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ESR of Cu^{2+} and Tl^{2+} in thallium borate glasses

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The electron spin resonance (ESR) and optical absorption spectra of Cu^{2+} were measured in thallium borate glasses in order to investigate the effects of glass transition temperature, T_g, upon the responses of cupric ion in alkali borate glasses. The ESR of Tl^{2+} induced by γ-ray irradiation was also obtained. An abrupt increase in the covalency of in-plane Cu^{2+}–O π-bonding was observed in the Tl_2O system as well as in the Na_2O system in a similar B_2O_3 composition range although T_g for the Tl_2O glasses has little dependency on the composition compared with the Na_2O glasses. The trend in the variation of the S-character of the Tl^{2+} unpaired electron with composition agreed with that of the covalency of in-plane Cu^{2+}–O π-bonding. The structure of the anion group present in Tl_2O glasses was also examined by laser reman spectroscopy.

1. Introduction

The co-ordination state of transition metal cations in a glass varies with its chemical composition. Wong and Angell [1] pointed out that there are two factors relating to the effects of the glass composition on the co-ordination of the cations. One is the change in the chemical nature of the ligands at different compositions and the other is the change in the glass transition temperature (T_g) which usually accompanies the change in glass composition. Since the four-fold co-ordination (the co-ordination constructed by the bondings of a higher covalency) is favoured in the melt and supercooled liquid, a higher T_g gives rise to the freezing of the larger proportion of the tetrahedrally co-ordinated ion, other factors being equal [1]. They considered that the change in the co-ordination state of the cations in alkali borate glasses with varying glass composition was due to the latter factor [1]. On the other hand, the marked change in the covalency of Cu^{2+}–O π-bonding in the $Cu^{2+}O_6$ complex (D_{4h} symmetry) in glasses with a 80–85 mol% B_2O_3 composition, is attributed to the change in the chemical nature of the ligands [2–4].

In this paper the effects of T_g on the co-ordination state of the cupric ion in Tl_2O–B_2O_3 glasses is investigated. The glass system was chosen as a host matrix because the glasses are expected to have a lower T_g than alkali systems (T_g's of alkali borate glasses give no marked alkali-type dependence [5, 6]) and the thallous ion has alkali-type chemical properties.

Electron spin resonance (ESR) and optical absorption spectra of Cu^{2+} in the glasses and the ESR spectra of Tl^{2+} induced by γ-irradiation were measured. Laser raman spectra were also obtained in order to examine the anion group structures in the glasses.

2. Experimental procedure

2.1. Sample preparation

Thallium borate glasses with 0.5 mol% CuO ranging from 5 to 30 mol% Tl_2O were prepared from reagent grade Tl_2CO_3, H_3BO_3 and CuO. The carefully mixed reagents were sintered and fused in platinum crucibles with a platinum cover at 600 to 900° C for 20 to 30 min. The melts were poured onto a stainless steel plate and pressed with another one into a thin glass plate. No annealing was done after the quenching of the melt. In order to check the variation of the chemical composition in the batch during the fusion process, the densities of the glasses, which are sensitive to the Tl_2O content, were measured by the Archimedes method. The density–composition relation is given in the paper of Sakka *et al.* [7]. The batch composition agreed with the calculated

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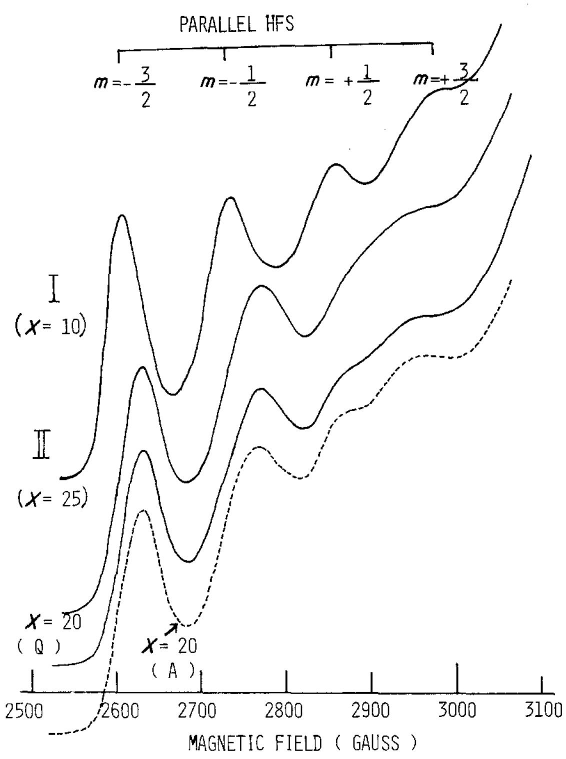

