^{125}Te NMR Study of $\text{MO}-\text{TeO}_2$ ($\text{M}=\text{Mg}, \text{Zn}, \text{Sr}, \text{Ba}$ and Pb) Glasses

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 $\text{MO}-\text{TeO}_2$ ($\text{M}=\text{Mg}, \text{Zn}, \text{Sr}, \text{Ba}$ and Pb) ガラスの ^{125}Te NMR 研究

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The structure of $\text{MO}-\text{TeO}_2$ ($\text{M}=\text{Mg}, \text{Zn}, \text{Sr}, \text{Ba}$ and Pb) glasses has been studied by means of ^{125}Te static NMR technique. The fraction of TeO_4 trigonal bipyramid (tbp), N_4 decreased and that of TeO_3 trigonal pyramid (tp), N_3 increased almost linearly up to 33.3 mol% MO and rapidly in the range of 33.3 to 40 mol% MO, with increasing MO content. It was found that the glasses containing MO in the range of 40 to 45 mol% MO consisted only of TeO_3 tp. On the basis of the structural model proposed in a previous paper, the fractions of TeO_4 tbp without a non-bridging oxygen (NBO) atom, $\text{TeO}_{4/2}$ (N_4^0), TeO_4 tbp with an NBO atom, $\text{O}_{3/2}\text{Te}-\text{O}^-$ (N_4^-) and TeO_3 tp with two NBO atoms, $\text{O}_{1/2}\text{Te}(=\text{O})-\text{O}^-$ (N_3^-) were calculated. The structural change for $\text{MO}-\text{TeO}_2$ glasses in the range of 0 to 33.3 mol% MO could be well represented by the model previously proposed for alkali tellurite binary glasses. A new model which represents the structural change for $\text{MO}-\text{TeO}_2$ glasses containing more than 33.3 mol% MO has been proposed.

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1. Introduction

Since tellurite glasses have some excellent physical properties, such as high refractive index, high infrared transmittance, high dielectric constants, good chemical durability and low temperature melting,¹⁻⁵⁾ they are considered to be a candidate for optical materials applicable to the optical switching devices⁶⁾ and optical amplifier hosts.⁷⁾

The structures of $\text{MO}-\text{TeO}_2$ ($\text{M}=\text{Mg}, \text{Zn}, \text{Sr}, \text{Ba}$ and Pb) glasses have been investigated by means of X-ray diffraction,⁸⁾ neutron diffraction,⁹⁾ infrared spectroscopy,^{10,11)} Raman spectroscopy,^{12,13)} EXAFS⁸⁾ and Mössbauer spectroscopy¹⁴⁾ so far. All these recent investigations claim that the addition of MO to TeO_2 glass changes the Te coordination polyhedron from TeO_4 trigonal bipyramids (tbp) to TeO_3 trigonal pyramid (tp). Suzuki determined the coordination numbers around Te atoms for $\text{BaO}-\text{TeO}_2$ glasses by neutron diffraction.⁹⁾ Himei et al.¹³⁾ estimated the molar ratio of $\text{TeO}_3/\text{TeO}_4$ for $\text{R}_2\text{O}-\text{TeO}_2$ ($\text{R}=\text{Li}, \text{Na}$ and K) and $\text{MO}-\text{TeO}_2$ ($\text{M}=\text{Ba}$ and Zn) glasses from the intensity ratio of Raman bands and proposed a structure model of these tellurite glasses. Nevertheless, the more detailed structure of $\text{MO}-\text{TeO}_2$ glasses has not been made clear yet.

In a previous paper,¹⁵⁾ ^{125}Te static NMR study of $\text{M}_2\text{O}-\text{TeO}_2$ ($\text{M}=\text{Li}, \text{Na}, \text{K}, \text{Rb}$ and Cs) glasses enabled us to discriminate between TeO_3 tp and TeO_4 tbp and to estimate quantitatively the fractions of TeO_3 tp and TeO_4 tbp. On the basis of these results, we proposed a structure model for $\text{M}_2\text{O}-\text{TeO}_2$ glasses. In the present work, ^{125}Te static NMR spectra are measured for $\text{MO}-\text{TeO}_2$ ($\text{M}=\text{Mg}, \text{Zn}, \text{Sr}, \text{Ba}$ and Pb) glasses in order to determine the more reliable fractions of TeO_3 tp and TeO_4 tbp of $\text{MO}-\text{TeO}_2$ glasses. Then, the structure of $\text{MO}-\text{TeO}_2$ glasses is discussed quantitatively.

2. Experimental

2.1 Preparation of glasses

To attain both shorter measuring time and higher S/N ratio by shortening relaxation times of Te nuclei with

$I=1/2$, TeO_2 , $\text{MgO}-\text{TeO}_2$, $\text{ZnO}-\text{TeO}_2$, $\text{SrO}-\text{TeO}_2$, $\text{BaO}-\text{TeO}_2$ and $\text{PbO}-\text{TeO}_2$ glasses containing 0.3 mol% Fe_2O_3 were prepared. The glass compositions are shown in Table 1. Reagent-grade $\beta\text{-TeO}_2$ (Mitsuwa Pure Chemicals, Osaka), Fe_2O_3 , MgO , SrCO_3 and PbO (Nacalai Tesque, Inc., Kyoto) and ZnO and BaCO_3 (Wako Pure Chemicals, Osaka) were used as starting materials. A 3 g batch of well-mixed reagents was melted in a Pt-5 % Au crucible at 800-970°C for 10 min in air. The melt was poured onto a stainless plate and immediately pressed by another stainless plate.

