JOURNAL OF MATERIALS SCIENCE 27 (1992) 3793–3798

Infrared and Raman spectra of binary tellurite glasses containing boron and indium oxides

QIU JIAN RONG, AKIYOSHI OSAKA, TOKURO NANBA, JUN TAKADA, YOSHINARI MIURA
Department of Applied Chemistry, Faculty of Engineering, Okayama University 3-3-1, Tsushima Naka, Okayama-shi, 700 Japan

The constitution of glasses in the systems M_2O_3–TeO_2 (M = B and In) was investigated by Raman and infrared spectroscopy. From the relation between the M_2O_3 content and the intensity ratios of the deconvoluted Raman peaks $I(720)/I(665)$ and $I(780)/I(665)$, it was concluded that In_2O_3 behaves as a network modifier to yield TeO_3^- units and that discrete BO_3 and BO_4 units construct a network of glasses containing boron oxide. A structural model for those glasses was derived which involves three-coordinated oxygen atoms and TeO_4 units of an intermediate configuration, $O_3Te^{\delta+} \ldots O^{\delta-}$.

1. Introduction

Although tellurium dioxide is hardly vitrified with a conventional melt-quenching technique [1], glasses with a wide range of composition are obtained [2–5] when it is combined with mono- or multi-valent metal oxides. TeO_2-based multi-component glasses have several interesting properties such as low melting temperatures, high refractive indices and large third-order non-linear susceptibility [6]. A tellurite network basically consists of TeO_4 trigonal bipyramid (TBP) units and TeO_3 trigonal pyramid (TP) units [2, 4], each of which has a lone pair of electrons [2, 7], while the constitution of binary glasses depends on the second metal oxides. Mochida *et al.* [2] reported that TBP units were converted to TP ones on addition of alkali and alkaline earth oxides. Suzuki [8] obtained similar results from a neutron scattering study on barium and sodium tellurite glasses. He proposed a mechanism (Equations 1 and 2) of the formation of the TP units:

$$3TeO_{4/2} + O^{2-} \rightarrow O_{2/2}Te\text{–}O + 2TeO_{3/2}O^- \tag{1}$$

$$O_{2/2}Te\text{–}O + 2TeO_{3/2}O^- + 2O^{2-} \rightarrow 3TeO_3^{2-} \tag{2}$$

where $O_{1/2}$ represents a bridging oxygen. These two reactions proceed as the content of a network modifying oxide increases until all the oxygen atoms of the TBP units become non-bridging (Equation 3).

$$TeO_{4/2} + O^{2-} \rightarrow TeO_3^{2-} \tag{3}$$

The three oxygens in the TeO_3^{2-} units are equivalent because of resonance. Yoko *et al.* [3] proposed a similar mechanism where they assumed other TP units, $O_{1/2}Te(=O)\text{–}O^-$. Dimitriev and co-workers proposed the change from TBP to TP for the tellurite glasses containing V_2O_5, MoO_3 and Bi_2O_3 as well as CuO [9, 10].

For the glasses in the system of $xB_2O_3\cdot(100 - x)TeO_2$, Göring *et al.* [11] measured B^{11}-NMR spectra, and reported that the fraction (N_{4B}) of four-coordinated boron atoms decreased from 0.56 to 0.43 as x increased from 20 to 25 mol %. They postulated formation of TeO_3^+ units to compensate a negative charge on a BO_4 unit. However, no crystals containing TeO_3^+ units have been found nor has valid experimental evidence which indicates the formation of the TeO_3^+ units been reported. Moreover, it is not yet clear whether BO_3 and BO_4 units form any borate groups. Thus, despite these studies, the structure of boron-oxide–tellurium-oxide glasses has not thoroughly been understood. We hence intended to investigate the constitution of those glasses. The present study primarily concerns their infrared and Raman spectra. Incidentally, Kaneko [12] suggested that of IIIb family elements In plays the role of an intermediate oxide in silicate glasses. Thus it is worth studying the role of In_2O_3 in tellurite glasses, and systematic comparison between the two systems will help understand the behaviour of both B and Te atoms in boron-oxide–tellurium-oxide glasses. Moreover, the Raman spectra of lithium tellurite and borate glasses will be of great help as a reference since their structural change with composition has been fairly well studied [2, 13].