Figure 1 Representative ESR spectra of Cu^{2+} in $X Tl_2O \cdot (100-X)B_2O_3$ glasses (parallel hyperfine structure). The spectrum (Q) for the quenched glass with $X = 20$ is regarded as the superposition of Spectra I and II. The contribution of Spectrum II to this spectrum is reduced in the Spectrum (A) for the annealed glass at the transformation temperature range.

composition within about 1 mol %. We will therefore discuss the glass composition with the batch composition. The use of $TlNO_3$ as the Tl_2O source gave the same results for following measurements.

2.2. ESR measurements

The ESR and optical absorption spectra of Cu^{2+} were measured as described in a previous paper [4]. The ESR measurements of Tl^{2+} were made under the following conditions. The thallium borate glasses without CuO were coarsely crushed after quenching of the melts, sealed in quartz glass tubes under degassing and subjected to γ-ray irradiation from a ^{60}Co-source with a dose of 9×10^5 rad at 77 K. The measurements were made at $-100°$ C without warm-up. The applied magnetic field and the resonating microwave frequency were calibrated by a proton nuclear magnetic resonance (NMR) marker and a cavity wave meter, respectively.

2.3. Determination of the glass transition temperature

Differential thermal analysis was used to determine T_g. The heating rate employed was $5° \text{C} \min^{-1}$. Glasses with a high B_2O_3-content (> 80 mol %) are hygroscopic. The glass samples were therefore crushed and pulverized in dry benzene in order to avoid the absorption of moisture. The measurements were conducted under degassing.

2.4. Laser raman spectra

Fibrous glasses drawn from the melts were used for the laser raman measurements. Hygroscopic samples were coated with liquid paraffin to prevent surface hydration. A Spex 1401 double spectrometer with an Ar-ion laser (488 nm) was employed.

3. Results

3.1. ESR and optical absorption spectra of Cu^{2+}

As in the case of alkali borate glasses, two representative ESR spectra were obtained over the covered glass-forming range in this study (from 5 to 30 mol % Tl_2O); the spectra were abbreviated as I and II in the preceding paper [4]. Spectrum I was observed in low alkali borate glasses (below 15 mol % alkali content) and Spectrum II was observed in high alkali glasses. In the composition range 17 to 20 mol % Tl_2O, the ESR spectra were regarded as the superposition of Spectra I and II as shown in Fig. 1. Such an overlapping has been reported for all the alkali borate glasses with similar compositions [2, 4, 8, 9]. The spin Hamiltonian parameters were determined by assuming an axial

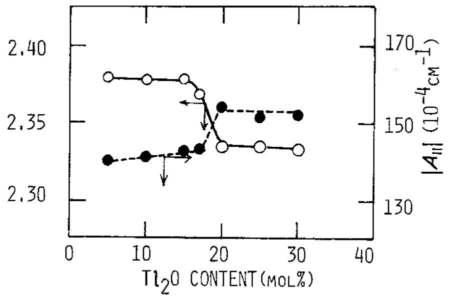

Figure 2 The variation of $g_{\parallel}$ and $A_{\parallel}$ with the Tl_2O content.

symmetry of the Cu^{2+}-complex and employing the first order perturbation theory [4]. Fig. 2 shows the relation between the ESR parameters and the Tl_2O content. A marked change was seen at about 20 mol% Tl_2O. Fig. 3 exhibits the variation of peak energy of the ligand field absorption band of Cu^{2+} with composition. A slight increase in the excitation energy was noticed near 20 mol% Tl_2O.

3.2. Glass transition temperature

Fig. 4 shows the relation between T_g and the B_2O_3 content of Na_2O– and Tl_2O–B_2O_3 glasses. For the soda system, the T_g–composition curve is divided into three regions: in the first region T_g increases linearly with the Na_2O content ($0 \leqslant Na_2O \leqslant 20$ mol%), in the second region T_g has little dependency on the composition ($20 \leqslant Na_2O \leqslant 35$ mol%) and in the last region T_g decreases monotonously ($40 \leqslant Na_2O \leqslant 70$ mol%). In contrast with the soda system, T_g of the thallium system is hardly dependent on the composition. T_g of thallium glasses is less than that of soda glasses with the same B_2O_3 content.