Small amounts of batches (50-100 mg for pure TeO_2 glass, 0.1-0.2 g for $40\text{BaO}\cdot 60\text{TeO}_2$ glass and 0.3-1.0 g for $x\text{PbO}\cdot (100-x)\text{TeO}_2$ ($x=30-45$) glasses) were melted in a Pt-5 % Au crucible at 830-950°C for 10 min in air. The melt was quenched by immersing the bottom of the crucible into a freezing mixture consisting of NaCl and ice water kept at about -10°C.

In most cases, the quenched melts were identified to be glassy by visual inspection. X-ray diffraction using a Rigaku Geigerflex RAD-IIA diffractometer was used in some cases to reconfirm visual observation.

2.2 NMR measurements

^{125}Te static NMR spectra of powdered tellurite glasses were measured at 126.32 MHz (9.4 T) on a JEOL JNM-GSX 400 MAS FT-NMR spectrometer. A single pulse sequence was used: a pulse length of 2.5 μs , the accumulation of 6000-20000 scans and a pulse delay of 2.5 s for $\text{MO}-\text{TeO}_2$ glasses. Telluric acid $\text{Te}(\text{OH})_6$ was used as a secondary standard whose chemical shift was $\delta=692.2$ ppm with reference to $(\text{CH}_3)_2\text{Te}$.¹⁶⁾

2.3 ^{125}Te static NMR spectra

The principal components of the chemical shift tensors, δ_1 , δ_2 and δ_3 were estimated by fitting the calculated theoretical spectra to the experimental static NMR spectra as described in a previous paper.¹⁷⁾ The isotropic chemical shift $\delta_{\text{iso}}(\text{static})$, the chemical shift anisotropy $\Delta\delta$ and the asymmetry parameter η were also determined by using the following definitions:^{18,19)}

Table 1. Chemical Shift Parameters Used in the Simulated Spectra, Chemical Shift Anisotropy and Asymmetry Parameter

Glass	Profile 1 (TeO ₄)							Profile 2 (TeO ₃)						
x/mol%	δ ₁	δ ₂	δ ₃	δ _{iso}	Δδ	η	Area/%	δ ₁	δ ₂	δ ₃	δ _{iso}	Δδ	η	Area/%
TeO ₂ glass	2220	1590	620	1477	-1285	0.74	100	-	-	-	-	-	-	0
xMgO·(100-x)TeO ₂ glasses														
x=10	2260	1630	660	1517	-1285	0.74	79	2220	2010	1320	1850	-805	0.39	21
x=20	2320	1690	720	1577	-1285	0.74	60	2240	2030	1340	1870	-805	0.39	40
x=30	2330	1700	730	1587	-1285	0.74	41	2220	2010	1320	1850	-805	0.39	59
x=33.3	2190	1560	590	1447	-1285	0.74	35	2220	2010	1320	1850	-805	0.39	65
x=35	2190	1560	590	1447	-1285	0.74	30	2180	1970	1280	1810	-805	0.39	70
x=40	-	-	-	-	-	-	0	2130	1920	1220	1757	-805	0.39	100
xZnO·(100-x)TeO ₂ glasses														
x=10	2290	1660	690	1547	-1285	0.74	79	2310	2130	1380	1940	-860	0.35	21
x=20	2320	1690	720	1577	-1285	0.74	59	2260	2080	1330	1890	-860	0.35	41
x=30	2250	1620	650	1507	-1285	0.74	41	2230	2050	1300	1860	-860	0.35	59
x=33.3	2160	1530	560	1417	-1285	0.74	36	2190	2010	1260	1820	-860	0.35	64
x=35	2180	1550	580	1437	-1285	0.74	31	2140	1960	1210	1770	-860	0.35	69
x=40	-	-	-	-	-	-	0	2220	2020	1260	1833	-860	0.35	100
x=45	-	-	-	-	-	-	0	2140	1960	1280	1793	-770	0.35	100
xSrO·(100-x)TeO ₂ glasses														
x=10	2380	1750	780	1637	-1285	0.74	80	2280	2060	1340	1893	-825	0.38	20
x=15	2400	1770	800	1657	-1285	0.74	70	2300	2080	1360	1913	-825	0.38	30
xBaO·(100-x)TeO ₂ glasses														
x=10	2340	1710	740	1597	-1285	0.74	80	2260	2060	1360	1898	-800	0.38	20
x=20	2310	1680	710	1567	-1285	0.74	61	2250	2050	1350	1888	-800	0.38	39
x=30	2270	1640	670	1527	-1285	0.74	42	2200	2000	1300	1833	-800	0.38	58
x=33.3	2140	1510	540	1397	-1285	0.74	35	2150	1950	1250	1783	-800	0.38	65
x=35	2220	1590	620	1477	-1285	0.74	29	2170	1970	1270	1803	-800	0.38	71
x=40	-	-	-	-	-	-	0	2030	1830	1130	1663	-800	0.38	100
xPbO·(100-x)TeO ₂ glasses														
x=10	2230	1600	630	1487	-1285	0.74	79	2270	2040	1300	1870	-855	0.40	21
x=20	2250	1620	650	1507	-1285	0.74	62	2290	2060	1320	1890	-855	0.40	38
x=30	2220	1590	620	1477	-1285	0.74	47	2380	2150	1410	1980	-855	0.40	53
x=33.3	2210	1580	610	1467	-1285	0.74	41	2300	2070	1330	1900	-855	0.40	59
x=35	2230	1600	630	1487	-1285	0.74	34	2260	2030	1290	1860	-855	0.40	66
x=40	-	-	-	-	-	-	0	2250	2020	1280	1850	-855	0.40	100
x=45	-	-	-	-	-	-	0	2050	1890	1210	1717	-760	0.32	100

All the values except η and area have a unit of ppm.