2. Experimental procedure

Glasses of the compositions $xLi_2O\cdot(1 - x)TeO_2$, $xB_2O_3\cdot(1 - x)TeO_2$ and $xIn_2O_3\cdot(1 - x)TeO_2$ (x in mol fraction) were prepared. They are hereafter denoted as lithium glasses, boron glasses and indium glasses, respectively. Appropriate mixtures of reagent grade Li_2CO_3, B_2O_3, In_2O_3 and TeO_2 were melted in platinum crucibles at 700–800 °C for 20 min in air. The melts were quenched between a sheet of steel plate

0022–2461

and a piece of iron. Clear glasses could only be obtained in the region $0.15 \leqslant x \leqslant 0.35$ for the lithium system, $0.15 \leqslant x \leqslant 0.30$ for the boron one, and $0.05 \leqslant x \leqslant 0.15$ for the indium one. The X-ray amorphous samples were then annealed for 30 min near T_g (obtained beforehand from their differential scanning calorimetry (DSC) traces) and served for measuring Raman and infrared spectra. Li_2TeO_3 crystal was prepared by cooling the corresponding melt to room temperature in an electric furnace whose power was turned off after the completion of melting. The obtained sample was identified as Li_2TeO_3 (JCPDS 19-728) with an X-ray diffraction measurement. IR spectra were taken with a KBr pellet method by using a Hitachi IR 270-30 spectrometer. Raman spectra were measured with Ar^+ laser (514.5 nm) by using a JASCO NR-1000 Raman spectrophotometer.

3. Results

3.1. Raman spectra of lithium tellurite glasses, Li_2TeO_3 crystal and $Li_2O \cdot 5B_2O_3$ glass

The Raman spectrum in Fig. 1a for Li_2TeO_3 crystal indicates that the TeO_3^{2-} units yield two strong peaks at 720 and 790 cm^{-1}. The spectrum in Fig. 1b for $Li_2O \cdot 5B_2O_3$ glass shows very sharp peaks at 772 and 803 cm^{-1}, which corresponds to a borate ring with BO_4 units and the boroxol group, respectively [13]. The full width at half maximum (FWHM) is 20 cm^{-1} for these two borate bands. Fig. 2 shows the Raman spectra of the lithium glasses of composition $xLi_2O \cdot (1-x)TeO_2$. The relative intensity of the 455 cm^{-1} and 665 cm^{-1} peaks decreases with x, while a shoulder peak at about 730 cm^{-1} for $x = 0.15$ grows accompanied by a blue shift up to 760 cm^{-1} for $x = 0.3$.

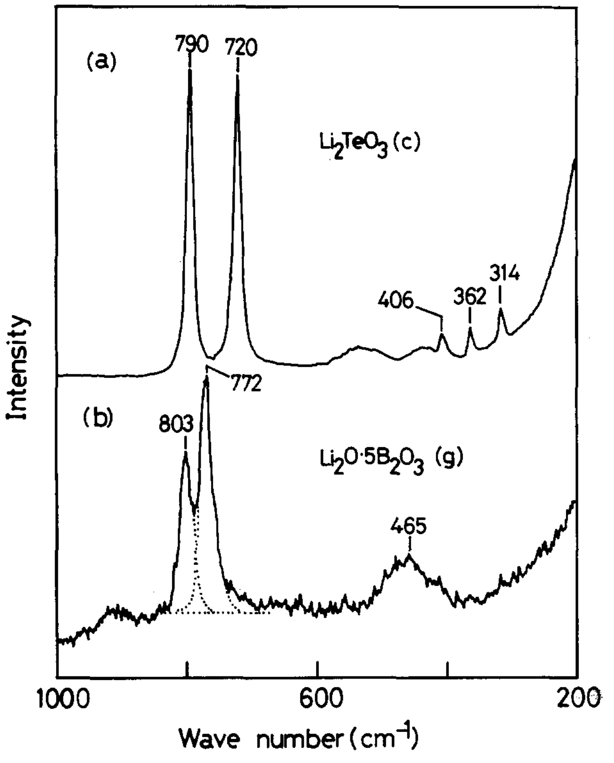

Figure 1 Raman spectra of Li_2TeO_3 crystal (a) and $Li_2 \cdot 5B_2O_3$ glass (b).