3.3. ESR spectra of Tl^{2+}

Two representative ESR spectra of Tl^{2+} in Tl_2O–B_2O_3 glasses are shown in Fig. 5. A set of doublet absorptions is assigned to the hyperfine (hf) structure due to ^{203}Tl ($I = 1/2$, 29.5%, $\mu = 1.596\ \beta_N$) and ^{205}Tl ($I = 1/2$, 70.5%, $\mu = 1.615\ \beta_N$) nuclei. The slight difference between the nuclear magnetic moments of these two isotopes is insufficient to split each hf absorption further [10].

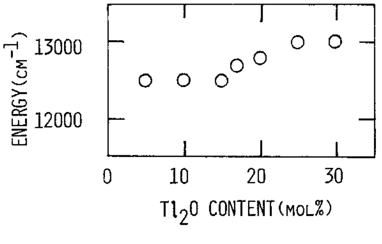

Figure 3 The variation in the peak energy of ligand field absorption band of Cu^{2+} with the Tl_2O content.

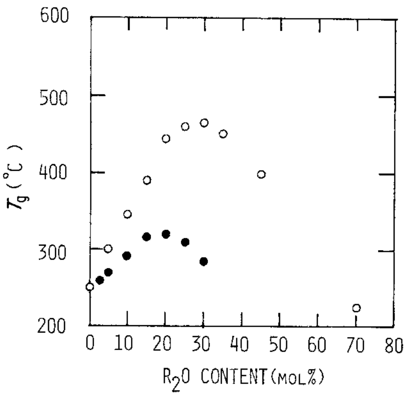

Figure 4 Glass transition temperature (T_g) ○: Na_2O–B_2O_3 glasses, ●: Tl_2O–B_2O_3 glasses. The glass with 45 mol% Na_2O contains 3 mol% Al_2O_3 (Al_2O_3 was added to the batch in order to vitrify the composition [4]).

The analysis of the spectra was made by assuming the following spin-Hamiltonian

$$\mathcal{H} = \beta s \cdot \tilde{g} \cdot H + I \cdot \tilde{A} \cdot s.$$

As a first approximation both $\tilde{g}$ and $\tilde{A}$ tensors are regarded as scalars (g and a). Then the solution of the Hamiltonian is given by the Breit–Rabi equation [11]. The ESR parameters were evaluated using the following equations [12]

$$a = h\nu \frac{(1+C) + [(1+C)^2 + 8(1-C)^2]^{\frac{1}{2}}}{2(C-1)}$$

$$g = \frac{2h\nu}{\beta H^-} \frac{a + h\nu}{2h\nu + a},$$

where C indicates the ratio H^+/H^- (H^+ and H^- mean the magnetic field where the high field and low field hf absorption curves cross the base line in the derivative spectrum, respectively). The ESR parameters obtained were plotted against the Tl_2O content in Fig. 6. It was noticed that the hf coupling constant a abruptly decreased beyond 20 mol% Tl_2O and then the g-shift $(2.002 - g)$ was enhanced simultaneously. Fig. 7 shows the composition dependence of the line widths measured at the peak-to-peak widths in the derivative spectrum. A remarkable change was again observed near the 20 mol% Tl_2O region.

