{XMnO} \cdot (40-X)\text{Fe}_2\text{O}_3 \cdot 60\text{B}_2\text{O}_3$ , here  $X=10, 15, 20$  and  $30$  in mol %.

### 2.2 X-ray diffraction measurements

The X-ray powder diffraction experiment was done at I.I.T. Roorkee. The Philips PW 1140/09 X-ray powder diffractometer was used. The details of operating conditions were as follows: generator rating, 35kv, 20mA; radiation  $\text{Cu-K}\alpha$  (angle range 5 to 90°) and step size 1cm/min. X-ray diffraction data was used to check for possible crystallinity of the sample after quenching and annealing. All samples were found to be completely amorphous in nature.

### 2.3 Infrared measurements

The vibration spectra of the various glasses were obtained at room temperature using the KBr pellet technique in the range 200-4000 $\text{cm}^{-1}$  on Jasco FT/IR-300E spectro-photometer. The investigated samples were ground to fine particles and then mixed with KBr in the ratio 2:200. The mixture was then subjected to a pressure of 5 ton/ $\text{cm}^2$ . The spectra were measured immediately after preparing the desired disks.

### 2.4 Mössbauer measurements

Samples were crushed to obtain fine powders and sieved through a 200  $\mu\text{m}$  gauge. The Mössbauer absorber was prepared by pressing the powder in the aluminum holder of diameter 10mm so that areal density was 50mg/ $\text{cm}^2$  with uniform spread and fixing the open ends with cellophane tapes. The absorption spectra were recorded in transmission geometry at room temperature with a constant acceleration Mössbauer drive and a 256-multichannel analyzer, using Austin Science Inc, U.S.A Mössbauer Spectrometer. A  $^{57}\text{Fe}(\text{Rh})$  source with initial activity of 10mCi was used. In general several runs were taken to check the reproducibility of the spectra. Total counts collected per channel were close to  $10^6$  or more. The Mössbauer spectrometer was calibrated using a 0.001 inch enriched  $\alpha\text{-Fe}$  foil. The outermost lines were separated through 10.68mm/s. This is in excellent agreement with an ideal absorption spectrum and calibration was done accordingly. One channel corresponds to a velocity of 0.0628mm/s. The experimental data were fitted using a least squares fitting program assuming Lorentzian lineshape with

$\chi^2$ . minimization technique. The solid line through the data points is the result of the computer fit of the data.

## 3 Results and Discussion

Five samples of the glass series  $\text{XMnO} \cdot 60\text{B}_2\text{O}_3$  ( $40-X$ )  $\text{Fe}_2\text{O}_3$ ;  $X = 0, 10, 15, 20$  &  $30$  were studied. In each of the sample one of the constituent i.e.,  $\text{B}_2\text{O}_3$  was kept fixed while iron oxide was replaced by manganese oxide