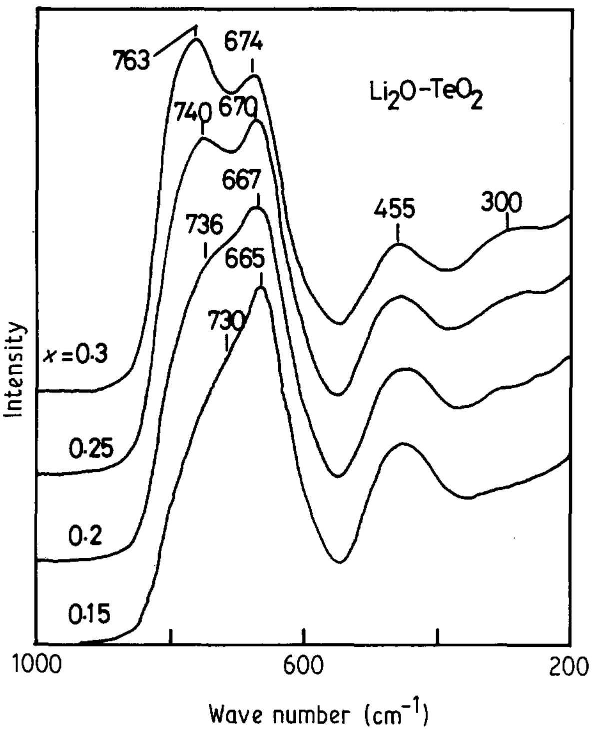

Figure 2 Raman spectra of $xLi_2O \cdot (1-x)TeO_2$ glasses.

3.2. Spectra of the binary tellurite glasses containing trivalent cations

Fig. 3a represents the infrared spectra for the boron glasses of composition $xB_2O_3 \cdot (1-x)TeO_2$, indicating a few peaks at 635, 930, 1240 and 1350 cm^{-1}. The 635 cm^{-1} peak has been assigned to TBP units [2, 4], and its relative intensity decreases with x. The peak at 930 cm^{-1} is assigned to BO_4 units while those at 1240 and 1350 cm^{-1} are assigned to BO_3 ones [13, 14]. The 930 cm^{-1} band intensity decreases with x relative to the 1350 cm^{-1} and 1240 cm^{-1} bands. The Raman spectra of the boron glasses in Fig. 3b have two strong peaks at 455 cm^{-1} and 665 cm^{-1} and a shoulder at about 745 cm^{-1} as well as a very weak shoulder peak at 850 cm^{-1}. The 665 cm^{-1} Raman band corresponds to the 635 cm^{-1} infrared peak. The spectral profile is quite similar to that of TeO_2 glass reported by Sekiya *et al.* [15].

Fig. 4 shows Raman spectra for the indium glasses of composition $xIn_2O_3 \cdot (1-x)TeO_2$. The intensity of the 665 cm^{-1} peak decreases with x, while a peak at about 730 cm^{-1} grows with a blue shift up to about 750 cm^{-1}. The spectral profile in the range from 600 to 800 cm^{-1} is similar to that of the lithium glasses, but it is quite different from that of the boron glasses though both In and B are of the IIIb family in the periodic table.

4. Discussion

4.1. Configuration of TeO_n polyhedra

It is characteristic of Te to yield $n+1$ or $n+2$ configurations which have one or two bonds longer than 0.23 nm in addition to n ordinary bonds of 0.18–0.22 nm in length [2, 4]. Wider distribution of