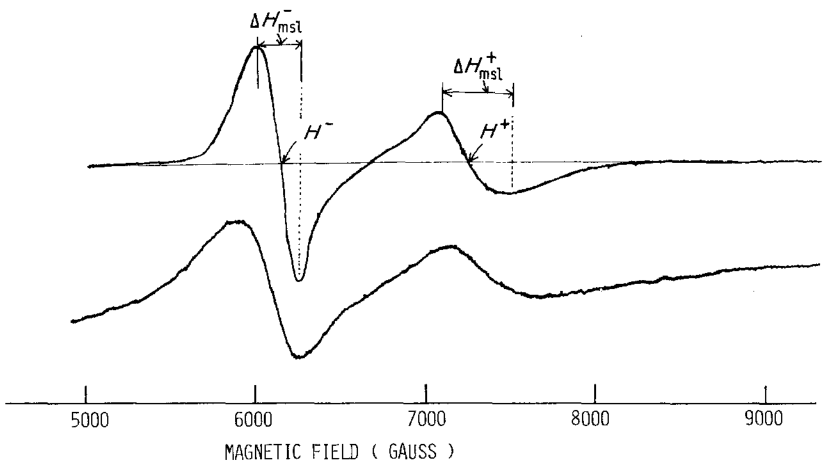

Figure 5 Representative ESR spectra of Tl^{2+} induced by γ-ray irradiation in $Tl_2O-B_2O_3$ glasses. The upper and lower spectra (abbreviated as A and B, respectively) are observed in the glasses with less than 20 mol% Tl_2O and the glasses with more than 20 mol% Tl_2O content, respectively. Note that the line width of the higher field hf absorption (HFS-H) is considerably wider than that of the lower field absorption (HFS-L) and the degree of the deformation in the line shape of HFS-H is larger than that of HFS-L. Such features are characteristic of ESR spectra of ns^1 centres ($a/2 > h\nu$) in the vitreous state [12].

3.4. Laser raman spectra

Two illustrative spectra of Tl_2O- and Na_2O-glasses are shown in Fig. 8. The two sharper peaks at $800\,cm^{-1}$ and $770–750\,cm^{-1}$ reveal the presence of a boroxyl group and 6-membered ring borate structures with one or two four-co-ordinated boron or borons, respectively [13, 14]. No significant difference was observed between the spectra of Na- and Tl-glasses with the same B_2O_3 content. However, the relative intensity of the peak at $800\,cm^{-1}$ to that at $770–750\,cm^{-1}$ was slightly different for both glasses, as shown in Fig. 9.

4. Discussion

4.1. The correlation between the covalent nature of the Cu^{2+}–O bond and T_g of the matrices

The covalences of σ- and in-plane $p\pi$-$d\pi$ Cu–O bondings ($\Gamma\sigma$ and $\Gamma\pi$) in the $Cu^{2+}O_6$ complex (D_{4h}) for $Tl_2O-B_2O_3$ glasses are shown in Fig. 10 as a function of the Tl_2O content. Those for Na_2O glasses are reproduced in Fig. 11 [4] for comparison. The covalences were evaluated from the ESR parameters and the ligand field absorption

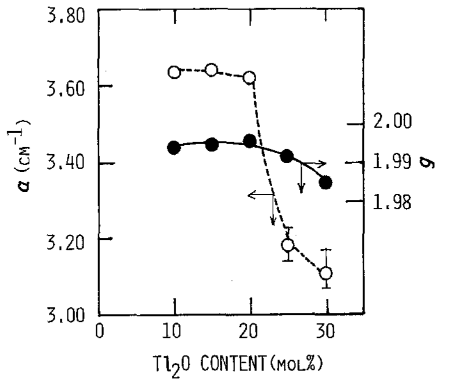

Figure 6 The change in ESR parameters for Tl^{2+} with the Tl_2O content in $Tl_2O-B_2O_3$ glasses.

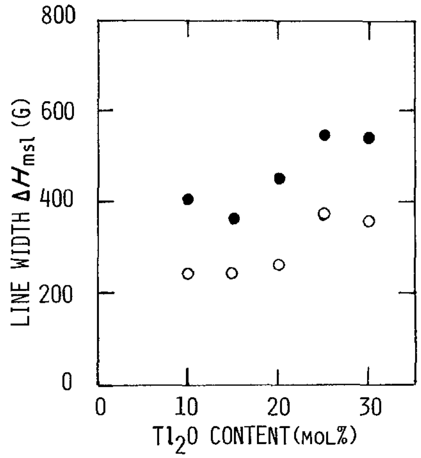

Figure 7 The variation in the line widths of Tl^{2+} with the Tl_2O content. ΔH^{-}_{msl}(○) and ΔH^{+}_{msl}(●) express the peak-to-peak widths of the HFS-L and -H in the derivative spectrum, respectively.

