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Infrared spectra, X-ray investigations and electrical conductivity of lithium borosilicate glasses containing transition metal oxides

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The conductivities of lithium borosilicate glasses containing 2.5 mol % V_2O_5, MnO, Cr_2O_3, Fe_2O_3 and CoO were measured for untreated and heat-treated glasses (for 5 h at 480, 580 and 680° C). Both IR and X-ray diffraction techniques were used to investigate the microstructure of these glasses before and after heat-treatment. Lithium metasilicate and lithium metaborate were the main separated phases in addition to lithium disilicate in samples containing Fe_2O_3. The silicon ions are coordinated to four oxygens in tetrahedral coordination and some borons changed from triangular to tetrahedral.

1. Introduction

The separation of borosilicate glasses into two liquid phases has been recognised for a long time. Phase separation may enhance the properties of a glass or change them in other ways. Furthermore, it is sometimes important for developing a uniform crystallization in glasses by means of heat-treatment.

Sastory and Hummel [1] studied some quenched lithium borosilicate glasses and they stated that only binary borate and binary silicate glasses were detected as long as the Li_2O content was less than 53 mol %. In certain compositions the opacity of the glasses is due to liquid immisibility and not to crystalline phases [2]. Maurer [3] and Hammel [4] studied the effect of nucleating agents on the crystallization of some Li_2O-SiO_2 glass systems. They showed that the size of the particles in the phase-separated area is larger than in the crystalline area.

Warren *et al.* [5] and Meller and Milberg [6] studied the X-ray diffraction of pure B_2O_3 glasses. They concluded that the structure was built up of BO_3 groups. Wong and Angell [7] studied vitreous SiO_2, and found that the structure was built up of SiO_4 groups.

Tenny and Wong [8] studied the structure of borosilicate glasses by infrared techniques. They observed that the strongest B–O band exists at 1270 cm^{-1}, while for the Si–O band it is at 1060 cm^{-1}.

Pliskin *et al.* [9] found that the intensity of the B–O–Si band at 440 cm^{-1} is mainly a function of composition.

Mackenzie [10] and Hansen [11] detected electronic conductivity in certain glasses containing multivalent transition ions.

Tosio [12] explained the properties of borosilicate glasses in terms of the various atomic groups which consist of one BO_4 tetrahedron with four BO_3 triangles.

In the present work lithium borosilicate glass systems containing 2.5 mol % of different transition metal oxides were prepared. The effect of the heat-treatment temperature and the type of transition metal oxide on the molecular structure, electrical conductivity and density were studied.

2. Experimental procedures

Powders of pure chemicals over 98.5% purity were mixed together thoroughly to form a homogeneous mixture. The homogeneous mixture was melted in an electric furnace at 1100° C for 5 h and then quenched in air to prepare a glass system according to the formula

$$34.44\,\text{mol}\,\%\ Li_2O-47.09\,\text{mol}\,\%\ SiO_2-15.94\,\text{mol}\,\% \times B_2O_3-2.5\,\text{mol}\,\%\ R_xO_y$$

where R_xO_y was V_2O_5, Cr_2O_3, MnO, Fe_2O_3 or CoO. The glass samples obtained were heat-treated for 5 h at 480, 580 and 680° C.

The heat-treated samples were crushed into powder form. The variation in the structure was examined using Cu$K\alpha$ radiation. The crystalline phases shown by X-ray diffraction were identified by comparison with ASTM cards. The infrared spectra for all the studied samples were recorded using a Beckman IR 4220 infrared spectrophotometer. The electrical conductivity was measured at temperatures ranging from 20 to 300° C using a VA-J-52 German-type electrometer.