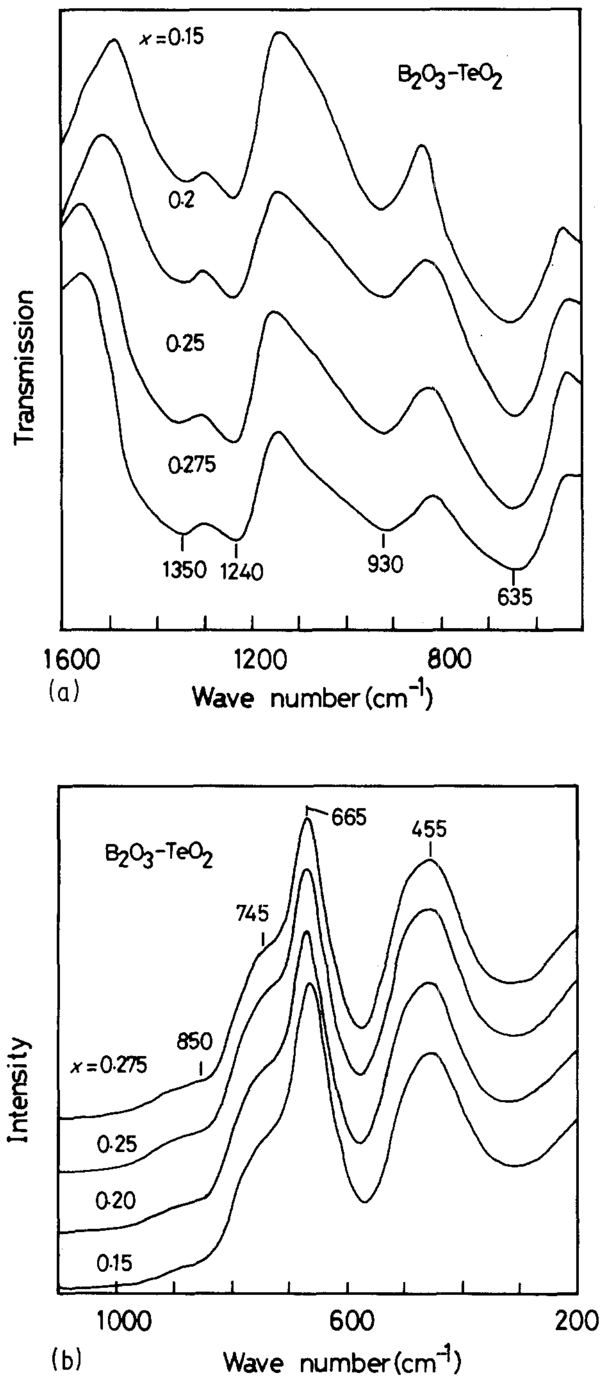

Figure 3 (a) Infrared and (b) Raman spectra of $xB_2O_3\cdot(1-x)TeO_2$ glasses.

the bond length is indicated for TeO_n polyhedra in crystals, and continuous variation of the fourth Te–O length has been noticed from about 0.2 nm in pure TBP units to about 0.3 nm in pure threefold coordination [16]. Such behaviour is explained in terms of a weak tendency of Te atoms towards threefold coordination [16]. Since we will discuss the constitution of glasses constructed by TeO_n polyhedra, it is necessary to define what are the TP and the TBP units with respect to configuration and bond length. TeO_3^{2-} units have shorter bonds (about 0.188 nm) [17], and $O_{2/2}Te$–O and $O_{1/2}Te(=O)O^-$ units [3, 8] are likely to have similar bond lengths. TeO_4 units have longer bonds, though the length depends on crystals. For instance, the Te–O bonds in tellurite are 0.188, 0.193, 0.207 and 0.219 nm long [18] while those in paratellurite are 0.190 and 0.208 nm long [19]. Thus one may assume that tellurite consists of the units of a TeO_{3+1} configuration; Suzuki [8] proposed such TeO_{3+1} units are the constituent ones of TeO_2 glass where three oxygen atoms are at 0.195 nm and the fourth one at 0.218 nm. However, in the present study, we take the bonds longer than 0.23 nm as the extra (+ 1 or + 2) ones to involve the constituent polyhedra of paratellurite into the category of TBP units. Hence TeO_2 glass is referred to as being composed of $TeO_{4/2}$ (TBP) units. When the fourth oxygen is getting far apart, the unit is represented as $O_{3/2}Te^{\delta+}\ldots\ldots O_{1/2}^{\delta-}$ like a $TeCl_3^+\ldots Cl^-$ unit in $TeCl_4$ crystal [20]. It becomes a $TeO_{3/2}^+$ unit in a limiting case where the fourth oxygen lies about 0.3 nm far from the Te atom.

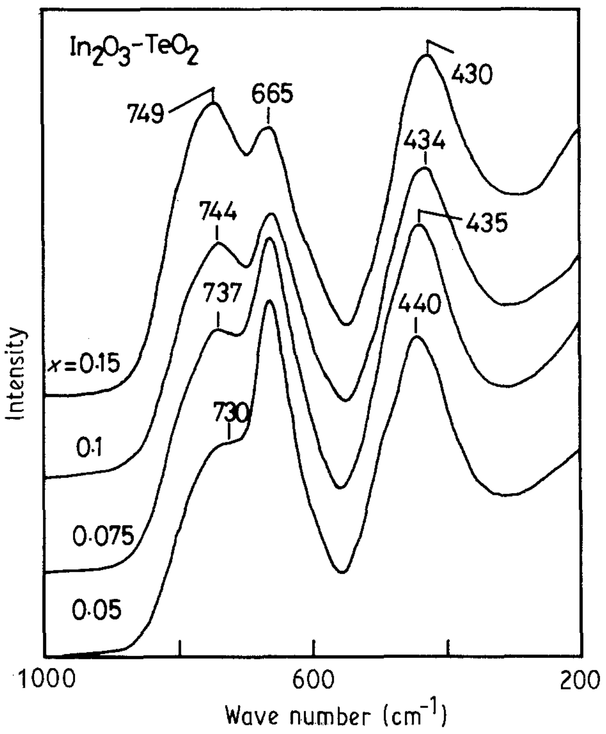

Figure 4 Raman spectra of $xIn_2O_3\cdot(1-x)TeO_2$ glasses.

