# Glass-Forming Region and Structure of Oxyhalide Tellurite Glasses Containing LiX(X=F and Br) and Li₂O

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## LiX(X=F, Br) 及び Li₂O を含むオキシハライドテルライトガラスのガラス化範囲及び構造

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*The glass-forming regions in the ternary systems LiX( X= F and Br)-Li₂O-TeO₂ were established in the present study. For X= Br the glass-forming region was found to be widened up to about 75 mol % LiBr on the LiBr rich side compared to the system containing LiCl which was studied previously, while the region for X=F was restricted to the Li₂O side, and no glass was formed in the binary LiF-TeO₂ system. These results were interpreted based on the glass structure which was mainly deduced from the IR measurement.*

## 1. Introduction

Crystalline TeO₂ has a unique structural unit, that is, an asymmetrical TeO₄ trigonal bipyramid, in which there are two different kinds of sites, two axial and three equatorial positions. One of the latter is occupied by a lone pair of electrons.

The authors[1],[2] have recently studied the glass-forming region, some physical properties and structure of glasses in the system LiCl-Li₂O-TeO₂. A very wide glass forming region from 15mol% up to about 60mol% LiCl was found to be present on the side rich in LiCl, while glass was formed in the very limited region from 15 to 33mol% Li₂O on the Li₂O rich side. It is generally known that alkali halides except fluorides do not modify the network structure of glasses consisting of typical network formers such as B₂O₃[3],[4] and P₂O₅,[4]-[6] that is, they just dissolve in the glass network without any significant interactions.

Contrary to these glasses, LiCl added to tellurite glasses was found to act as a network modifier just like Li₂O based on the IR spectroscopic study.[1],[2] Moreover, it was revealed that the introduced Cl atoms are situated preferentially in an equatorial position to form Te-Cl_eq bonds. This phenomenon was explained by the Bent rule that an atom with the small electronega-

tivity compared to the other, in this case oxygen atom, is subject to take an equatorial position rich in s-character. The observed large area of glass formation on addition of LiCl was then attributed to the inhibition of formation of a TeO₃ tetrahedron† with a lone pair of electrons which is supposed to promote devitrification, due to the formation of Te-Cl_eq bonds. [1],[2]

In the present study, the effects of LiF and LiBr on the glass-forming region and structure of tellurite glasses have been investigated. It should be noted that the F atom has an electronegativity larger than both O and Cl atoms, while that of Br atom is smaller than those.

## 2. Experimental

Reagent grade Li₂CO₃(Nakarai Chemicals Co. Ltd.), LiF(Wako Chemicals Co. Ltd.), LiBr (Morton Thiokol Inc., U.S.A.) and β-TeO₂ (Nakarai Chemicals and Mitsuwa Chemicals) were used as the starting materials for preparing glasses. 3g of well mixed glass batches were melted at 650°-800°C for 15-30min in a Pt crucible lined with gold by evaporation. The molten glasses were poured on the iron plate and immediately pressed by the cold iron. Some LiF-containing glasses which devitrified when this

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† Here after is called a TeO₃ trigonal pyramid from its apparent shape.

method was applied were obtained by immersing the bottom of Pt crucible containing 0.2-0.3 g of glass melt directly into a freezing mixture (ice and NaCl) kept at −10°C. Hereafter, this is called a rapid quenching method for convenience.

Glass formation was judged by X-ray diffraction. The IR spectra of glasses were taken by the KBr pellet method using a type 202 IR spectrometer (Japan Spectroscopic Co. Ltd.).

### 3.   Results

#### 3.1   Glass forming region

The glass-forming region of the ternary LiX(X =F and Br)-Li₂O-TeO₂ systems determined by the iron pressing method in the present study are shown in **Figs. 1** ( a ) and ( b ), respectively and summarized in Fig. 1 ( c ) together with the result for the ternary LiCl-Li₂O-TeO₂ system.[1] In the system containing LiF the region giving transparent glasses is restricted to the Li₂O side. As denoted in Fig. 1 ( a ) the glass became opaque

beyond the LiF content more than 10mol%. No glasses were obtained in the area on the LiF side, where $\alpha$-TeO₂ and LiF were precipitated out depending on the TeO₂ and LiF contents, respectively. Some of these samples, however, became glassy in very small amounts (0.2-0.3g) using the rapid quenching method.

On the other hand, the glass-forming region in the system LiBr-Li₂O-TeO₂ was widened up to about 75mol% on the halide side compared to the system LiCl-Li₂O-TeO₂, although the minimum content of LiBr necessitated for glass formation was almost the same as in the latter system.

#### 3.2   IR spectroscopy

All the tellurite glasses containing LiF for the present IR study were prepared by the rapid quenching method, while glasses without LiF were prepared by the iron pressing method and subjected to IR measurements.