3. Results and discussion

3.1. Infrared measurements

Figs 1 to 5 show the infrared spectra of untreated and heat-treated samples containing V_2O_5, Cr_2O_3, MnO, Fe_2O_3 and CoO, respectively. Three broad bands were observed in all IR spectra of the untreated samples. The first band, observed at 1420 cm^{-1}, was attributed to B–O–B vibration [13]. The second band, appearing

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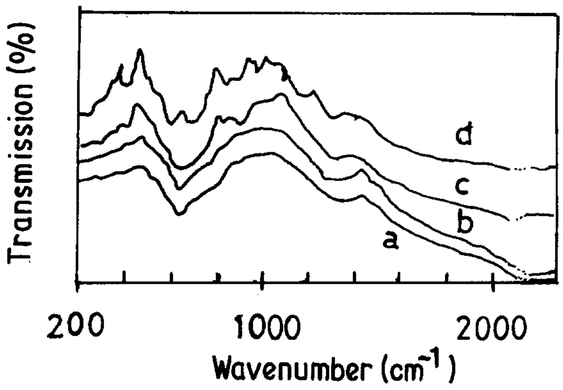

Figure 1 The infrared spectra of samples containing V_2O_5: (a) untreated and heat-treated at (b) 480° C, (c) 580° C, (d) 680° C.

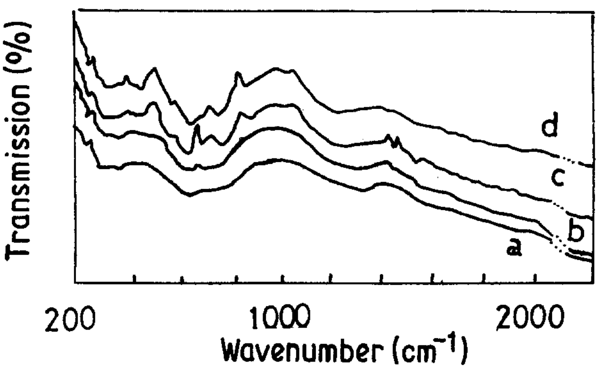

Figure 3 The infrared spectra of samples containing MnO: (a) untreated and heat-treated at (b) 480° C, (c) 580° C, (d) 680° C.

at 1030 cm^{-1}, was due to Si–O–Si and B–O–B stretching vibrations [14, 15]. The third band, appearing at 460 cm^{-1}, was attributed to bending vibrations of Si–O and B–O bonds [14, 15]. The intensities of these bands increased and new bands appeared as the temperature of heat treatment increased.

The infrared spectra of the heat treated glass samples showed the following features:

1. Heat treatment at 480° C for all samples caused an increase in the intensities of the three broad bands mentioned above.

2. Heat treatment at 580° C caused the splitting of the observed broad bands as follows:

(a) Nine bands in the infrared spectra of the glasses containing V_2O_5. The band at 1376 cm^{-1}, which is due to boron–oxygen triangles, changed to tetrahedra to form diborate vibrations [16]. The band at 1080 cm^{-1} may be due to Si–O–Si vibrations, and two bands at 1020 and 1110 cm^{-1} are due to disilicate–Si–O–Si–vibrations [17]. The band at 850 cm^{-1} indicates the formation of non-bridging oxygen B–O–B$^{\diagup \mathrm{O}^-}$ [5]. The band at 656 cm^{-1} may be due to B–O–B, and the last two bands at 460 and 390 cm^{-1} are due to Si–O–Si vibrations.

(b) Six bands in the infrared spectra of the glasses containing Cr_2O_3. The band at 1420 cm^{-1} showed no variation, and new bands could be observed at 850 and 735 cm^{-1} which are due to B–O–B vibrations [18]. The bands at 500, 450 and 410 cm^{-1} are due to Si–O–Si vibrations [19].

(c) Seven bands in the infrared spectra of the glasses containing MnO. The band at 1412 cm^{-1} may be the same band as at 1420 cm^{-1} but shifted to lower frequency. Other new bands were observed at 1075 cm^{-1} which is due to Si–O–Si [20] at 975 cm^{-1} which is due to SiO_3^-, at 844 cm^{-1} which is due to B–O–B$^{\diagup \mathrm{O}^-}$, at 735 cm^{-1} which is due to B–O–B, and at 515 and 450 cm^{-1} which are due to Si–O–Si vibrations.

(d) Ten bands in the infrared spectra of the glasses containing Fe_2O_3. The band at 1500 cm^{-1} results from B–O vibration, while that at 1415 cm^{-1} is due to Si–O–B [21]. The band at 1375 cm^{-1} which is due to boron–oxygen triangles changed to boron–oxygen tetrahedra forming the diborate, and another at 695 cm^{-1} is due to B–O–Si [8]. Bands at 1075, 980, 515, 450 and 410 cm^{-1} were also observed.