4.2. Ratios of Raman band intensities $I(720)/I(665)$ and $I(780)/I(665)$

Relative intensities of the Raman bands assigned to TBP and TP units stand for the fractions of these two units in glass. For the qualitative analysis of the intensity ratio, the Raman spectra in the range 350–1000 cm^{-1} have been deconvoluted into component bands after Mysen *et al.* [21]. A typical example is demonstrated in Fig. 5 for (a) $Li_2O\cdot 4TeO_2$ glass and (b) $B_2O_3\cdot 4TeO_2$. The spectrum of the lithium glass consists of a few components at 455, 610, 665, 720, and 780 cm^{-1}. Here the 780 cm^{-1} band corresponds to the 790 cm^{-1} band for Li_2TeO_3 shown in Fig. 1. The boron glass has similar components at 457, 610, 665, 725 and 772 cm^{-1} as well as a weak band at 850 cm^{-1}. According to Sekiya *et al.* [15] paratellurite and tellurite crystals have strong peaks in the vicinity of 650 cm^{-1} with another few strong ones near 200 cm^{-1} as well as weak peaks in

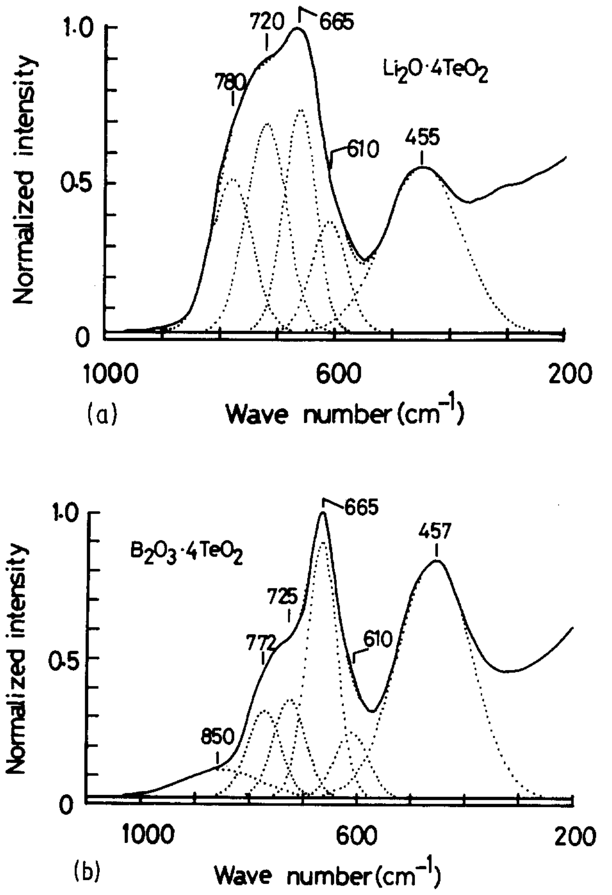

Figure 5 Deconvolution of the Raman spectrum for $Li_2O{\cdot}4TeO_2$ glass (a) and $B_2O_3{\cdot}4TeO_2$ glass (b).

the range 350–800 cm^{-1}. We hence attribute the 665 cm^{-1} component in Fig. 5a and b to TBP units. The 720 and 780 cm^{-1} component bands for the lithium glasses are due to the TP units of $O_{1/2}Te(=O)O^-$ [3] or $O_{2/2}Te–O^-$ [8] configurations because their relative intensity increases with x as indicated in Fig. 2. It is surprising, however, that two component peaks have been deconvoluted at 716 and 773 cm^{-1} from the Raman spectrum of pure TeO_2 glass [15], which correspond to the component at 725 and 772 cm^{-1} for $B_2O_3{\cdot}4TeO_2$ glass. These peaks should accordingly be assigned to TBP units [15] although they have already been assigned to the TeO_3^{2-} units in Fig. 1 (Li_2TeO_3). It is thus very confusing that the TBP units in TeO_2 glass show Raman bands similar in position to the TP units. We can discriminate the assignments only by the change of the band intensity due to composition. That is, a systematic variation of the ratios $I(720)/I(665)$ and $I(780)/I(665)$ will be noticed as the fraction of TP units varies with composition; they will increase when the TP units increase, or they will not change when the coordination state of Te atoms remains constant.