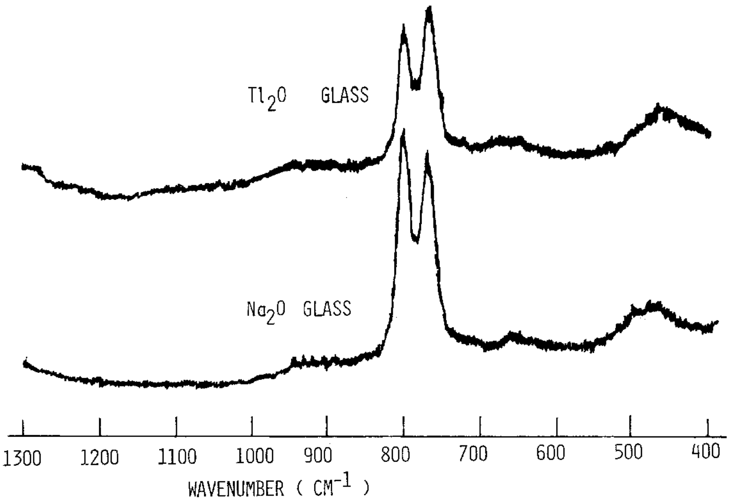

Figure 8 Laser raman spectra of $15R_2O \cdot 85\ B_2O_3$ glasses.

energies by the LCAO–MO method of Maki and McGarvey [15, 16]. An abrupt increase of $\Gamma\pi$ was observed for Tl_2O glasses as well as alkali glasses at a similar composition in spite of the absence of a marked change in the T_g–composition curve.

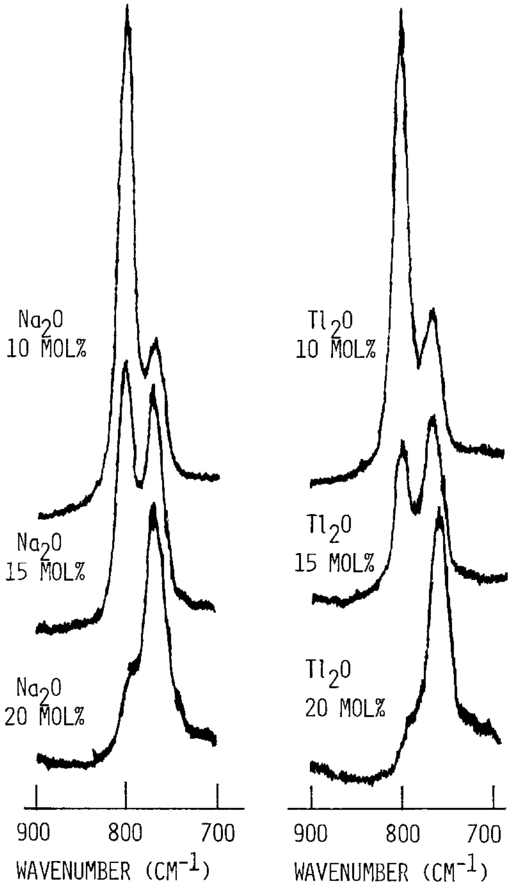

Figure 9 Laser raman spectra of $XR_2O \cdot (100-X)$ B_2O_3 glasses (700 to 900 cm^{-1} region).

These results lead to the conclusion that in alkali borate glasses the predominant factor controlling the co-ordination state of the Cu^{2+}-complex is not the glass transition temperature of the matrices.

4.2. Chemical bonding of Tl–O

Roughly speaking, the Tl^+ ion, the precursor of Tl^{2+}, has the nonbonding electron pair ($6S^2$). As the basicity of the ligand oxygens increases, the participation of the 6S level in the Tl–O bond is enhanced resulting in the promotion of the 6S level to the d^msp^n hybridized orbital. Therefore, it is considered that the S-character decreases with the strengthening of the Tl–O bond, which is defined by the following expression

$$\text{S-character} = \frac{g_1 a_{\text{glass}}}{g a_{\text{free}}} = \frac{|\psi(0)|^2_{\text{glass}}}{|\psi(0)|^2_{\text{free}}},$$

where $|\psi(0)|$ is the density of the unpaired electron

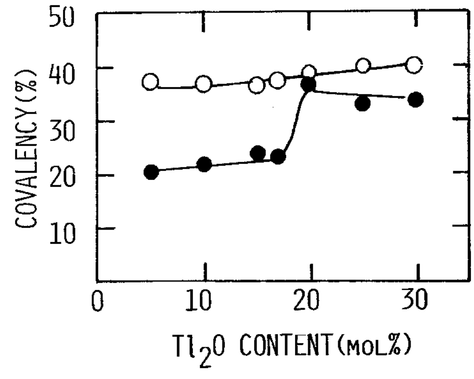

Figure 10 The composition dependence of the covalences of Cu^{2+}–O bonding in Tl_2O–B_2O_3 glasses. $\Gamma\sigma$(○) and $\Gamma\pi$(●) are the covalences for σ- and in-plane pπ-dπ bonds, respectively.

