Hyperfine Interact (2006) 170:127–130
DOI 10.1007/s10751-006-9466-3

^{57}Fe Mössbauer spectroscopic study of $(25-x)$MnO–xZnO–15Fe$_2$O$_3$–60B$_2$O$_3$ glasses

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Abstract The ^{57}Fe Mössbauer technique has been used to investigate the effect of zinc oxide substitution in $(25-x)$MnO–xZnO–15Fe$_2$O$_3$–60B$_2$O$_3$ glass system (x=0, 5, 10, 15 and 20 mol% of ZnO). Mössbauer absorption spectra for all the samples recorded at room temperature suggest the existence of the two paramagnetic quadrupole doublets. The observed variations in hyperfine parameters have been explained on the basis of cations distribution and exchange interaction at the lattice sites and it is concluded that B–B interaction increases while the metal–metal interaction decreases due to replacement of manganese oxide by zinc oxide. These results suggest that the present glass system exhibits a paramagnetic behaviour that changes towards the weak paramagnetic when manganese oxide was replaced with zinc oxide.

Key words Mössbauer technique · zinc oxide substitution · absorption spectra

1 Introduction

^{57}Fe Mössbauer technique is an excellent tool to study the magnetic behaviour in magnetic materials e.g. ferrites, alloys and glasses. Generally glasses are disordered materials having non-periodic arrangement of atoms. Several metal oxides like ZnO, MnO, PbO, CuO, etc. are mixed with B$_2$O$_3$ to form glasses.

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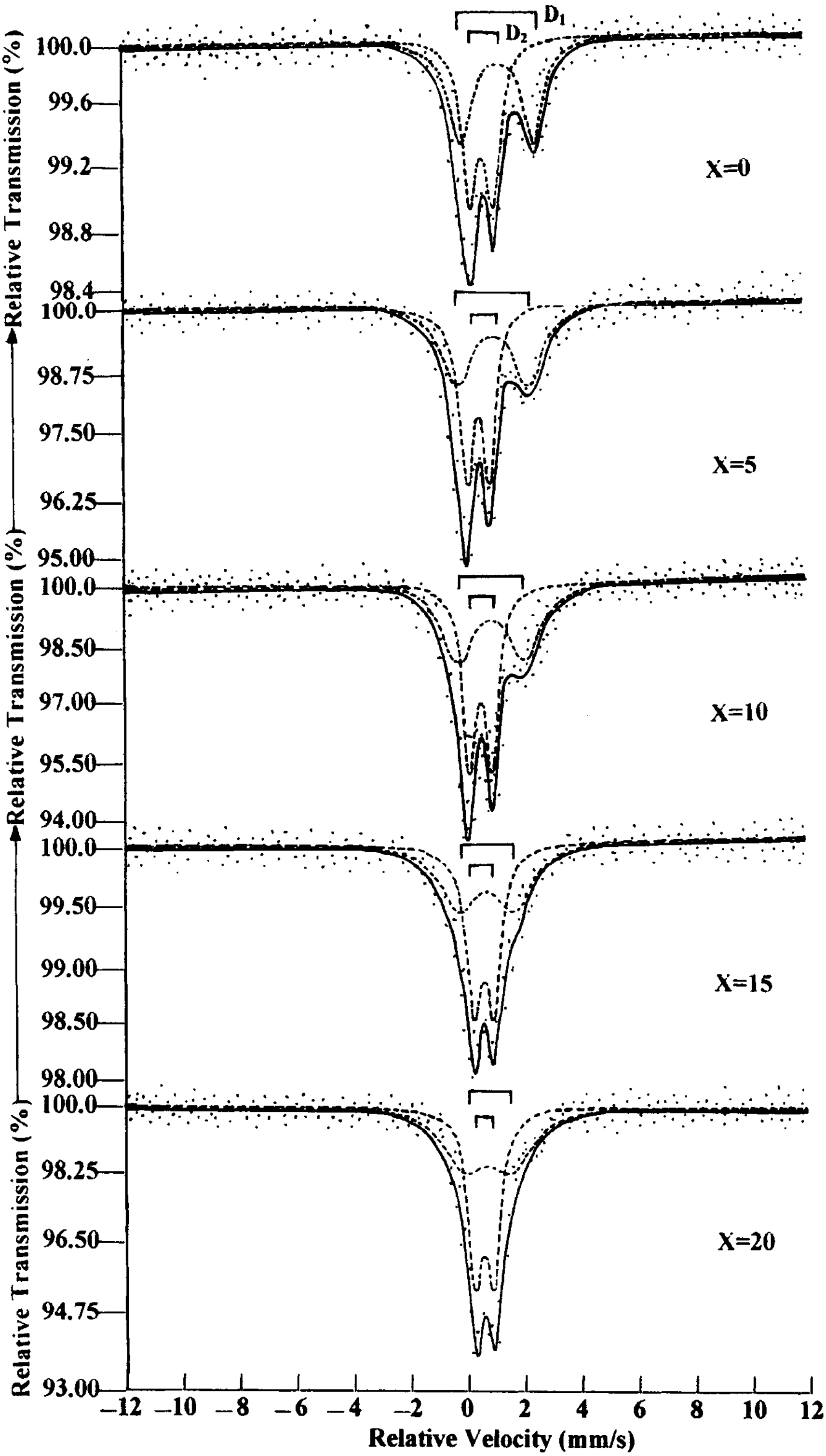