As discussed above, the ratios of the peak intensity $I(720)/I(665)$ and $I(780)/I(665)$ can be used as a parameter representing the fraction of TP units in the glasses. Then, the deconvolution is carried out for all the glasses. The boron glasses yield bands near 440, 610, 665, 720 and 780 cm^{-1} while the indium glasses near 455, 610, 665, 720 and 780 cm^{-1}. A weak band observed at 850 cm^{-1} for the boron glasses may be related to a Te–O–B mode. The blue shift of the peak near 730 cm^{-1} observed in Figs 2 and 4 is then ascribed to the growth of the two components near 720 and 780 cm^{-1}. Incidentally, borate groups with one or two BO_4 units cause a very sharp Raman band near 770 cm^{-1} [13] (spectrum in Fig. 1b). However, the 780 cm^{-1} band deconvoluted for the present boron glasses is not ascribed to the borate groups. This will be discussed in Section 4.2. The intensity ratios have been plotted in Fig. 6 as a function of $x/(1-x)$. Fig. 6 illustrates that those for the lithium and indium glasses increase linearly with $x/(1-x)$, whereas those for the boron glasses are almost independent of it. The lines are drawn according to least-squares fitting for the ratio $I(720)/I(665)$, and the slopes and y-cut values for both ratios are tabulated in Table I. The y-cut values are almost independent of the second oxide; about 0.5 and 0.4 for $I(720)/I(665)$ and $I(780)/I(665)$, respectively. By taking experimental uncertainty for the deconvolution into account, we regard that the slopes for the indium glasses are three times as large as those for the lithium glasses, whereas those for the boron glasses are null. It follows that each oxygen introduced by In_2O_3 and Li_2O yields

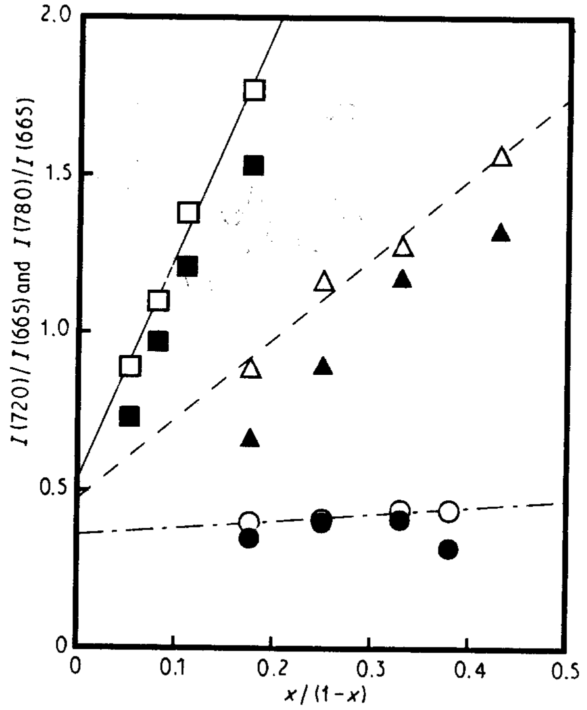

Figure 6 Linear relations between the ratios of the Raman band intensities versus $x/(1-x)$ for the glasses of composition $xM_mO_n{\cdot}(1-x)TeO_2$ (M = Li, In and B). The lines represent least-squares fitting for the ratio $I(720)/I(665)$.

TABLE I Linear relations between the ratios of the Raman band intensities versus $x/(1-x)$ for the glasses of compositions $xM_mO_n{\cdot}(1-x)TeO_2$ (M = Li, In and B)

	$I(720)/I(665)$		$I(780)/I(665)$	
M_mO_n	Slope	y-cut	Slope	y-cut
Li_2O	2.5	0.47	2.6	0.23
In_2O_3	7.2	0.53	6.4	0.44
B_2O_3	0.2	0.36	− 0.1	0.39

almost the same amount of TP units. On this basis we conclude that indium oxide behaves as a network-modifying oxide in the indium glasses like Li_2O in the lithium glasses. Moreover, not only the coincidence of the *y*-cut values (i.e. the ratios extrapolated to pure TeO_2 glass) of the three series of glasses but the non-zero values of them indicate that the TBP units in these glasses take configuration similar to that in pure TeO_2 glass.