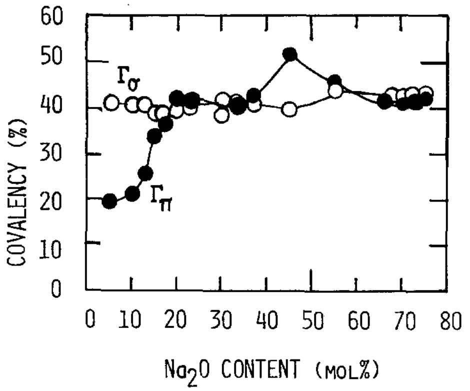

Figure 11 The composition dependence of the covalences of Cu^{2+}–O bonding in Na_2O–B_2O_3 glasses [4].

at the position of nucleus. The value of a_{free} (hf coupling constant of Tl^{2+} in a free space) is 5.85 cm^{-1} [17]. The S-character was used as a measure of the covalency of the Tl–O bond and is shown in Fig. 12 as a function of the Tl_2O content. A marked reduction of the S-character is found at about 20 mol% Tl_2O. The result is interesting in that this is the composition at which the $\Gamma\pi$ value increased abruptly (Fig. 10) and the pronounced down-field shift of ^{205}Tl–NMR, which means the increase of the covalent character of Tl–O bond occurred, which was observed by Nomii and Nachtrieb [18].

4.3. Distribution of the bonding state of Cu^{2+}–O and Tl–O in the glasses

In general, the ESR line shape for glass exhibits a pronounced line-broadening compared with that for polycrystalline matter. This extra-broadening is brought about by the site-to-site fluctuation of the bonding state of the centre in glass and was analysed by introducing the distribution of spin-Hamiltonian parameters [2, 19–21].

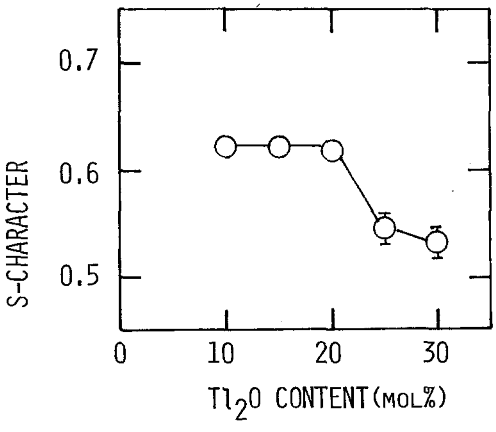

Figure 12 The change in the S-character of the Tl^{2+} unpaired electron with the Tl_2O content in thallium borate glasses.

In the case of ESR of Cu^{2+} in glass, the line width of parallel hf shoulders increases with increasing nuclear magnetic quantum number m. Such a feature was explained by introducing the fluctuation of $g_{\parallel}$- and $A_{\parallel}$-values originating from the structural distribution [2]. It was pointed out that the magnitude of $g_{\parallel}$-distribution (and $A_{\parallel}$-distribution) for Spectrum II is greater than that for Spectrum I [4]. On the other hand, the line-broadening of the spectra for the ns^1 centre in glass can be analysed by assuming the fluctuation of a single parameter, a [12, 22]. This assumption is supported by the fact that g is almost independent of the glass composition, while a is highly dependent as noted in Fig. 6. The line width for Spectrum B (observed in the glasses with greater than 20 mol% Tl_2O) is about two times larger than that for Spectrum A (less than 20 mol% Tl_2O) as seen in Fig. 5. Both Spectrum A of Tl^{2+} and Spectrum I of Cu^{2+} with the narrower distribution of the ESR parameter are observed in the glass with 10 to 20 mol% content, whereas Spectra B and II with a wider distribution are obtained in the composition range 25 to 30 mol% Tl_2O.