(e) Six bands in the infrared spectra of the glasses containing CoO appeared at 1420, 1080, 980, 850, 735 and 460 cm^{-1}.

3. The heat treatment at 680° C caused an increase in the intensities of some of the above-mentioned bands for the case of samples heat-treated at 580° C, and the following new bands were observed:

(a) Thirteen bands in the infrared spectra of the glasses containing V_2O_5 at 1375, 1080, 1020, 656, 545, 460, and 390 cm^{-1}. The band at 850 cm^{-1} has shifted to 890 cm^{-1}, which indicates the presence of non-bridging oxygen vibrations; the band at 780 cm^{-1} has shifted to 790 cm^{-1} and a new band is observed at 1220 cm^{-1} which is due to stretching vibrations of the boroxal ring [22]. The band at 980 cm^{-1} is due to the

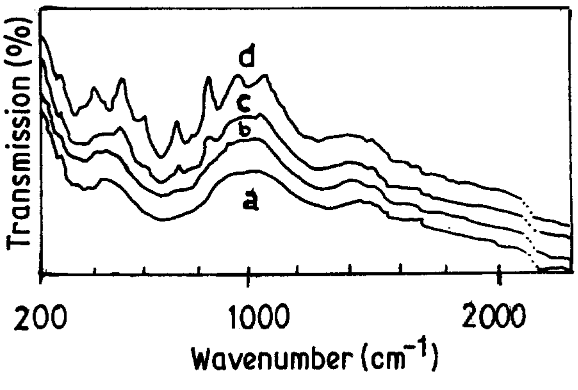

Figure 2 The infrared spectra of samples containing Cr_2O_3: (a) untreated and heat-treated at (b) 480° C, (c) 580° C, (d) 680° C.

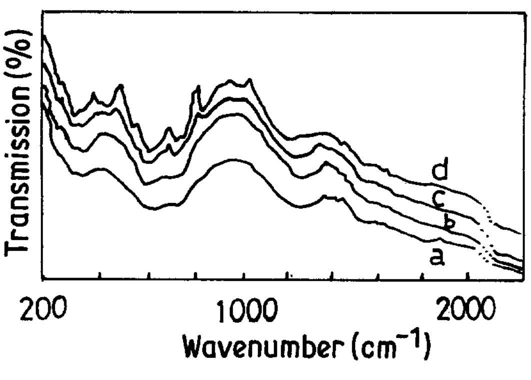

Figure 4 The infrared spectra of samples containing Fe_2O_3: (a) untreated and heat-treated at (b) 480° C, (c) 580° C, (d) 680° C.

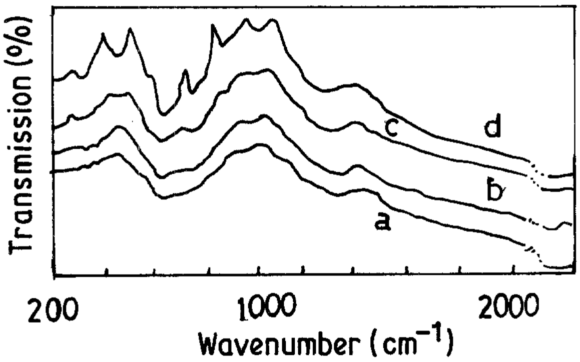

Figure 5 The infrared spectra of samples containing CoO: (a) untreated and heat-treated at (b) 480° C, (c) 580° C, (d) 680° C.

SiO$_3^{2-}$ group and that at 940 cm^{-1} shows the presence of B–O–Si [23]. The last band at 760 cm^{-1} indicates the presence of boron–oxygen triangles.

(b) Twelve bands in the infrared spectra of the glasses containing Cr_2O_3. Two bands were at 850 and 735 cm^{-1}. Three bands at 515, 445, and 394 cm^{-1} may be the same as the bands at 500, 450 and 410 cm^{-1} but shifted to lower frequency. New bands are observed at 1070, 980, and 602 cm^{-1} which are due to Si–O$^-$ vibration [19], and one at 680 cm^{-1} which is due to B–O–Si vibration [8, 24].

