

STRUCTURE OF LITHIUM BORATE –TRANSITION METAL OXIDE SYSTEM

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ABSTRACT

Structural properties of some lithium borate–transition metal oxide system have been investigated by means of X–ray diffraction studies and Infrared spectroscopy. Analysis of the network structures were carried out based on 1) networks modified by Li_2O and 2) networks modified by V_2O_5 . Networks modified by Li_2O are formed by three–dimensional arrangement of BO_3 , BO_4 groups, non–bridging and bridging oxygens, while the networks modified by V_2O_5 are made by three–dimensional array of clusters with BO_3 and BO_4 groups.

Key words: Lithium Borate, Transition Metal Oxide, XRD, IR Spectra.

INTRODUCTION

Boron atoms have coordination numbers three or four in borates and form the fundamental triangular BO_3 and tetrahedral BO_4 groups. The connections of several groups make a stable cluster, which forms a network structure. The network structure of pure boron oxide is thought to consists predominantly of connected boroxol rings built up of only BO_3 groups¹, while borate structure containing network modifiers involve BO_3 and BO_4 groups in clusters². A number of spectroscopic studies such as IR, NMR, Raman, X–ray spectra, etc and Molecular Dynamics (MD) simulation have been carried out so as to know the geometry and distribution conduction sites responsible for ionic migration^{3–5}. System containing transition metal oxides such as V_2O_5 , Fe_2O_3 , WO_3 with different glass forming substances P_2O_5 , TeO_2 , B_2O_3 , etc. have been reported to possess semiconducting properties^{6–8}. In this paper, results of X–ray diffraction and infrared spectra of the system made at room temperature were investigated to understand the changes in the network structure.

EXPERIMENTAL

The system has a general formula as $(26 + x) \text{V}_2\text{O}_5 - 39 \text{B}_2\text{O}_3 - (35 - 2x) \text{Li}_2\text{O} - x \text{WO}_3$, for $x = 0, 1.5, 3$ and 4.5 ; x varies by 1.5 for four different compositions. System with $x = 0, 1.5, 3$ and 4.5 are referred as A_1, A_2, A_3, A_4 samples, respectively. These samples were synthesized using reagent grade of starting materials V_2O_5 , H_3BO_3 , Li_2CO_3 , H_2WO_4 . The corresponding four oxides in appropriate amounts of well–dried and desiccated ingredients were thoroughly wet–mixed in an agate mortar for about 2 hrs in acetone. The well–mixed and dried oxides were

melted in a silica crucible for 2 hrs at around 1100 °C. The melt was then finally vitrified onto aluminium plate.

X-ray powder diffraction data of the system were obtained on Philips PW 1700 X-ray powder diffractometer. The IR absorption spectra of the system were obtained in KBr pellet, using Specord-75 spectrophotometer to understand the changes in the network structure.

RESULTS AND DISCUSSION

X-ray Diffraction: The X-ray diffraction spectra of the system for four different compositions are shown in figure 1. The system shows amorphous character. It is clear from the spectrum that the ternary system ($x = 0$) is completely amorphous. Some traces of glassy phases are observed in quaternary samples with reduction of Li_2O .

Figure 2 exhibits the ir absorption spectra of the system. To assign various peaks observed in the above spectrum, the ir spectra of 50 Li_2O : 50 B_2O_3 (hereafter referred as 50 L-B) and 50