**Figure 2** shows IR spectra for $x$LiF·$(1-x)$ TeO₂ glasses. A well-developed peak at about
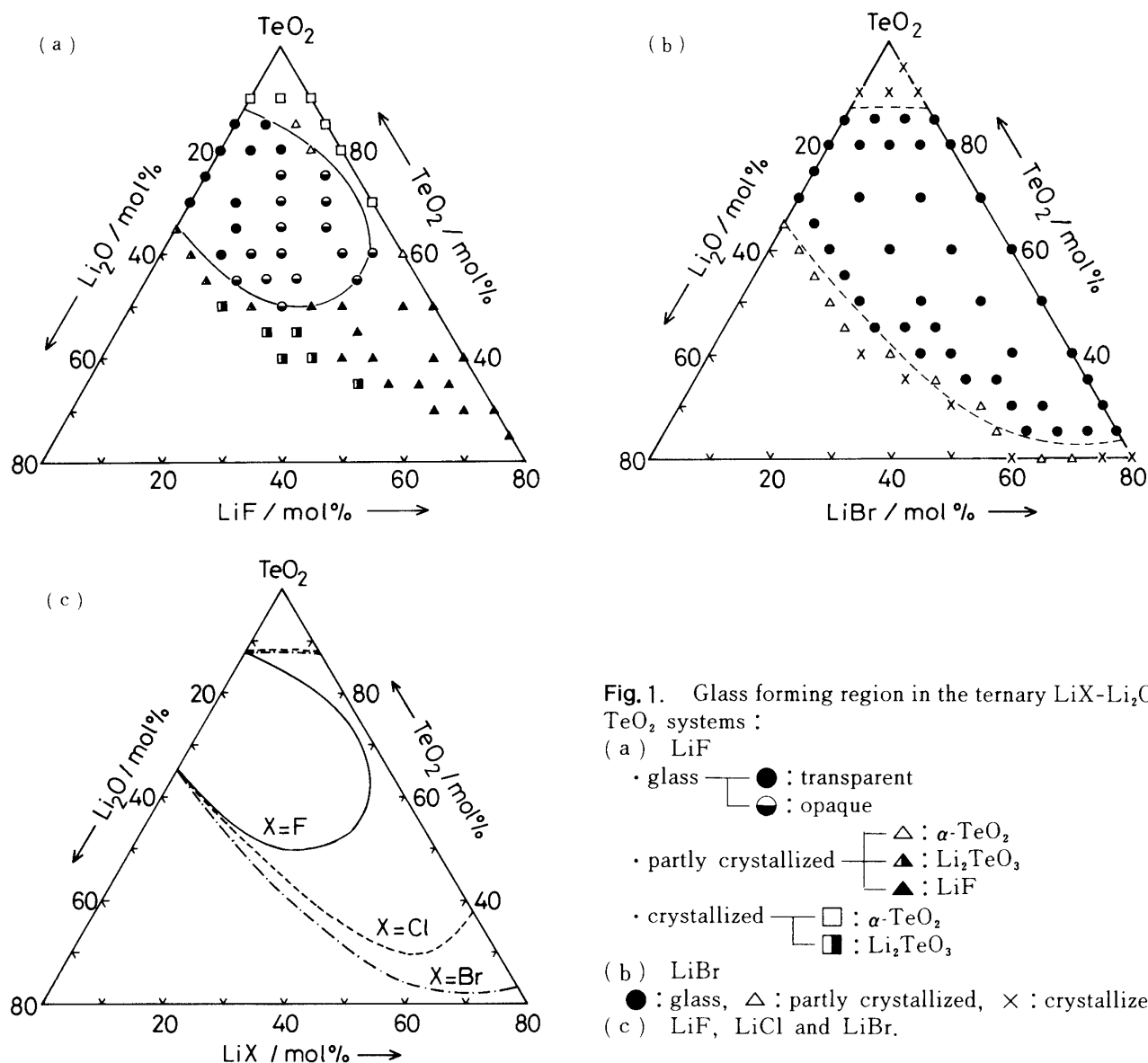


( a )



( b )



( c )

Fig. 1.   Glass forming region in the ternary LiX-Li₂O-TeO₂ systems :
( a )   LiF
   · glass ⌐● : transparent
       └◖ : opaque
   · partly crystallized ⌐△ : $\alpha$-TeO₂
       ├▲ : Li₂TeO₃
       └▲ : LiF
   · crystallized ⌐□ : $\alpha$-TeO₂
       └▣ : Li₂TeO₃
( b )   LiBr
   ● : glass,  △ : partly crystallized,  × : crystallized
( c )   LiF, LiCl and LiBr.
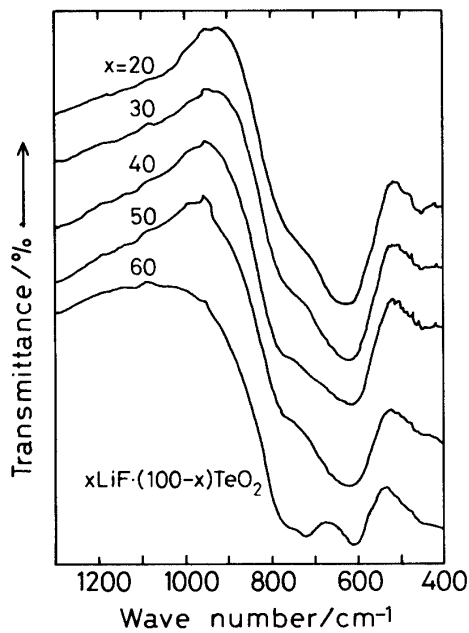
Fig. 2.   IR spectra of $x$LiF·$(100-x)$TeO$_2$ binary glasses.