### 3.1 Infrared measurements

The vibrational modes of the borate network are seen to be mainly active in three infrared regions, which are similar to those reported earlier<sup>3-6</sup>. The first group of bands that occur at 1200-1600  $\text{cm}^{-1}$  is due to the asymmetric stretching relaxation of B-O bond of the tetragonal  $\text{BO}_3$  units. The second group lies between 800-1200  $\text{cm}^{-1}$  and is due to B-O bond stretching of the tetrahedral  $\text{BO}_4$  units. The third group is observed around 700  $\text{cm}^{-1}$  and is due to bending of B-O-B linkages in the borate network. The infrared spectra of the present glass systems show nine to ten absorption peaks as shown in Fig.1. The peaks are sharp, medium and broad. In the pure  $\text{B}_2\text{O}_3$  glass, the absorption peak at 806  $\text{cm}^{-1}$  is the characteristic of boroxol ring (boron in III coordination). The absence of the band at 806  $\text{cm}^{-1}$  signifies that no boroxol ring is present in the glass system under study. This corresponds to the progressive substitution of boroxol ring by  $\text{BO}_3$  &  $\text{BO}_4$  groups. These groups may be attached in the form of random network. This type of behaviour has also been observed in  $\text{B}_2\text{O}_3 \cdot \text{Li}_2\text{O}$  glass by other workers<sup>7-8</sup>. In the present glass system  $\text{XMnO}(40-X)\text{Fe}_2\text{O}_3 \cdot 60\text{B}_2\text{O}_3$ , when Mn is absent i.e. for  $X=0$ , nine peaks are observed as shown in Fig. 1. The first absorption band is located in the region 1194-1470  $\text{cm}^{-1}$  and is associated with the fundamental asymmetrical stretching vibration of the B-O bond of the trigonal  $\text{BO}_3$  units (Table 1). The other group is located in the region 925-1019  $\text{cm}^{-1}$  and originates from B-O bond stretching of the tetrahedral  $\text{BO}_4$  units and is due to vibration of some boron atoms attached to non-bridging oxygen in the form of  $\text{BO}_4$  vibrations<sup>9</sup>. The shoulder at 1020  $\text{cm}^{-1}$  indicates the formation of diborate group in the present glasses. In I.R. spectra of  $\text{PbO}_2 \cdot \text{B}_2\text{O}_3 \cdot \text{ZnO}$  glasses the absorption band at about 993 $\text{cm}^{-1}$  is attributed to a B-O stretching vibration of B-O-Pb linkage<sup>10</sup>. In the present glasses a lower frequency band observed at  $\sim 925\text{cm}^{-1}$  is most probably due to the greater M-O interaction in B-O-M

linkage resulting in weakening of B-O bond and hence lowers its frequency in comparison to the value

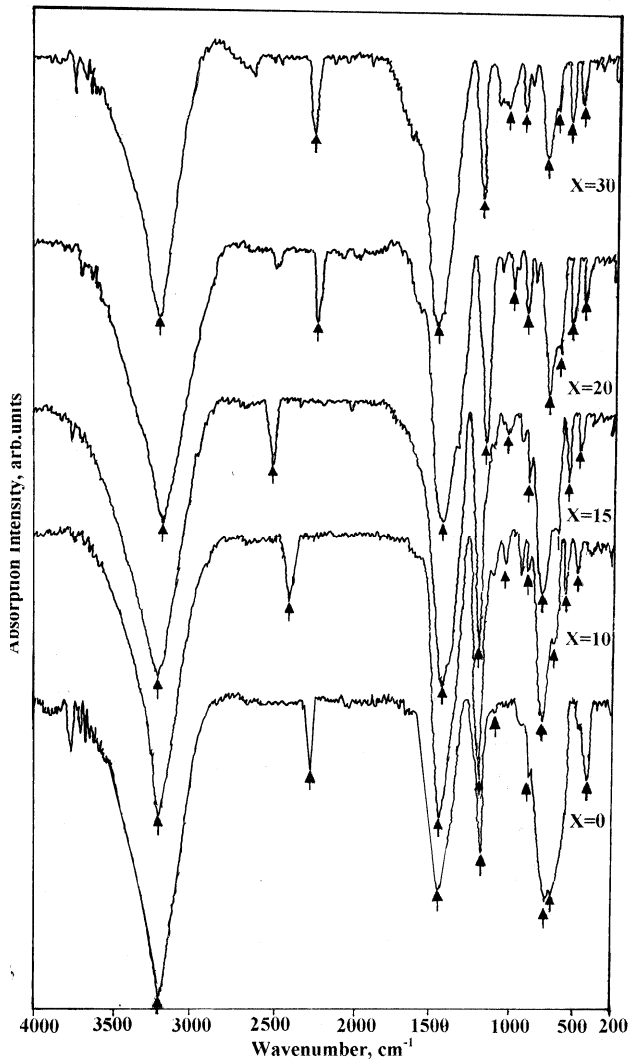


Fig. 1 — IR absorption Spectra for  $\text{XMnO} \cdot (40\text{-X})\text{Fe}_2\text{O}_3 \cdot 60\text{B}_2\text{O}_3$  glass system, for  $X=0, 10, 15, 20, 30$  mol %. Peak positions of each ten bands as listed in Table 1 are indicated by an arrow in the same order as assigned in Table 1