Fig. 1 Mössbauer absorption spectra for X=0, 5, 10, 15 and 20 recorded at room temperature

Table 1 Hyperfine interaction parameters computed from Mössbauer spectra recorded at room temperature,'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	χ^2/degree of freedom
X=0	D$_1$	0.87	4.82	0.93	0.39
	D$_2$	0.37	1.53	0.63	
X=5	D$_1$	0.78	4.62	1.19	0.32
	D$_2$	0.23	1.48	0.55	
X=10	D$_1$	0.58	4.44	1.28	0.33
	D$_2$	0.23	1.48	0.52	
X=15	D$_1$	0.33	3.65	1.47	0.43
	D$_2$	0.25	1.32	0.59	
X=20	D$_1$	0.38	3.06	1.67	0.31
	D$_2$	0.29	1.25	0.57	

D$_1$ and D$_2$ corresponds to doublet one and two

Recently the study of zinc oxide in the form of zinc ferrite thin film [1, 2] as well as magnetic properties of zinc substituted manganese ($Mn_{1-X}Zn_XFe_{2-X}O_4$) ferrites system [3] received considerable attention due to their structural characteristics and its uses in different commercial applications [4].

When manganese ferrite diluted with zinc then it shows a ferromagnetic to a week paramagnetic behaviour. So we plan to prepare such system in the form of borate glasses in order to study its magnetic behavior.

2 Experimental

Zinc substituted Manganese doped iron borate glasses were prepared from regent grade powders of ZnO, MnCO$_3$, Fe$_2$O$_3$ and H$_3$BO$_3$ by solid-state reaction technique. The general formula was $(25-x)$MnO–xZnO–15Fe$_2$O$_3$–60B$_2$O$_3$, here x=0, 5, 10, 15 and 20 in mol% of zinc oxide. The X-ray diffraction patterns shows that all the samples are completely amorphous in nature. Mössbauer absorption spectra of all the samples recorded at room temperature and were fitted to two paramagnetic quadrupole doublets as shown in Fig. 1.

3 Results and discussion

From the experimental observations such as IR and Mössbauer study, it has been observed [5, 6] that no tetrahedral formation occur which suggest that Mn^{2+}(MnO) probably changes to Mn^{3+} at higher temperature.

The variation in observed hyperfine parameters has been explained on the basis of cation distribution and exchange interactions between iron ions and zinc ions at the octahedral (B) and tetrahedral (A) sites. It has been reported that Mn^{3+} has strong preference to occupying only the octahedral B-site, however ZnO (Zn^{2+} ion) has strong chemical preferentially occupy A-site.

When zinc oxide is introduced at the cost of Manganese oxide, there is consistent decrease in hyperfine parameters listed in Table 1. This is due to the fact that some of the zinc oxide is lost (during firing process as zinc oxide is more volatile having lowest values of melting point and vapour pressure than those for other elements) while the remaining zinc ion migrate iron ions from A to B site in view of the site preferences for different ions as mentioned above. This increases the iron concentration at B site. However as zinc oxide concentration increases, the iron ions left at A site being small in number, the A–B interaction experienced by B-site iron ions decreases. Also, the increased number of iron ions at the B site increases the B–B interaction; resulting in spin canting consequently, the hyperfine parameters decrease. Moreover, the possible interactions at the B-site are as follows : (1) Fe^{3+}–Fe^{3+}, (2) Fe^{3+}–Mn^{3+}, (3) Mn^{3+}–Mn^{3+}. Out of these Fe^{+3}–Fe^{3+} and Fe^{3+}–Mn^{3+} interactions are very weak while Mn^{3+}–Mn^{3+} interaction is strong antiferromagnetic. As the manganese oxide concentration is being replaced by zinc oxide concentration due to which metal–metal interaction at the lattice site B decreases which causes the depletion in the hyperfine parameters.

Present study shows that when the manganese doped iron borate glasses are diluted with ZnO, show a paramagnetic to a week paramagnetic behavior. However when this system was formed in the form of ferrite [3], showed a ferromagnetic to a weak paramagnetic behavior when diluted with zinc oxide.

On the basis of these results it is concluded that magnetic behaviour of the system depends upon the method of preparation as well as on the sintering temperature.

4 Conclusion

It is concluded that the present glass system shows a paramagnetic behaviour that decreases to a week paramagnetic behaviour when manganese oxide was replaced by zinc oxide.

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