The errors of δ₁, δ₂ and δ₃ are ±10 ppm. The errors of area are ±2 %.

$$\delta_{\text{iso (static)}} = \frac{\delta_1 + \delta_2 + \delta_3}{3} \quad (1)$$

$$\Delta\delta = \delta_3 - \frac{\delta_1 + \delta_2}{2} \quad (2)$$

$$\eta = \frac{\delta_2 - \delta_1}{\delta_3 - \delta_{\text{iso (static)}}} \quad (3)$$

The principal components of the chemical shift tensors can be determined based on the next relation

$$|\delta_3 - \delta_{\text{iso (static)}}| \geq |\delta_1 - \delta_{\text{iso (static)}}| \geq |\delta_2 - \delta_{\text{iso (static)}}| \quad (4)$$

3. Results

Figure 1 shows the ^{125}Te static NMR spectra of $\text{ZnO}-\text{TeO}_2$ glasses together with that of ZnTeO_3 crystal. All the spectra of glasses consisted of one broad peak without splitting in the range of 500 to 2800 ppm. The intensity of the peaks in the range of 500 to 1800 ppm decreased with increasing ZnO content, suggesting that the local structure around Te atoms in glasses changes with the ZnO content. The ^{125}Te static NMR line profiles of $\text{MO}-\text{TeO}_2$ ($\text{M}=\text{Mg}$, Sr , Ba and Pb) glasses which are not shown here were basically similar to those of $\text{ZnO}-\text{TeO}_2$ glasses.

4. Discussion

4.1 ^{125}Te static NMR spectra and local structure of tellurite glasses

In a previous paper,¹⁷⁾ the local structure around Te atoms has been classified into five groups based on the structural units present in tellurite crystals as illustrated in Fig. 2. These are (1) TeO_3 type which consists of isolated TeO_3 type and terminal TeO_3 type, (2) TeO_{3+1} type and (3) TeO_4 type which consists of $\alpha\text{-TeO}_2$ type and $\beta\text{-TeO}_2$ type. Isolated TeO_3 type means the TeO_3 tp structural unit present as a free anion, the terminal TeO_3 type the TeO_3 tp one of the corners of which is connected with neighboring TeO_n polyhedron, and the TeO_{3+1} type the TeO_3 tp having an additional O atom at a remote distance from 0.22 to 0.25 nm. Furthermore, $\alpha\text{-TeO}_2$ type contains the TeO_4 tbp structural units which are connected by sharing their corners, and $\beta\text{-TeO}_2$ type the Te_2O_6 units consisting of two edge-

shared TeO_4 tbps. Figure 3 shows the relationship between the asymmetry parameter η and the absolute value of the chemical shift anisotropy $|\Delta\delta|$ for different structural units as found in various tellurite crystals, which was obtained previously.¹⁷⁾ A region determined by both η and $|\Delta\delta|$, which corresponds to each structural unit shown in Fig. 2, is depicted in this $\eta-|\Delta\delta|$ diagram.

As clearly seen from Fig. 1, the line profile of ^{125}Te static NMR spectra of $\text{ZnO}-\text{TeO}_2$ glasses varies with increasing ZnO content and is getting close to that of ZnTeO_3 crystal containing only TeO_3 tp as a structural unit. This suggests that the formation of TeO_3 tp takes place on addition of ZnO to TeO_2 glass and the content increases with increasing ZnO concentration. Especially, since the spectra of glasses containing 40 and 45 mol% ZnO consist of one broad peak without splitting in the range of 1200 to 2600 ppm, it is predicted that those glasses are composed only of TeO_3 tp. The principal components of the chemical shift tensor, δ_1 , δ_2 and δ_3 , were estimated from the measured spectra and the isotropic chemical shift $\delta_{\text{iso}}(\text{static})$, $\Delta\delta$ and η were calculated from Eqs. (1)–(3). The results obtained for $\text{MO}-\text{TeO}_2$ ($\text{M}=\text{Mg}$, Zn , Ba and Pb) glasses containing 40 and 45 mol% MO are listed in Table 1 and are plotted in the $\eta-|\Delta\delta|$ diagram (Fig. 3). Since all the points determined from both $\Delta\delta$ and η of these glasses are located just in the region of terminal TeO_3 type, it can be safely said that all these glasses are mainly composed of TeO_3 tps of terminal TeO_3 type.

Since TeO_2 glass is composed of TeO_4 tbps of $\alpha\text{-TeO}_2$ type (Fig. 3),¹⁵⁾ it seems reasonable to assume that $\text{MO}-\text{TeO}_2$ glasses are mainly composed of TeO_4 tbp and TeO_3 tp structural units, their fractions depending on the composition. To confirm this assumption, the experimental ^{125}Te static NMR spectra of $\text{MO}-\text{TeO}_2$ glasses are deconvoluted by using two spectral components: the profile 1 is due to TeO_4 tbp and the profile 2 due to TeO_3 tp.

An example of line profile deconvolution performed for $\text{ZnO}-\text{TeO}_2$ glasses is shown in Fig. 4. Here the principal components of the chemical shift tensor, δ_1 , δ_2 and δ_3 , for TeO_2 glass and $40\text{MO}\cdot 60\text{TeO}_2$ ($\text{M}=\text{Mg}$, Zn , Ba and Pb) glasses are used as the initial values for the profile 1 and profile 2, respectively. The values obtained by the spectral deconvolution for the present $\text{MO}-\text{TeO}_2$ glasses are summarized in Table 1. The NMR parameters, η and $\Delta\delta$, of the profile 2 obtained for respective glass systems are shown in Fig. 3. It is interesting to note that all the values are situated in the area which is assigned to the structural unit TeO_3 tp of terminal TeO_3 type. This result confirms that the assumption that the present $\text{MO}-\text{TeO}_2$ glasses mainly consist of TeO_4 tbp and TeO_3 tp is reasonable.