(c) Eight bands in the infrared spectra of the glasses containing MnO. All the bands at 1412, 1075, 975, 844, 735, 515 and 450 cm^{-1} were observed in the spectrum of the sample heat-treated at 580° C but with different intensities. In addition to these bands a new one was observed at 790 cm^{-1}.

(d) Ten bands in the infrared spectra of the glasses containing Fe_2O_3. Bands at 1375, 1105, 1020 and at 960 cm^{-1} may be due to disilicate vibrations. Bands at 955 and 675 cm^{-1} are due to B–O–Si [8]. The last at 850 cm^{-1} is due to $\mathrm{B{-}O{-}B}^{\diagup \mathrm{O}^-}$.

(e) Eight bands in the infrared spectra of glasses containing CoO. They are at 1375, 1080, 980, 520, 460, 445, 410 and 602 cm^{-1}.

In all samples it was found that some BO_3 changed to BO_4 forming non-bridging oxygens, while in the sample containing Cr_2O_3, some SiO_3 also changed to SiO_4. The silicon ions are coordinated to four oxygens in a tetrahedral coordination and the lithium ion surrounds itself with non-bridging oxygens in the network. Boron changes its coordination from triangular with three oxygens to tetrahedral coordination because of the high field strength.

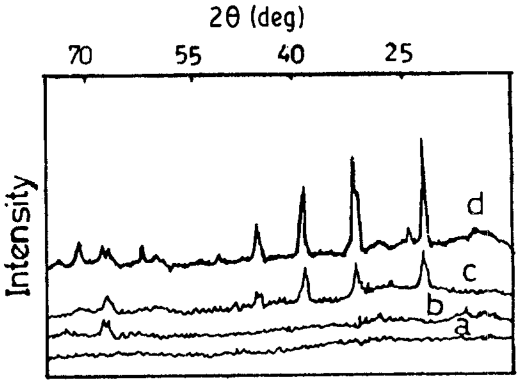

Figure 7 The X-ray diffraction patterns of untreated and heat-treated glasses containing Cr_2O_3: (a) untreated and heat-treated at (b) 480° C, (c) 580° C, (d) 680° C.

3.2. X-ray measurements

Figs 6 to 10 show the X-ray diffraction patterns of untreated and heat-treated glasses containing V_2O_5, Cr_2O_3, MnO, Fe_2O_3 and CoO, respectively. From the figures it can be seen that:

1. The untreated and all heat-treated samples at 480° C are completely in the glassy state.

2. The heat treatment at 580° C for all samples caused the following:

(a) Samples containing V_2O_5 are completely glassy.

(b) Lithium metaborate and lithium metasilicate are separated in samples containing Cr_2O_3, MnO, Fe_2O_3 and CoO.

3. The heat-treatment at 680° C for all samples caused the following:

(a) Lithium disilicate and tridymite have been separated in the sample containing V_2O_5.

(b) Lithium metaborate and lithium metasilicate are separated in samples containing Cr_2O_3, MnO and CoO.

(c) Lithium disilicate, lithium metasilicate and lithium metaborate are separated in samples containing Fe_2O_3.

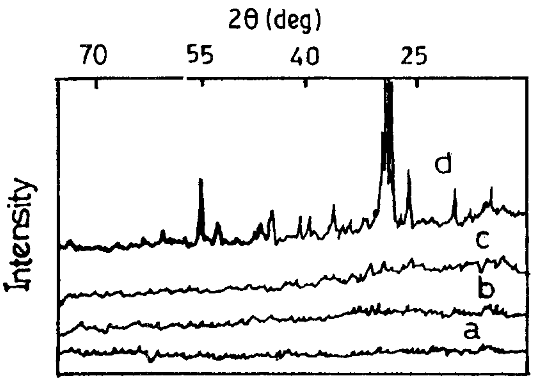

Figure 6 The X-ray diffraction patterns of untreated and heat-treated glasses containing V_2O_5: (a) untreated and heat-treated at (b) 480° C, (c) 580° C, (d) 680° C.