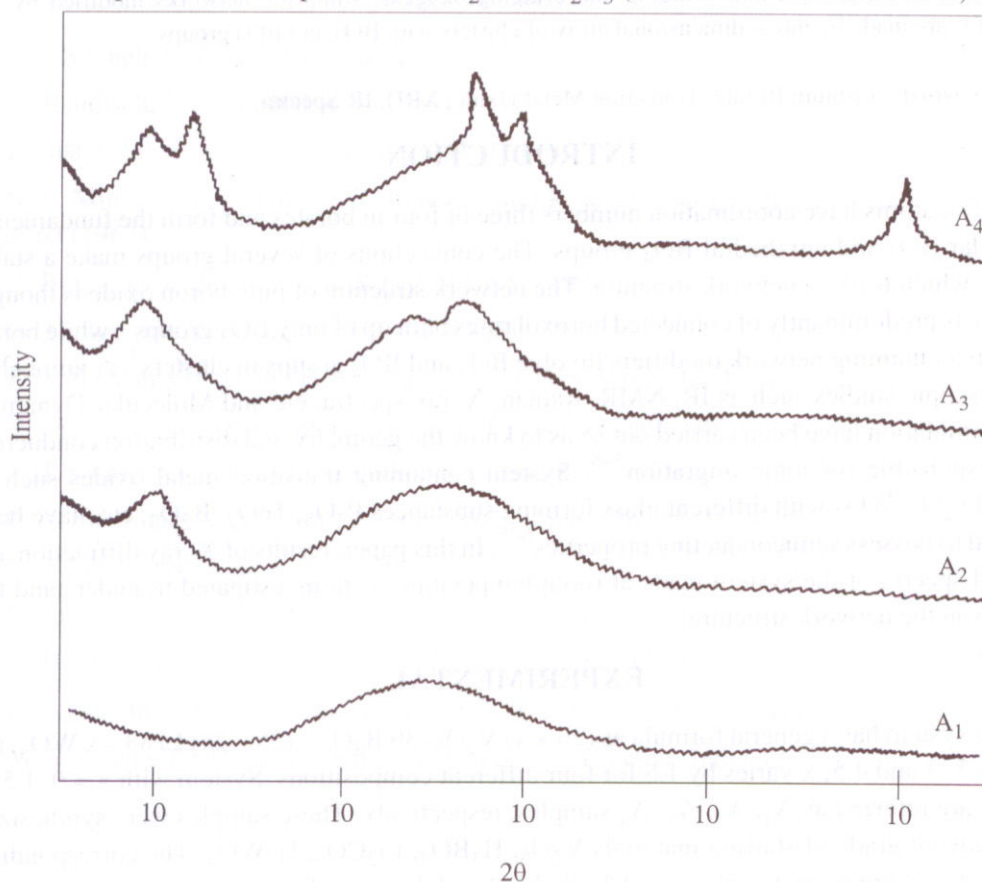


Figure 1.

V_2O_5 : 50 B_2O_3 (hereafter referred as 50 V-B) glasses, which are prepared by similar method as used in the present work and shown for comparison. The ir spectra of 50 L-B glass exhibits three absorption bands at 1350 cm^{-1} , 1100 cm^{-1} and 700 cm^{-1} while the ir spectra of 50 V-B glass exhibits bands at 1430 cm^{-1} , 1180 cm^{-1} , 1020 cm^{-1} , 800 cm^{-1} and a shoulder at 480 cm^{-1} . Bands in the region $1300 - 1450\text{ cm}^{-1}$ are due to B-O stretching of BO_3 units. The bands in the region $800 - 1200\text{ cm}^{-1}$ are due to B-O stretching of BO_4 units and band around 700 cm^{-1} is a characteristic of bending of B-O-B linkage in borate networks.

First of all, the band in the region $1300 - 1400\text{ cm}^{-1}$ is detected in A_1 . As the network of vitreous B_2O_3 is formed with connected boroxol rings, the infrared spectrum of vitreous B_2O_3 consists predominantly of the vibrations of BO_3 groups, the boroxol rings and B-O-B bridging oxygens. This band is due to the vibrations of the BO_3 group, built up in the molten state.^{1,9-13} A shoulder appears in the same region in A_2 which results in reduction of BO_3 groups. In A_3 , two bands at 1400 cm^{-1} and 1320 cm^{-1} appeared by disappearance the shoulder and are thought to be due to vibration of BO_3 groups associated with V_2O_5 and Li_2O , respectively.