Figure 5 plots the fractions of TeO_4 tbp (N_4) and TeO_3 tp (N_3) as a function of MO content in the $\text{MO}-\text{TeO}_2$ glasses. N_3 increases and N_4 decreases almost linearly below 33.3 mol% MO with increasing MO content. N_3 increases and N_4 decreases rapidly in the range of 33.3 to 40 mol% MO with increasing MO content. The glasses containing MO between 40 and 45 mol% consist only of TeO_3 tp.

Here let's compare the structures of glasses and crystals with the compositions of $\text{MgO}\cdot 2\text{TeO}_2$ and $2\text{MO}\cdot 3\text{TeO}_2$ ($\text{M}=\text{Mg}$, Zn and Pb). The ^{125}Te static NMR spectra of glasses and crystals of MgTe_2O_5 and $\text{Mg}_2\text{Te}_3\text{O}_8$ are compared in Fig. 6 as an example. The line profiles of these crystals are quite different from those of the glasses having the same compositions. MgTe_2O_5 crystal consists only of TeO_{3+1} polyhedra,²⁰⁾ whereas corresponding glass contains both TeO_4 tbp and TeO_3 tp. Furthermore, $\text{M}_2\text{Te}_3\text{O}_8$ ($\text{M}=\text{Mg}$, Zn and Pb) crystals contain TeO_4 tbp and TeO_{3+1} polyhedra,^{21)–23)} while $40\text{MO}\cdot 60\text{TeO}_2$ ($\text{M}=\text{Mg}$, Zn and Pb) glasses TeO_3 tp only. Thus, it can be said that the

Fig. 1. ^{125}Te static NMR spectra of $x\text{ZnO}\cdot(100-x)\text{TeO}_2$ ($x=0$, 10, 20, 30, 33.3, 35, 40 and 45) glasses and ZnTeO_3 crystal.

Fig. 2. Classification of structural units of (1) TeO_3 type: (i) isolated TeO_3 type and (ii) terminal TeO_3 type, (2) TeO_{3+1} type, and (3) TeO_4 type: (i) $\alpha\text{-TeO}_2$ type and (ii) $\beta\text{-TeO}_2$ type.

Fig. 3. Plots of the η vs. the $|\Delta\delta|$ for tellurite glasses. Profile 1 is based on the line profile of TeO_2 glass. Profile 2 is based on those of $40\text{MO}\cdot 60\text{TeO}_2$ glasses ($\text{M}=\text{Mg}, \text{Zn}, \text{Ba}$ and Pb) and $\text{SrO}-\text{TeO}_2$ glasses.

structures are quite different between the glasses and crystals with the compositions of $\text{MgO}\cdot 2\text{TeO}_2$ and $2\text{MO}\cdot 3\text{TeO}_2$ ($\text{M}=\text{Mg}, \text{Zn}$ and Pb). This result can explain the ex-

perimental fact that $\text{MO}-\text{TeO}_2$ glasses have high resistance against crystallization and hence a wide glass-forming region.

The broken curves in Fig. 5 denote the theoretical amounts of TeO_3 tp and TeO_4 thp produced when the added MO is completely used to transform TeO_4 into TeO_3 . The theoretical values of N_3 and N_4 can be given by Eqs. (5) and (6), respectively.

$$N_3(\%) = 200x / (100 - x) \quad (5)$$

$$N_4(\%) = 100 - N_3(\%) \quad (6)$$

where x is the MO content (mol%). As seen in Fig. 5, the discrepancy between the experimental and theoretical values at the same composition increases with the increase of MO content, indicating that all the MO added are not used to form TeO_3 tp.

4.2 Structure model of tellurite glasses

A model presenting a structural change on addition of a network modifying oxide to TeO_2 glass is proposed by Himei et al.¹³⁾ The vitrification reaction can be described as

where a , b and c are the fractions and $a+b=1$. Equation (7) holds only when $0 \leq y \leq 0.5$. When $y > 0.5$, Eq. (7) cannot be used since $(1-2y-cy) < 0$. $[\text{O}_{2/2}\text{Te}(\text{O})_2]^{2-}$ (TeO_4 thp with two non-bridging oxygens (NBO)) and isolated TeO_3^{2-} (TeO_3 tp) are considered to be hardly formed when $0 \leq y \leq 0.5$ ($0 \leq \text{MO}(\text{mol}\%) \leq 33.3$). The molar ratio of $\text{TeO}_3/\text{TeO}_4$ is thus represented by Eq. (8) as a function of b , c and y

$$\frac{[\text{TeO}_3]}{[\text{TeO}_4]} = \frac{(2b+c)y}{1 - (2b+c)y} \quad (8)$$

Since their method does not give unique values of b and c , the molar ratios of the structural units in tellurite glasses cannot be determined. However, from the result of a molecular orbital calculation on clusters modeling TeO_2 glass by Uchino and Yoko,²⁴⁾ it was demonstrated that the $\text{O}_{2/2}\text{Te}=\text{O}$ unit does not exist in tellurite glasses, that is, $c=0$. Therefore, Eq. (7) is rewritten using $c=0$ and $a=1-b$:

Fig. 4. Simulated and experimental ^{125}Te static NMR spectra of $x\text{ZnO} \cdot (100-x)\text{TeO}_2$ ($x=0, 10, 20, 30, 33.3, 35, 40$ and 45) glasses.