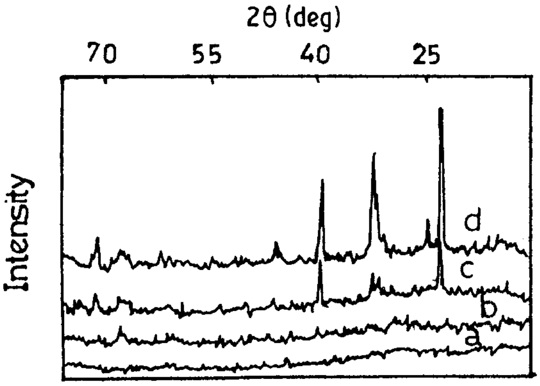

Figure 8 The X-ray diffraction patterns of untreated and heat-treated glasses containing MnO: (a) untreated and heat-treated at (b) 480° C (c) 580° C, (d) 680° C.

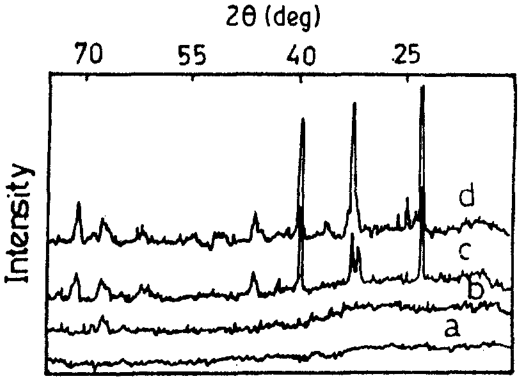

Figure 9 The X-ray diffraction patterns of untreated and heat-treated glasses containing Fe_2O_3: (a) untreated and heat-treated at (b) 480° C, (c) 580° C, (d) 680° C.

The absence of phase-separation in all samples studied after heat treatment at 480° C may be due to the fact that the crystallization temperature has not yet been reached. In term of the ionic potential Z/R (the ratio of the ionic charge Z to the atomic radius R), Z/R for V_2O_5 is greater than for other oxides. No phase separation was observed when the sample containing V_2O_5 was heat-treated at 580° C. This means that thermal energy is then expected to have been used to form the stable disilicate phase from the metasilicate phase which is separated in the samples heat-treated without V_2O_5 at the same temperature [25], and this concentration of V_2O_5 increases the nucleating temperature range and the homogeneity of the glass. In the case of samples containing Fe_2O_3, the phases separated were lithium metasilicate, lithium metaborate and lithium disilicate, while the separated phases were lithium metaborate and lithium metasilicate in the case of samples containing MnO and Cr_2O_3. This can be understood according to the fact that Z/R for iron is greater than for manganese and chromium. Although the ratio of Z/R for cobalt is greater than that for iron, the separated phases in the sample containing cobalt were less than for the sample containing iron. This observation can be interpreted according to the fact that the addition of CoO increases the transfer of boron–oxygen triangles to boron–oxygen tetrahedra, which in turn decreases the area of the immiscibility region [26].

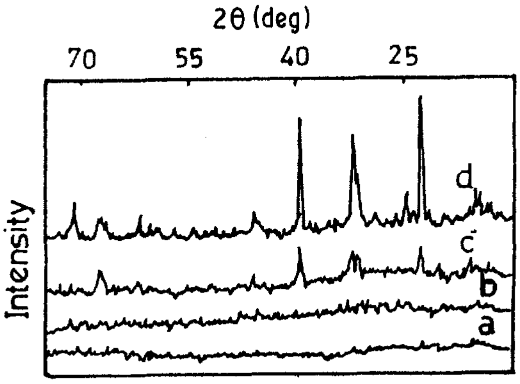

Figure 10 The X-ray diffraction patterns of untreated and heat-treated glasses containing CoO: (a) untreated and heat-treated at (b) 480° C, (c) 580° C, (d) 680° C.

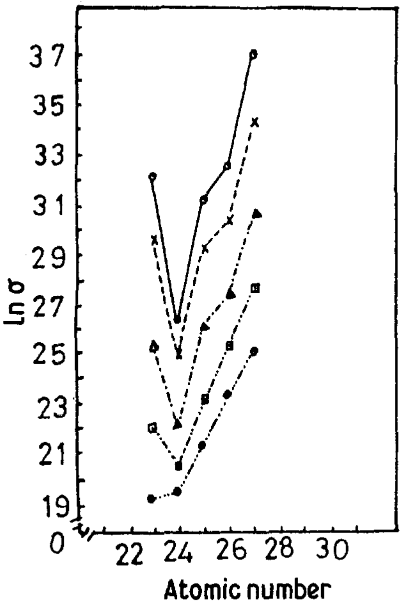

Figure 11 The relation between d.c. conductivity for the untreated glasses and the atomic number of the transition element used. (○) 50° C, (x) 100° C, (△) 150° C, (□) 200° C, (●) 250° C.