observed in  $\text{PbO}_2 \cdot \text{B}_2\text{O}_3 \cdot \text{ZnO}$  glasses. This can be attributed to B-O stretching vibration of B-O-M linkage where M represents a metal ion ( $\text{Mn}^{3+}/\text{Fe}^{3+}$ ). The third group of band is observed at  $720 \text{ cm}^{-1}$  and is due to bending of B-O-B linkage in the borate network. The absorption band observed at  $646 \text{ cm}^{-1}$  is due to bending of O-B-O linkage<sup>10</sup>. This possibility is more in borate glasses where boroxol ring is absent. Boron is a network forming cation, it may occupy the centers of oxygen triangles or tetrahedral sites. The low frequency band observed at  $\sim 354 \text{ cm}^{-1}$  is assigned to Fe-O stretching vibration<sup>11</sup>. Besides the vibrational bands due to borate network, the spectra also reveal, a group of prominent absorption bands in the near-infrared range from  $2200\text{-}3200 \text{ cm}^{-1}$  due to hydroxyl or water groups<sup>4</sup> and these are persistent in all compositions. The fundamental frequency<sup>10</sup> at  $960 \text{ cm}^{-1}$  due to  $\text{BO}_3^{3-}$  groups is not observed in the present glasses. This may be due to the fact that the structure of borate glasses heavily depends on their thermal history. The different rates of cooling of the melt and quenching temperature also affect the structure of the borate glasses.

On addition of Mn i.e at  $X=10$ , the appearance of an additional band  $\sim 370 \text{ cm}^{-1}$  is assigned to Mn-O[Mn(III)] stretching unit<sup>11</sup>. The absorption band lying in the region  $925\text{-}1194 \text{ cm}^{-1}$  gets slightly intensified. On further addition of Mn in the glasses no structural changes are observed in the IR spectra, which shows that the structure of the present glasses is independent of composition. This also supports that  $\text{Fe}^{3+}$  ions are being replaced by  $\text{Mn}^{3+}$  ion. In present glasses, it is found that there is no frequency band observed at  $\sim 840 \text{ cm}^{-1}$ , which is a characteristic of the formation of tetrahedral  $\text{MO}_4$  units<sup>10</sup>. The absence of this band in the IR spectra clearly indicates the absence of tetrahedral formation of Mn( $\text{MnO}_4$ ) in the present glass system. Also, no boroxol ring formation

Table 1— Peak frequencies from IR spectra for  $\text{XMnO} \cdot (40\text{-X})\text{Fe}_2\text{O}_3 \cdot 60\text{B}_2\text{O}_3$

Glass No.	Composition (Mol%)			Peak Positions (cm-1)									
	MnO	$\text{Fe}_2\text{O}_3$	$\text{B}_2\text{O}_3$	Mn-O	Fe-O	O-B-O	B-O-B	B-O-M	$\text{BO}_4$	$\text{BO}_3$	hydroxyl group		
A	0	40	60	354	--	646	720	925	1019.8	1194	1470	2260	3221
B	10	30	60	352	372	645.8	719.2	924	1021.0	1194	1460	2510	3220
C	15	25	60	353	373	644.2	720.8	925	1020.2	1193.9	1466	2510	3215
D	20	20	60	355	371	642	718.7	926	1020.2	1194	1466.7	2521	3221.6
E	30	10	60	354	372	643.4	719.0	924	1023.0	1194.8	1484	2516	3215

is observed. It is concluded that the structure of Mn doped iron borate glasses consists of randomly connected  $\text{BO}_3$  &  $\text{BO}_4$  groups.