The ratio $[\text{TeO}_3]/[\text{TeO}_4]$ is described as follows:

$$\frac{[\text{TeO}_3]}{[\text{TeO}_4]} = \frac{2yb}{1-2yb} \quad (10)$$

The y value is known from the glass composition. Since the ratio $[\text{TeO}_3]/[\text{TeO}_4]$ is directly obtained in this NMR work, Eq. (10) gives the b values. N_4^0 , N_4^- and N_3^- , which indicate the fractions of $\text{TeO}_{4/2}$, $\text{O}_{3/2}\text{Te}-\text{O}^-$ and $\text{O}_{1/2}\text{Te}(=\text{O})-\text{O}^-$, respectively, can be calculated from b values. $\text{TeO}_{4/2}$, $\text{O}_{3/2}\text{Te}-\text{O}^-$ and $\text{O}_{1/2}\text{Te}(=\text{O})-\text{O}^-$ mean TeO_4 tbp without a non-bridging oxygen (NBO), TeO_4 tbp with an NBO and TeO_3 tp with two NBO's, respectively. Since N_4^0 becomes 0 % at 33.3 mol% MO according to Eq. (9), the remaining two units, $\text{O}_{3/2}\text{Te}-\text{O}^-$ and $\text{O}_{1/2}\text{Te}(=\text{O})-\text{O}^-$, will exist in the glasses containing 33.3 mol% MO. Over 33.3 mol% MO, further addition of MO are considered to change the $\text{O}_{3/2}\text{Te}-\text{O}^-$ and $\text{O}_{1/2}\text{Te}(=\text{O})-\text{O}^-$ units into the $\text{O}_{2/2}\text{Te}-\text{O}_2^{2-}$ (TeO_4 tbp with two NBO's) and the isolated TeO_3^{2-} (TeO_3 tp with three NBO's) units, respectively. Hence, it may be reasonable to assume that $\text{O}_{3/2}\text{Te}-\text{O}^-$, $\text{O}_{2/2}\text{Te}-\text{O}_2^{2-}$, $\text{O}_{1/2}\text{Te}(=\text{O})-\text{O}^-$ and isolated TeO_3^{2-} units exist in the glasses over 33.3 mol% MO. Since a model presenting a structural change shown above cannot be employed over 33.3 mol% MO, N_4 and N_3 obtained over 33.3 mol% MO exhibit ($N_4^- + N_4^{2-}$) and ($N_3^- + N_3^{2-}$), respectively, where N_4^{2-} and N_3^{2-} denote the fractions of $\text{O}_{2/2}\text{Te}-\text{O}_2^{2-}$ and isolated TeO_3^{2-} units, respectively. Because N_4^- , N_4^{2-} , N_3^- and N_3^{2-} cannot individually be determined over 33.3 mol% MO, their sums $N_4^* (=N_4^- + N_4^{2-})$ and $N_3^* (=N_3^-$

Fig. 5. Plots of the fraction of N_4 (top) and N_3 (bottom) vs. MO content in the $\text{MO}-\text{TeO}_2$ ($M=\text{Mg, Zn, Sr, Ba}$ and Pb) glasses. The broken curves denote the theoretical curves (see text).

Fig. 6. ^{125}Te static NMR spectra of MgTe_2O_5 (top) and $\text{Mg}_2\text{Te}_3\text{O}_8$ (bottom) crystals together with corresponding glasses.

+ N_3^{2-}) are taken into consideration in this work. The values of N_4^0 , N_4^- , $N_4^* (=N_4^- + N_4^{2-})$, N_3^- , $N_3^* (=N_3^- + N_3^{2-})$, $N_4^-/(N_3^- + N_4^-)$ and the average coordination number of Te atoms N_{ave} obtained for the present MO-

TeO₂ glasses are summarized in Table 2. As clearly seen from this table, all these values are not sensitive to MO and show similar composition dependences to each other.

Variations of N_4^0 , N_4^- , N_4^* ($=N_4^-+N_4^{2-}$), N_3^- and N_3^* ($=N_3^-+N_3^{2-}$) with the ZnO content in the ZnO-TeO₂ glass system are shown in Fig. 7 as an example. N_4^0 decreases, while N_4^- and N_3^- increase up to 33.3 mol% ZnO with increasing ZnO content. N_4^0 becomes 0 % over 33.3 mol% ZnO. N_3^* increases and N_4^* decreases rapidly over 33.3 mol% ZnO with increasing ZnO content. N_3^* and N_4^* are 100 and 0 %, respectively, over 40 mol% ZnO. It is interesting to note that the initial addition of ZnO to TeO₂ glass results in the formation not of N_4^- but of N_3^- , and the N_4^- increases rapidly in the range of 20 to 33.3 mol% ZnO. This behavior is attributed to the repulsion between the lone pairs of electrons of excessive $\text{O}_{1/2}\text{Te}(=\text{O})-\text{O}^-$ tp groups as described in a previous paper.¹⁵⁾ Variations of N_4^0 , N_4^- , N_4^* , N_3^- and N_3^* with the MO content in the MO-TeO₂ (M=Mg, Sr, Ba and Pb) glass systems were very similar to those in the ZnO-TeO₂ glass system.

It is also interesting to note that the composition dependences of N_4^0 , N_4^- and N_3^- in the MO-TeO₂ glass systems are very similar to those in the M₂O-TeO₂ (M=Li, Na, K, Rb and Cs) glass systems.¹⁵⁾ Therefore, it can be said that the model which presents the structural change for M₂O-TeO₂ glasses holds for the present MO-TeO₂ glasses in the range of 0 to 33.3 mol% MO.