Secondly a shoulder at 1100 cm^{-1} is detected in A_1 and A_2 with decrease in intensity in the latter, and it is thought to be due to vibration of BO_4 groups. Decrease in Li_2O content decreases the intensity of shoulder, which decreases the BO_4 groups. This shoulder disappears in A_3 and A_4 and three bands appeared at 1175 cm^{-1} , 1100 cm^{-1} and 1050 cm^{-1} . A weak band at 950 cm^{-1} in A_1 , becomes more intense and broad in A_2 and a band at 1100 cm^{-1} in A_3 and A_4 are due to vibration of BO_4 groups coexist with Li_2O . An additional band arises in A_3 and A_4 , at 910 cm^{-1} which becomes sharper in A_4 with

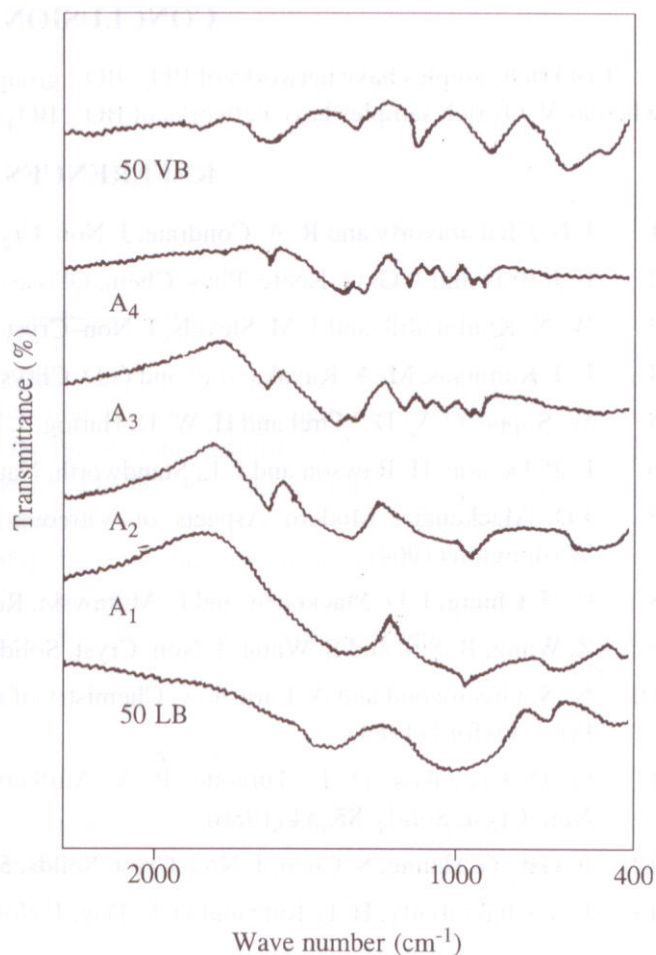


Figure 2

reduction in the intensity of band at 950 cm^{-1} . Bands at 1175 cm^{-1} and 910 cm^{-1} in A_3 and A_4 are due to vibrations of BO_4 groups, which coexist with V_2O_5 particles. Band at 1050 cm^{-1} is due to the vibration of the non-bridging oxygen at the cost of BO_3 and BO_4 .

A weak broad band appears in the region $600\text{--}700\text{ cm}^{-1}$ in A_1 , which is shifted to lower frequency side in A_2 in region $450\text{--}550\text{ cm}^{-1}$, disappearance in A_3 and A_4 is thought to be due to bridging oxygens between BO_3 groups.

Peculiar characteristic between 50 V-B and 50 L-B spectra is the broadness. The addition of Li_2O leads to a broadening and a shift of the main peak towards lower frequencies. This shift is due to an increase of the B-O distance. The broadening of the main band can be explained by the increased width of the distribution of B-O distances.

CONCLUSION

Li_2O rich samples have networks of BO_3 , BO_4 groups non-bridging and bridging oxygens whereas V_2O_5 rich samples have networks of BO_3 , BO_4 groups.

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