### 3.2 Mössbauer measurements

Mössbauer absorption spectra of all the samples i.e.  $X=0,10,15,20$  &  $30$  were recorded at room temperature as shown in Fig. 2. The spectra were computer fitted and the hyperfine parameters i.e. Isomer shift ' $\delta$ ' mm/s, quadrupole splitting ' $\Delta$ ' mm/s, line width ' $\Gamma$ ' mm/s and hyperfine field ' $H_{\text{int}}$ ' kOe were computed using normal procedure<sup>12</sup> and are listed in Table 2. The Mössbauer absorption spectra for the samples  $X=0,10,15,20$  were analyzed for two quadrupole doublets, and the sample  $X=30$  was analyzed for single quadrupole doublet. It is generally observed that addition of cobalt in these glasses increases  $T_C$ , atleast at low concentration, while addition of Mn decreases<sup>13</sup> the values of  $T_C$ ,  $T_C$  also increases with an increase in the boron concentration as explained by Rao<sup>14</sup>. In our work the boron concentration is kept fixed, where as the iron concentration is decreased and the manganese concentration is increased. It is evident that the manganese ions have substituted the corresponding iron ions as the size of manganese ion is comparable to that of iron ion<sup>15-16</sup>. As observed in I.R absorption spectra of glasses there is no tetrahedral formation of  $\text{MnO}(\text{MnO}_4)$ , this suggests that only  $\text{Mn}^{3+}$  ion replaces the corresponding  $\text{Fe}^{3+}$  ions at B-site. This tendency of manganese is due to dual role of  $\text{Mn}^{3+}$  cations in glass structure. In glass structure  $\text{Mn}^{3+}$  cations play the role of network modifier when these cations are ionically bonded. On the other hand, if Mn-O bond is covalent  $\text{Mn}^{3+}$  cation will act as a glass modifier. From the experimental observations such as I.R. & Mössbauer study, it has been observed that  $\text{Mn}^{2+}(\text{MnO})$  probably changes to  $\text{Mn}^{3+}$  at higher temperatures ( $>1000^\circ\text{C}$ ). Similar results have also been reported by Ch Sumalatha *et al.*<sup>17</sup> in  $\text{MnO-Bi}_2\text{O}_3\text{-PbO}$  glasses. In our present investigation, the possible interactions at the B-site are as follows: (1)  $\text{Fe}^{3+}-\text{Fe}^{3+}$ , (2)  $\text{Fe}^{3+}-\text{Mn}^{3+}$ , (3)  $\text{Mn}^{3+}-\text{Mn}^{3+}$ . Out of these,  $\text{Fe}^{3+}-\text{Fe}^{3+}$  &  $\text{Fe}^{3+}-\text{Mn}^{3+}$  interactions are very weak<sup>17-18</sup> while  $\text{Mn}^{3+}-\text{Mn}^{3+}$  interaction is strong antiferromagnetic<sup>18,20</sup>. As the size of the iron ion is comparable to that of Mn ion and both occupy A & B sites respectively. Although iron ion prefer B-site and Mn ion A-site<sup>21</sup>, however in our study  $\text{Mn}^{2+}$  is being converted into  $\text{Mn}^{3+}$  and the latter prefers B-site. In the absence of Mn doping the possible interaction at