With reference to our previous model,²⁵⁾ we propose an

Table 2. Fractions of Several Tellurite Structural Units; N_4^0 , N_4^- , N_4^* ($=N_4^-+N_4^{2-}$), N_3^- and N_3^* ($=N_3^-+N_3^{2-}$), the Ratio $N_4^-/(N_3^-+N_4^-)$, and the Average Coordination Number N_{ave} of Te Atoms

Glass x/mol%	N_4^0 /%	N_4^- /%	N_4^* /%	N_3^- /%	N_3^* /%	$N_4^-(N_3^-+N_4^-)$	N_{ave}
TeO ₂ glass	100.0	0.0	-	0.0	-	-	4.00
xMgO·(100-x)TeO ₂ glasses							
x=10	77.8	1.2	-	21.0	-	0.06	3.79
x=20	50.0	10.0	-	40.0	-	0.20	3.60
x=30	14.3	26.7	-	59.0	-	0.31	3.41
x=33.3	0.0	35.0	-	65.0	-	0.35	3.35
x=35	0.0	-	30.0	-	70.0	0.30	3.30
x=40	0.0	-	0.0	-	100.0	0.00	3.00
xZnO·(100-x)TeO ₂ glasses							
x=10	77.8	1.2	-	21.0	-	0.06	3.79
x=20	50.0	9.0	-	41.0	-	0.18	3.59
x=30	14.3	26.7	-	59.0	-	0.31	3.41
x=33.3	0.0	36.0	-	64.0	-	0.36	3.36
x=35	0.0	-	31.0	-	69.0	0.31	3.31
x=40	0.0	-	0.0	-	100.0	0.00	3.00
x=45	0.0	-	0.0	-	100.0	0.00	3.00
xSrO·(100-x)TeO ₂ glasses							
x=10	77.8	2.2	-	20.0	-	0.10	3.80
x=15	64.7	5.3	-	30.0	-	0.15	3.70
xBaO·(100-x)TeO ₂ glasses							
x=10	77.8	2.2	-	20.0	-	0.10	3.80
x=20	50.0	11.0	-	39.0	-	0.22	3.61
x=30	14.3	27.7	-	58.0	-	0.32	3.42
x=33.3	0.0	35.0	-	65.0	-	0.35	3.35
x=35	0.0	-	29.0	-	71.0	0.29	3.29
x=40	0.0	-	0.0	-	100.0	0.00	3.00
xPbO·(100-x)TeO ₂ glasses							
x=10	77.8	1.2	-	21.0	-	0.06	3.79
x=20	50.0	12.0	-	38.0	-	0.24	3.62
x=30	14.3	32.7	-	53.0	-	0.38	3.47
x=33.3	0.0	41.0	-	59.0	-	0.41	3.41
x=35	0.0	-	34.0	-	66.0	0.34	3.34
x=40	0.0	-	0.0	-	100.0	0.00	3.00
x=45	0.0	-	0.0	-	100.0	0.00	3.00

Fig. 7. Plots of the fractions of several tellurite structural units; N_4^0 , N_4^- , N_4^* ($=N_4^-+N_4^{2-}$), N_3^- and N_3^* ($=N_3^-+N_3^{2-}$) vs. composition in the ZnO-TeO₂ glasses.

additional model to explain the rapid increase of TeO₃ tps over 33.3 mol% MO. As stated before, the $\text{O}_{3/2}\text{Te}-\text{O}^-$ and $\text{O}_{1/2}\text{Te}(=\text{O})-\text{O}^-$ units both exist in the glasses containing 33.3 mol% MO. The $\text{O}_{3/2}\text{Te}-\text{O}^-$ units are connected by sharing their corners to form a glass network and the $\text{O}_{1/2}\text{Te}(=\text{O})-\text{O}^-$ units are connected with the $\text{O}_{3/2}\text{Te}-\text{O}^-$ units by sharing their corners to form a terminal. When MO content exceeds 33.3 mol%, the $\text{O}_{3/2}\text{Te}-\text{O}^-$ and $\text{O}_{1/2}\text{Te}(=\text{O})-\text{O}^-$ units will change into the $\text{O}_{2/2}\text{Te}-\text{O}_2^{2-}$ (TeO_4 tpb with two NBO's) and the isolated TeO_3^{2-} (TeO_3 tp with three NBO's) units, respectively, by the further addition of MO. The $\text{O}_{1/2}\text{Te}(=\text{O})-\text{O}^-$ unit seems more stable than the $\text{O}_{2/2}\text{Te}-\text{O}_2^{2-}$ unit owing to the resonance between the $\text{Te}-\text{O}^-$ and $\text{Te}=\text{O}$ bonds and therefore the latter unit is considered to change into the former unit. Since $\text{O}_{2/2}\text{Te}-\text{O}_2^{2-}$ units are connected with the $\text{O}_{3/2}\text{Te}-\text{O}^-$ or $\text{O}_{1/2}\text{Te}(=\text{O})-\text{O}^-$ units by sharing their corners, they have three kinds of linkage modes;

- $\text{O}_{2/2}\text{Te}-\text{O}_2^{2-}$ unit connected with one $\text{O}_{3/2}\text{Te}-\text{O}^-$ and one $\text{O}_{1/2}\text{Te}(=\text{O})-\text{O}^-$ units.
- $\text{O}_{2/2}\text{Te}-\text{O}_2^{2-}$ unit connected with two $\text{O}_{1/2}\text{Te}(=\text{O})-\text{O}^-$ units.
- $\text{O}_{2/2}\text{Te}-\text{O}_2^{2-}$ unit connected with two $\text{O}_{3/2}\text{Te}-\text{O}^-$ units.