4.3. Structure models of glasses in the system B_2O_3–TeO_2

A Raman band near 770 cm^{-1} for borate glass has been assigned to borate groups involving one or two BO_4 units [13]. Then one may assign the 780 cm^{-1} component in Fig. 6 to such groups since the difference of 10 cm^{-1} in band position is within the experimental uncertainty. If this assignment were true, the relative intensity of the Raman bands $I(780)/I(665)$ would change in accordance with the change in the fraction of the BO_4 units. Fig. 3a reveals that the 930 cm^{-1} band assigned to the BO_4 units decreases relative to the 1350 and 1240 cm^{-1} bands due to the BO_3 units as the boron oxide content, x, increases. This obviously indicates the decrease in the fraction of the BO_4 units, and is in accordance with the results of an NMR study by Göring *et al.* [11]. However, the ratio remains constant for the boron glasses in Fig. 6. Furthermore, FWHM of the 780 cm^{-1} component in the range 600–800 cm^{-1} is about 60 cm^{-1}, whereas FWHM of the band due to the borate groups is about 20 cm^{-1} in the spectrum of Fig. 1b, 1/3 as wide as the deconvoluted 780 cm^{-1} component. The 780 cm^{-1} band is therefore due to a Te–O mode. Moreover, the deconvolution could not yield a band near 800 cm^{-1} assignable to boroxol rings. From these results we have concluded the absence of any borate groups in the present glasses. It follows that the boron atoms are distributed as discrete BO_3 and BO_4 units.

A negative charge on a BO_4 unit can be balanced by either some structure groups or positively charged units. One of the latter units probable in the present glass is the $TeO_{3/2}^{+}$ unit in the limiting case of an intermediate $TeO_3^{\delta+} \ldots O^{\delta-}$ configuration. This positively charged unit would have a C_{3v} symmetry and give very strong Raman bands similar to those of the TeO_3^{2-} units in the spectrum of Fig. 1a, and those bands would decrease with increase in the boron oxide content. The present results described in §4.1 show that such is not the case.

With the intermediate configuration of $TeO_{4/2}$ units the fourth oxygen atom is more basic than the other three and will be a target of an electrophilic attach of a boron atom as represented in Equation 4. Here the boron atom is four-coordinated while the TBP configuration is conserved.

$$TeO_{4/2} + BO_{3/2} \rightarrow TeO_{3/2}^{\delta+} \ldots {}^{\delta-}O\text{–}BO_{3/2} \quad (4)$$

However, the left-hand side of Equation 4 needs $O_{1/2}$ for completion of the equation. Since no free oxygen atoms like those of alkali oxides are available in the present system, the oxygen connecting the Te and B atoms in Equation 4 must be shared by another network-forming cation. That is, it is inevitable to assume three-coordinated oxygens within the constraints that TBP configuration is to be held for Te, no non-bridging bonds are allowed, and a fraction of B atoms are four-coordinated. The three-coordinated oxide ions have been established in several tellurite crystals like $CuTeO_3$ [22] or $Te_4O_5(PO_4)_2$ [23]. Two possible groups involving such oxygens are:

$$O_{3/2}BO^{*}(\text{–}TeO_{3/2})_2 \qquad \text{(group I)}$$

$$O_{3/2}TeO^{*}(\text{–}BO_{2/2})(\text{–}BO_{3/2}) \qquad \text{(group II)}$$

Here, the oxygen with an asterisk combines two Te atoms and one B in group I, and two B atoms with one Te in group II. A greater positive charge may lie on the Te atom in group II because the Te atom in group II is connected to two borate units while the two Te atoms in group I share one negative charge on the BO_4 unit. Three-coordinated boron atoms are much more electrophilic due to open $2p_z$ orbitals than In or Te. They will attack a more basic oxygen, which might be the fourth one at a longer distance from Te. That oxygen accordingly behaves like the one in alkali or alkaline earth oxides. The role of indium oxide as a network modifier is then ascribed to its lower acidity or electronegativity [24].

5. Summary

Raman spectra of xM_2O_3 (M = In, B)·$(1-x)TeO_2$ glasses have been deconvoluted into component peaks. From the reference spectra of lithium tellurite glasses the 720 and 780 cm^{-1} bands are attributed to the formation of TeO_3 units, and 665 cm^{-1} band to TeO_4 ones. The intensity ratios of $I(720)/I(665)$ and $I(780)/I(665)$ for $xIn_2O_3 \cdot (1-x)TeO_2$ glasses linearly increase with increasing In_2O_3 content, and the slopes due to least-squares fitting are almost three times as large as those of $xLi_2O \cdot (1-x)TeO_2$ glasses. It is concluded, therefore, that In_2O_3 behaves as a network-modifying oxide in tellurite glass like Li_2O.