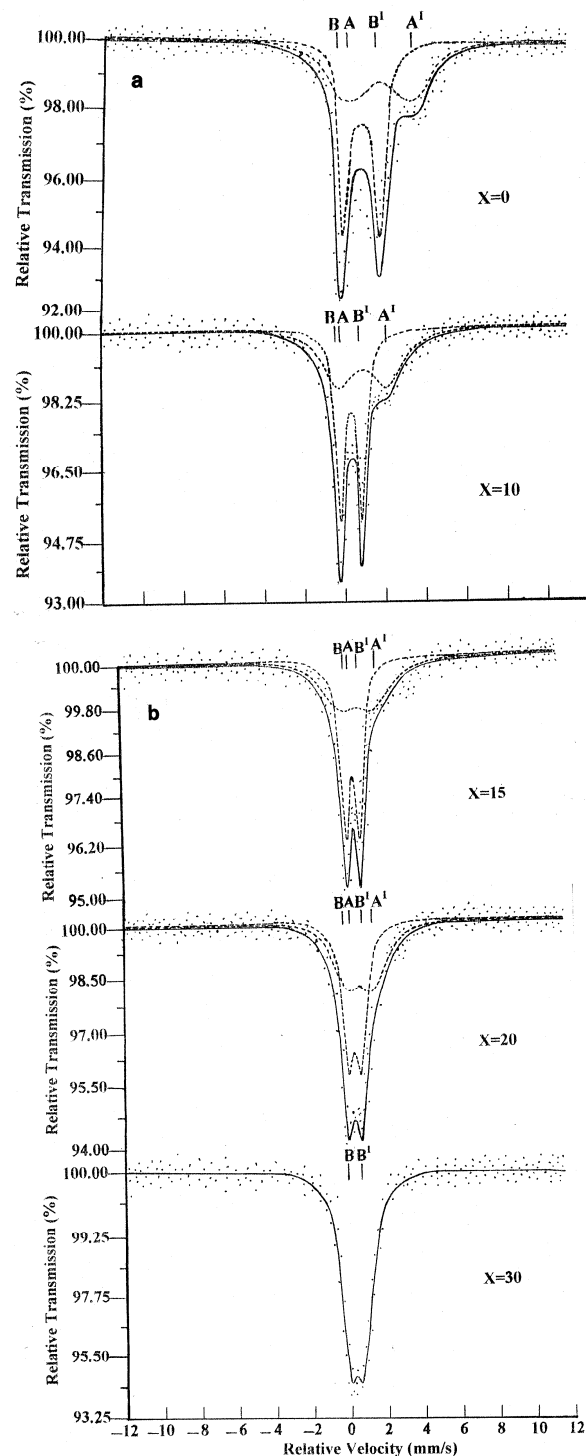


Fig. 2 — Mössbauer absorption spectra of  $X=0,10,15,20,30$  mol% of the glass system recorded at room temperature. (Data points represent experimental observation. The dashed line gives the curve obtained by fitting the experimental points and the solid line gives the total envelope of the fitted curves).

B-site is  $\text{Fe}^{3+}-\text{Fe}^{3+}$ . On addition of Mn,  $\text{Fe}^{3+}$  ions occupying B-site are replaced by  $\text{Mn}^{3+}$  ions, which

Table 2 — Hyperfine interaction parameters computed from Mössbauer absorption spectra recorded at room temperature, Isomer shift 'δ' is given relative to α-Fe.

Composition X (Mol. %)	Site	Isomer shift ( $\delta \pm 0.01$ ) mm/s	Quadrupole splitting ( $\Delta \pm 0.01$ ) mm/s	Line Width ( $\Gamma \pm 0.01$ ) mm/s	$\chi^2$ /degree of freedom	$H_{\text{int}}$ ( $\pm 1$ ) kOe
X=0	AA <sup>I</sup>	0.91	4.97	2.27	0.51	134
	BB <sup>I</sup>	0.56	3.17	0.52		
X=10	AA <sup>I</sup>	0.70	3.80	1.74	0.62	75
	BB <sup>I</sup>	0.29	1.77	0.48		
X=15	AA <sup>I</sup>	0.69	2.52	1.50	0.31	67
	BB <sup>I</sup>	0.33	1.29	0.44		
X=20	AA <sup>I</sup>	0.67	2.02	1.28	0.49	62
	BB <sup>I</sup>	0.32	1.13	0.58		
X=30	BB <sup>I</sup>	0.33	1.24	0.80	0.48	49

causes the depletion in  $\text{Fe}^{3+}/\text{Fe}^{2+}$  ratio and  $\text{Mn}^{3+}$ - $\text{Mn}^{3+}$  (metal-metal) interaction at B-site decreases, which tends to lower the magnetic field. On further addition of Mn more & more iron ions are being replaced by  $\text{Mn}^{3+}$ , due to which metal-metal interaction further decreases and greatly reduce the magnetic field. A similar trend has also been observed by Blasse<sup>18</sup> in  $\text{ZnFe}_{2-x}\text{Mn}_x\text{O}_4$  system. It is also clear from the Mössbauer absorption spectra that there is a continuous decrease in the hyperfine field. In the present series of glasses the concentration of magnetic ion ( $\text{Fe}^{3+}$ ) on A-site remains lower compared to that on B-sites and the mol % of iron decreases with addition of Mn. On the basis of hyperfine parameters it is concluded that a transition from ferromagnetic to paramagnetic state occurs in the present glass systems. Similar trend has also been observed by I.K.Rao<sup>14</sup> in Mn doped iron borate metallic glasses.