Figure 8(i) shows three possible mechanisms which explain the structural change of the $\text{O}_{2/2}\text{Te}-\text{O}_2^{2-}$ unit connected with one $\text{O}_{3/2}\text{Te}-\text{O}^-$ and one $\text{O}_{1/2}\text{Te}(=\text{O})-\text{O}^-$ units by sharing the corners; (1) the $\text{O}_{2/2}\text{Te}-\text{O}_2^{2-}$ unit with two NBO atoms at two equatorial sites, (2) the $\text{O}_{2/2}\text{Te}-\text{O}_2^{2-}$ unit with two NBO atoms at two axial sites and (3) the $\text{O}_{2/2}\text{Te}-\text{O}_2^{2-}$ unit with two NBO atoms at one equatorial and one axial sites. Since the $\text{O}_{1/2}\text{Te}(=\text{O})-\text{O}^-$ unit seems more stable than the $\text{O}_{3/2}\text{Te}-\text{O}^-$ unit due to the resonance between the $\text{Te}-\text{O}^-$ and $\text{Te}=\text{O}$ bonds, the structural change possibly occurs at $\text{O}_{3/2}\text{Te}-\text{O}^-$ and $\text{O}_{2/2}\text{Te}-\text{O}_2^{2-}$ units. Considering the rapid increase of TeO₃ tps over 33.3 mol%

(i) one $O_{3/2}\text{Te-O}^-$ and one $O_{1/2}\text{Te(=O)-O}^-$ units(1) Non-bridging oxygens O^- at two O_{eq} sites (2) Non-bridging oxygens O^- at two O_{ax} sites (3) Non-bridging oxygens O^- at one O_{eq} and one O_{ax} sites (ii) two $O_{1/2}\text{Te(=O)-O}^-$ units (iii) two $O_{3/2}\text{Te-O}^-$ units

Fig. 8. Mechanisms for the structural change of $O_{2/2}\text{Te-O}_2^{2-}$ (TeO_4 tbp) connected with (i) one $O_{3/2}\text{Te-O}^-$ (TeO_4 tbp) and one $O_{1/2}\text{Te(=O)-O}^-$ (TeO_3 tp), (ii) two $O_{1/2}\text{Te(=O)-O}^-$ and (iii) two $O_{3/2}\text{Te-O}^-$ units by sharing the corners.

MO, the structural change probably results in the formation of TeO_3 tps. A Te-O_{ax} bond in $O_{2/2}\text{Te-O}_2^{2-}$ unit may be cleaved by the electron transfers and succeeding a Te-O_{eq} bond in $O_{2/2}\text{Te-O}_2^{2-}$ unit receives an electron, forming a $O_{1/2}\text{Te(=O)-O}^-$ unit. As a result, the $\text{Te}_2\text{O}_5^{2-}$ unit is considered to be formed by sharing the corners of two TeO_3 tps. As seen in Fig. 8(i), in all the cases the $\text{Te}_2\text{O}_5^{2-}$ and $O_{2/2}\text{Te-O}_2^{2-}$ units are formed. The $\text{Te}_2\text{O}_5^{2-}$ unit is not connected with other TeO_n polyhedra but exists as an isolated unit.

The $O_{2/2}\text{Te-O}_2^{2-}$ unit, when connected with (ii) two $O_{1/2}\text{Te(=O)-O}^-$ or (iii) two $O_{3/2}\text{Te-O}^-$ units by sharing their corners, also undergoes structural changes similarly to the mechanism shown in Fig. 8(i). An example is shown in Figs. 8(ii) and (iii), showing that the structural units eventually formed are as follows;

(ii) two $O_{1/2}\text{Te(=O)-O}^-$ units $\rightarrow \text{Te}_2\text{O}_5^{2-}$ unit and isolated TeO_3^{2-} unit

(iii) two $O_{3/2}\text{Te-O}^-$ units $\rightarrow O_{2/2}\text{Te-O}_2^{2-}$ unit and $O_{3/2}\text{Te-O}^-$ unit connected with the corner of a $O_{1/2}\text{Te(=O)-O}^-$ unit

The $O_{2/2}\text{Te-O}_2^{2-}$ unit thus produced in (iii) immediately changes to the $O_{1/2}\text{Te(=O)-O}^-$ unit as described above. That is, in this respect the $O_{2/2}\text{Te-O}_2^{2-}$ unit is taken as an intermediate. The $O_{3/2}\text{Te-O}^-$ unit connected with the corner of a $O_{1/2}\text{Te(=O)-O}^-$ unit produced in (iii) will change into the $O_{2/2}\text{Te-O}_2^{2-}$ by the further addition of MO. Thus, the isolated $\text{Te}_2\text{O}_5^{2-}$ and TeO_3^{2-} units increase and the $O_{3/2}\text{Te-O}^-$ units decrease with increasing MO content over 33.3 mol% by three types of structural changes of the $O_{2/2}\text{Te-O}_2^{2-}$ units illustrated in Figs. 8(i)–(iii). As a result, the isolated $\text{Te}_2\text{O}_5^{2-}$ and TeO_3^{2-} units containing only TeO_3 tps exist in the glasses containing 40 mol% MO.