The intensity of an infrared peak of $xB_2O_3 \cdot (1-x)TeO_2$ glasses at 930 cm^{-1} decreases slightly with increase in x relative to 1350 cm^{-1} and 1240 cm^{-1} bands. This confirmed the presence of BO_4 units and their variation with composition, whereas borate rings are not formed in the present glasses. The intensity ratios of the Raman bands $I(720)/I(665)$ and $I(780)/I(665)$ for $xB_2O_3 \cdot (1-x)TeO_2$ glasses are independent of x, and the profile of Raman spectra is similar to that of TeO_2 glass. Thus the absence of TeO_3 units is concluded. From consideration of TeO_4 units in an intermediate configuration $TeO_3^{\delta+} \ldots {}^{\delta-}O$, two groups involving a three-coordinated oxide ion, $O_{3/2}TeO^{*}(\text{–}BO_{2/2})(BO_{3/2})$ and $O_{3/2}BO^{*}(TeO_{3/2})_2$, have been derived.

References

1. E. F. LAMBSON, G. A. SAUNDERS, B. BRIDGE and R. A. EL-MALLAWANY, *J. Non-Cryst. Solids* **69** (1984) 117.
2. N. MOCHIDA and K. TAKAHASHI, *Yogyo-Kyokai-Shi* **86** (1978) 317.

3. T. YOKO, K. KAMIYA, K. TANAKA, H. YAMADA and S. SAKKA, *Nippon Seramikkusu Kyokai Gakujutsu Ronbunshi* **97** (1989) 289.
4. M. ARNAUDOV, V. DIMITROV, Y. DIMITRIEV and L. MARKOVA, *Mater. Res. Bull.* **17** (1982) 1121.
5. M. IMAOKA and T. YAMASAKI, *Yogyo-Kyokai-Shi* **76** (1968) 160.
6. H. NASU, O. MATSUSITA, K. KAMIYA, H. KOBAYASHI and K. KUBODERA, *J. Non-Cryst. Solids* **124** (1990) 275.
7. J. E. HUHEEY, "Inorganic chemistry", 3rd Edn (Harper and Row, New York, 1983) Ch. 5.
8. K. SUZUKI, *J. Non-Cryst. Solids* **95/96** (1987) 15.
9. Y. DIMITRIEV, V. DIMITROV and M. ARNAUDOV, *J. Mater. Sci.* **18** (1983) 1353.
10. M. DIMITROVA-PANKOVA, Y. DIMITROV, M. ARNAUDOV and V. DIMITROV, *Phys. Chem. Glasses* **30** (1989) 260.
11. R. GÖRING, H. BÜRGER, H. NASS and B. SCHNABEL, *Physica Status Solidi* (*a*) **68** (1981) k29.
12. Y. KANEKO, H. NAKAMURA, M. YAMANE, K. MIZOGUCHI and Y. SUGINOHARA, *Yogyo-Kyokai-Shi* **91** (1983) 321.
13. W. L. KONIJNENDIJK and J. M. STEVELS, *J. Non-Cryst. Solids* **18** (1975) 30.
14. A. BHARGAVA, R L. SNYDER and R. A. CONDRATE, Sr. *Mater. Res. Bull.* **22** (1987) 1603.
15. T. SEKIYA, N. MOCHIDA, J. OHTSUKA and M. TONOKAWA, *Nippon Seramikkusu Kyokai Gakujutsu Ronbunshi* **97** (1989) 1435.
16. O. LINDQVIST, W. MARK and J. MORET, *Acta Crystallogr.* **B31** (1975) 1255.
17. R. MASSE, J. C. GUITEL and I. TORDJMAN, *Mater. Res. Bull.* **15** (1980) 431.
18. H. MEYER, *Z. Kristallogr.* **124** (1967) 228.
19. O. LINDQVIST, *Acta Chem. Scand.* **22** (1968) 977.
20. B. BUSS and B. KREBS, *Inorg. Chem.* **10** (1971) 2795.
21. B. MYSEN, W. LARRY, W. FINGER, O. VIRGO and F. A. SEIFERT, *Amer. Mineral.* **67** (1982) 686.
22. G. MENORAH and J. GARY, *Acta Crystallogr.* **B27** (1972) 602.
23. N. MOCHIDA, T. SEKIYA, J. OHTSUKA and TONOKAWA, *Nippon Seramikkusu Kyokai Gakujutsu Ronbunshi* **96** (1988) 973.
24. J. E. HUHEEY, "Inorganic chemistry", 3rd Edn (Harper and Row, New York, 1983) Ch. 3.

Received 18 March
and accepted 1 July 1991