### 3. Conclusion

It is concluded that the structure of Manganese-doped iron borate glasses consists of randomly connected  $\text{BO}_3$  and  $\text{BO}_4$  groups. The structure of the present glass system is independent of composition. In these glasses no tetrahedral formation of MnO occurs. Similarly the boroxol ring formation is not observed. The I.R. & Mössbauer study of the samples indicate that ferromagnetic to paramagnetic behavior of the system is observed due to decrease in hyperfine field with increase in manganese concentration.

### Acknowledgement

The authors are thankful to Prof. Nawal Kishore, Head, Department of Applied Physics, G J University,

Hissar & Prof. S.P. Taneja, Department of Physics, M D University, Rohtak, for useful discussions and help in preparing the samples.

### References

- Kingrey W D, *Introduction to ceramics* (Marcell Dekker Inc.), (1976) 102.
- Soppe W, Kleerebezem J & Hartog den H W, *J Non-Cryst Solids* 93 (1987) 142.
- Yawale S P, S V Pakade & Adgaonkar, *Indian J pure & Appl Phys*, 33 (1995) 34.
- Khalifa F A, Batal H a El & Azooz A, *Indian J Pure & Appl Phys*, 36 (1998) 314.
- Batal H A El, Khalifa F A & Azooz M A, *Indian J Pure & Appl Phys*, 39 (2001) 565.
- Ahmed A A, Elshafi N Abd & Eltohamy M R, *Indian J Pure & Appl Phys*, 36 (1998) 335.
- Panicker V G, Upadhyay R V, Rao S N & Kulkarni R G, *J Mat Sci Lett*, 3 (1983) 385.
- Galeener F L, Lucovsky G & Mikkelsen J C, *Phys Review B* 22 (1980) 3983.
- Ito Y, Miyauchi K & O J T, *J Non-Cryst Solids*, 57 (1983) 389.
- Motke S G, Yawale S P & Yawale S S, *Bulletin Material Science*, 25, 1 (2002) 75.
- Nakamoto K, *Infrared & Raman spectra of Inorganic and Coordination compounds*, 4<sup>th</sup> edition, Johan Wiley & Sons, New-York (1992)
- Bancroft G M, *Mössbauer Spectroscopy- An introduction for inorganic chemists and geochemists* (McGraw-Hill, New York), 1973, p. 197.
- Moskalewicz R & Zych W, *Phys Status Solidi a* (Germany), 97 (1986) K 43.
- Rao I K, *Indian J Pure & Appl Phys*, 36 (1998) 335.

- 15 Reddy V R, Das D, Mukhopadhyay P K, Chintalapudi S N & Reddy K Rama, *Proceedings of the Solid State Phys Symposium*, 42 (1999) 581.
- 16 Ahn K H, Wu X W, Liu K, & Chien C L, *Physical Review B* 54, 21 (1996) 15299.
- 17 Ch Sumalatha, Sreedhar B, Yamazuki M et al, *J Non-Cryst. Solids* 203 (1996) 84.
- 18 Blasse G, *Philips Res Rep (Netherlands)*, 20 (1965) 528.
- 19 Lotgering F K, *J Phys & Chem Solids (GB)*, 27 (1966) 139.
- 20 O 'les A, *Phys Status-Solidi a (Germany)*, 3 (1970) 569.
- 21 Smit J & Wijn H P J, *Ferrites (Philips Tech Lib Eindhoven, Netherland)*, (1959) 149.