A model showing a modification of TeO_2 glass network by MO is summarized in Fig. 9. When MO is added to TeO_2 glass in the range of 0 to 33.3 mol% MO (see the left half of Fig. 9), $\text{TeO}_{4/2}$ units first change to $O_{3/2}\text{Te-O}^-$ units which then are transformed into $O_{1/2}\text{Te(=O)-O}^-$ units depending on the composition in the same manner as that for $M_2\text{O-TeO}_2$ ($M=\text{Li, Na, K, Rb and Cs}$) glasses described in a previous paper.¹⁵⁾

In the composition range of 33.3 to 40 mol% MO, the $O_{3/2}\text{Te-O}^-$ and $O_{1/2}\text{Te(=O)-O}^-$ units change to the $O_{2/2}\text{Te-O}_2^{2-}$ and isolated TeO_3^{2-} units, respectively, by the addition of MO (arrows (1) and (2) in Fig. 9). The $O_{2/2}\text{Te-O}_2^{2-}$ unit changes to the $O_{1/2}\text{Te(=O)-O}^-$ unit as described above (arrows (3) and (4) in Fig. 9). At the same time, $O_{2/2}\text{Te-O}_2^{2-}$ and isolated TeO_3^{2-} units are newly formed from the $O_{3/2}\text{Te-O}^-$ and $O_{1/2}\text{Te(=O)-O}^-$ units, respectively (broken arrows (5) and (6) in Fig. 9). As a result, the $O_{3/2}\text{Te-O}^-$ units decrease, and the $\text{Te}_2\text{O}_5^{2-}$ and isolated TeO_3^{2-} units increase with increasing MO content. Finally, the glasses with 40 mol% MO consist of the isolated $\text{Te}_2\text{O}_5^{2-}$ and TeO_3^{2-} units containing only TeO_3 tps.

In the range of 40 to 45 mol% MO, the glasses consist of the isolated $\text{Te}_2\text{O}_5^{2-}$ and TeO_3^{2-} units containing only TeO_3 tps. An oxide ion in MO further breaks the Te-O-Te linkage in the $\text{Te}_2\text{O}_5^{2-}$ (TeO_3 tp) unit with the increase of MO content, producing two isolated TeO_3^{2-} (TeO_3 tp) units (arrow (7) in Fig. 9). The fact that the values of $|\Delta\delta|$ for 40MO·60 TeO_2 ($M=\text{Zn and Pb}$) glasses are slightly larger than those for 45MO·55 TeO_2 glasses (Fig. 3) may suggest this structural change. Although it is obvious according to Fig. 3 that the TeO_3 tps in glasses of 40 and 45 mol% MO belong to the terminal TeO_3 type, the isolated TeO_3^{2-} units (isolated TeO_3 type) are also considered to be present in the glasses if one takes into account the structural change as shown in Fig. 9.

Therefore, we can say that the 40MO·60 TeO_2 and 45MO·55 TeO_2 glasses consist of the isolated $\text{Te}_2\text{O}_5^{2-}$ and TeO_3^{2-} units containing only TeO_3 tps. It is, however, impossible to form a glass network by TeO_3 tps only. We have recently obtained by X-ray diffraction the result that the average coordination number of Zn^{2+} ions in 40ZnO·60 TeO_2 glass is about 4.²⁶⁾ This strongly suggests that ZnO_4 polyhedra play an important role in forming glass network together with the isolated $\text{Te}_2\text{O}_5^{2-}$ and TeO_3^{2-} units in 40MO·60 TeO_2 and 45MO·55 TeO_2 glasses. The more detailed aspects of the network structure in the MO- TeO_2 ($M=\text{Zn and Ba}$) glass systems will be discussed based on our results obtained by the X-ray radial distribution function analysis.²⁶⁾

5. Conclusion

The ^{125}Te static NMR spectra have been measured for

Fig. 9. A model showing a modification of TeO_2 glass network by MO.

$\text{MO}-\text{TeO}_2$ ($\text{M}=\text{Mg}, \text{Zn}, \text{Sr}, \text{Ba}$ and Pb) glasses containing 0.3 mol% Fe_2O_3 . The following conclusions were obtained.

(1) N_4^0 which exhibits the fraction of $\text{TeO}_{4/2}$ (TeO_4 tbp without a non-bridging oxygen (NBO)) decreases, and N_4^- and N_3^- which denote the fractions of $\text{O}_{3/2}\text{Te}-\text{O}^-$ (TeO_4 tbp with an NBO atom) and $\text{O}_{1/2}\text{Te}(=\text{O})-\text{O}^-$ (TeO_3 tp with two NBO atoms), respectively, increase with increasing MO content up to 33.3 mol% MO.

(2) $\text{TeO}_{4/2}$ (TeO_4 tbp) unit first changes to $\text{O}_{3/2}\text{Te}-\text{O}^-$ (TeO_4 tbp) unit and then to $\text{O}_{1/2}\text{Te}(=\text{O})-\text{O}^-$ (terminal TeO_3 tp) unit by the addition of MO to TeO_2 glass up to 33.3 mol% MO, similarly to the case for $\text{M}_2\text{O}-\text{TeO}_2$ ($\text{M}=\text{Li}, \text{Na}, \text{K}, \text{Rb}$ and Cs) glasses.

(3) In the range of 33.3 to 40 mol% MO, the $\text{O}_{3/2}\text{Te}-\text{O}^-$ (TeO_4 tbp) unit decreases and the isolated $\text{Te}_2\text{O}_5^{2-}$ (consisting of two TeO_3 tps) and TeO_3^{2-} (TeO_3 tp with three NBO's) units increase with increasing MO content. Finally, the glasses containing 40 mol% MO consist of the isolated $\text{Te}_2\text{O}_5^{2-}$ and TeO_3^{2-} units containing TeO_3 tps only.

(4) In the composition range of 40 to 45 mol% MO, the glasses consist of the isolated $\text{Te}_2\text{O}_5^{2-}$ and TeO_3^{2-} units containing only TeO_3 tps. The $\text{Te}-\text{O}-\text{Te}$ linkage in the $\text{Te}_2\text{O}_5^{2-}$ (TeO_3 tp) unit will be broken on further addition of MO, producing two isolated TeO_3^{2-} (TeO_3 tp) units.

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