4.4. The structure of the anion group

According to the results of the ^{11}B–NMR study by Baugher and Bray [23], the values of N_4 (the fraction of four-co-ordinated boron) of Tl_2O–B_2O_3 glasses [23] are considerably greater than those for alkali or silver borate glasses [24] as shown in Fig. 13. This result suggests that the anion group structures present in Tl_2O–B_2O_3 glasses are fairly different from those in alkali systems. The raman spectra for both systems exhibit only a small difference; the relative intensity (K) of the peak at 800 cm^{-1} to that at 770–750 cm^{-1} for the Tl_2O system is slightly smaller than that for the Na_2O system. However, compared with the K-values for Tl_2O– and Na_2O–B_2O_3 glasses with iso-N_4 values, the former has a considerably high value than the latter. This result suggests that the conversion from three-co-ordinated boron to four-co-ordinated boron with the addition of Tl_2O to B_2O_3 occurs in such a manner so as to preserve the boroxyl group and modify other BO_3 groups to BO_4 units. The boroxyl group is stabilized by the delocalization of

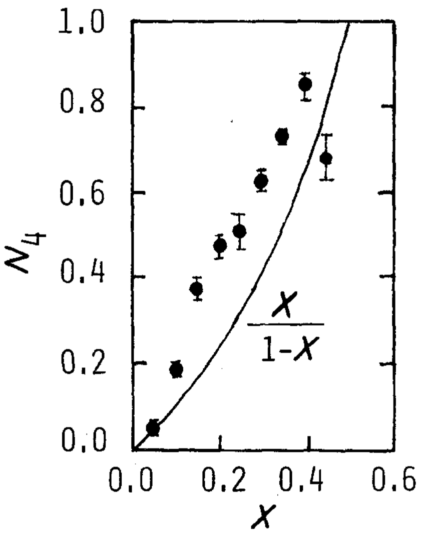

Figure 13 The fraction, N_4, of four-co-ordinated boron atoms plotted against the Tl_2O content in $XTl_2O \cdot (1-X) B_2O_3$ glasses. The solid line shows the value of N_4 that would be obtained if each Tl_2O unit converted two boron atoms from three-to four-co-ordination. The values of N_4 in $XR_2O \cdot (1-X)B_2O_3$ glasses follow the relation $X/(1-X)$ in the region from $X = 0$ to 0.3 [23].

pπ-electrons on the 6-membered borate ring [3].

The group structures with three-co-ordinated oxygens whose existence is suggested by the NMR study [23] were not detected directly in our raman spectra. All the boron atoms in crystalline $SrO \cdot 2B_2O_3$ are four-fold co-ordinated and three-co-ordinated oxygens are contained in it (in the proportion of two to fourteen oxygens [25, 26]). The raman spectrum for this polycrystal has peaks below 650 cm^{-1} [12]. As the peaks of the raman spectra except those at 800 and 770–750 cm^{-1} were greatly spread out in borate glasses due to the fluctuation of the structure [27, 28], it is difficult to observe these peaks distinctly. Thus, the present study does not offer information about the existence of the three-co-ordinated oxygen.

5. Summary

ESR and optical absorption spectra of the incorporated Cu^{2+} and the ESR of Tl^{2+} induced by γ-ray irradiation were measured for $Tl_2O–B_2O_3$ glasses. Laser raman spectra were also taken for the glasses. The results obtained are summarized as follows:

(1) The covalency of in-plane $Cu^{2+}–O$ π-bonding for the Tl_2O system changed distinctly in a similar composition range (80 to 85 mol% B_2O_3) as the Na_2O system irrespective of the absence of a pronounced composition dependence of T_g in contrast with the Na_2O system;

(2) The S-character of the unpaired electron of Tl^{2+} in the glasses with greater than 20 mol% Tl_2O is smaller than that in the glasses with less Tl_2O content;

(3) The magnitude of the distribution of the ESR parameters for both Cu^{2+} and Tl^{2+} in glasses with greater than 20 mol% Tl_2O is greater than those in the glasses with less Tl_2O content;

(4) The relative raman scattering intensity of the peak at 800 cm^{-1} to that at 770–750 cm^{-1} for the Tl_2O glasses is smaller than that for the Na_2O glasses with the same B_2O_3 content.

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