3.3. D.c. Electrical conductivity measurments

The electrical conductivities of all glasses were measured as a function of temperature, from which activation energy values were calculated. Figs 11 to 14 show the d.c. conductivity for the untreated and heat-treated glasses at 480, 580 and 680° C, respectively, as a function of the atomic number of the type of transition metal ion. The electrical conductivity of untreated and heat-treated samples was found to increase as the measuring temperature increased. From Figs 11 to 14 it was observed that the electrical conductivity increased when the samples were heat-treated at 480 and 580° C, while it decreased when they were heat-treated at 680° C. This observation

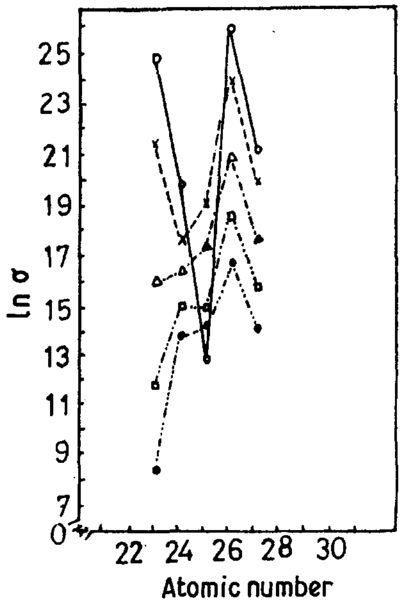

Figure 12 The relation between d.c. conductivity for glasses heat-treated at 480° C and the atomic number of the transition element used. (○) 50° C, (x) 100° C, (△) 150° C, (□) 200° C, (●) 250° C.

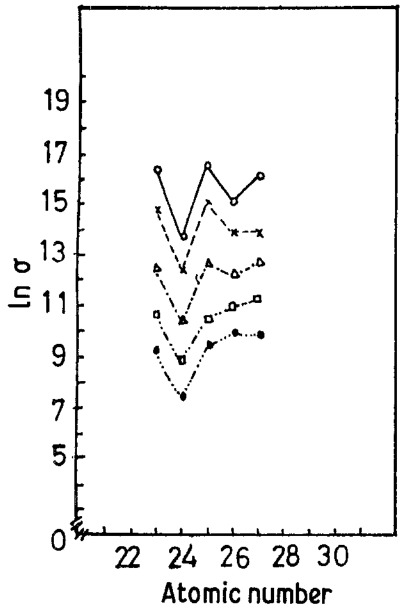

Figure 13 The relation between d.c. conductivity for glasses heat-treated at 580° C and the atomic number of the transition element used. (○) 50° C, (x) 100° C, (△) 150° C, (□) 200° C, (●) 250° C.

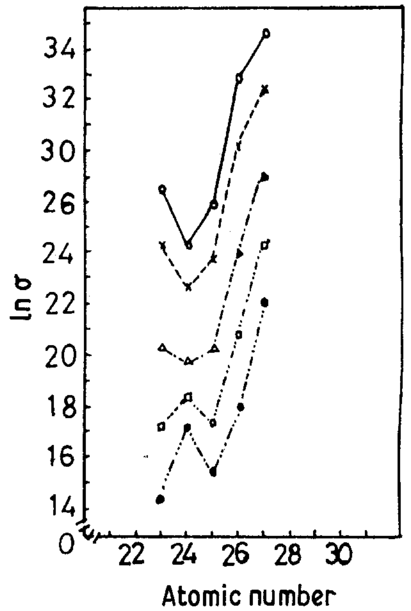

Figure 14 The relation between d.c. conductivity for glasses heat-treated at 680° C and the atomic number of the transition element used. (○) 50° C, (x) 100° C, (△) 150° C, (□) 200° C, (●) 250° C.

could be explained in terms of a change in the microstructure of the samples caused by the heat-treatment.

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