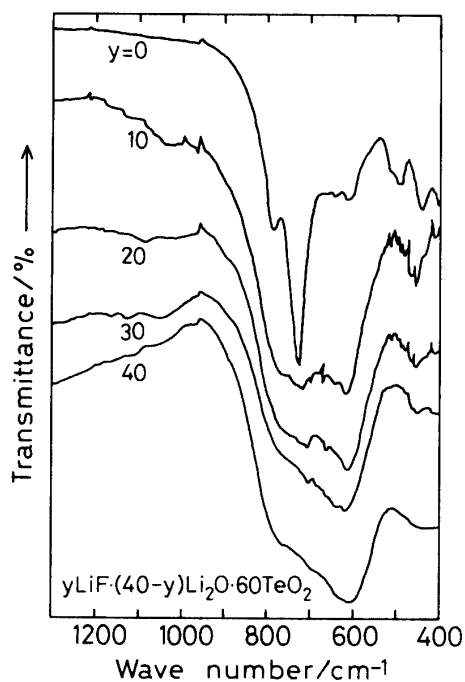Fig. 4.   IR spectra of $x$LiBr·$(100-x)$TeO$_2$ binary glasses.



Fig. 3.   IR spectra of $y$LiF·$(40-y)$Li$_2$O·60TeO$_2$ ternary glasses.
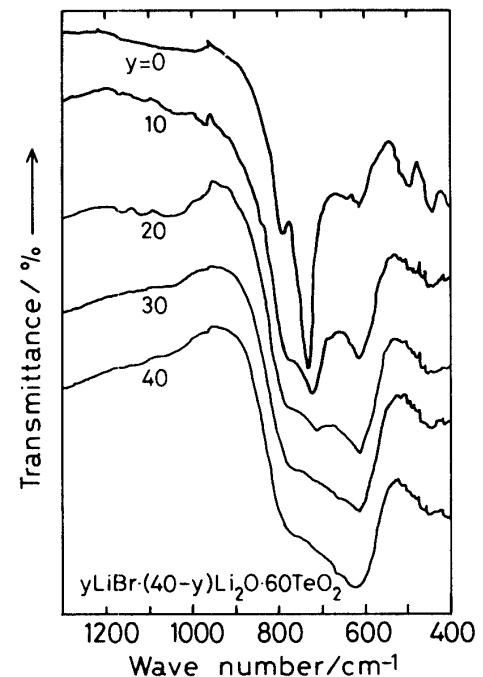


Fig. 5.   IR spectra of $y$LiBr·$(40-y)$Li$_2$O·60TeO$_2$ ternary glasses.

630cm$^{-1}$ and a shoulder at about 780cm$^{-1}$ are clearly seen for $x=20$. These are assigned to the symmetrical vibration of Te-O$_{ax}$ bond and asymmetric one of Te-O$_{eq}$ bond of the TeO$_4$ trigonal bipyramid, respectively, according to the previous studies.[1),2),7)-9)] With an increase in $x$, the former peak decreases in intensity and shifted towards lower wave numbers, and on the contrary the latter one becomes clearer. In the glass with $x$ =60, an additional peak appears around 720cm$^{-1}$, which will be discussed later.

Figure 3 shows IR spectra for $y$LiF·$(40-y)$

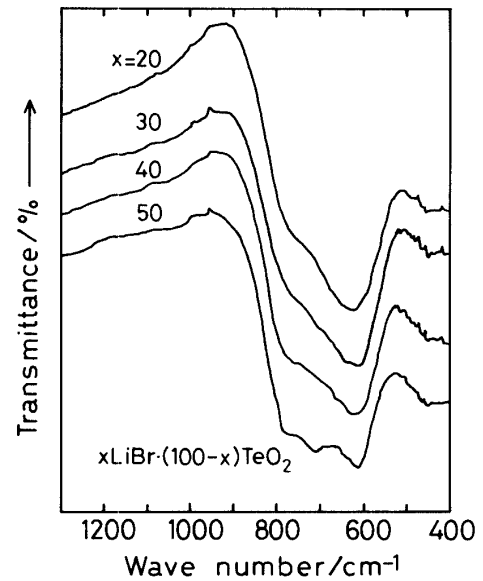Li$_2$O·60 TeO$_2$ glasses, among which, however, the sample with $y=0$ completely crystallized. The precipitated crystal is identified to be LiTeO$_3$ by X-ray diffraction.[1),2)] Therefore, a sharp peak observed at 720cm$^{-1}$ for $y=0$ is unequivocally attributed to the Te-O stretching vibration in TeO$_3$ trigonal pyramid. It is very interesting to note that this peak decreases drastically by substituting Li$_2$O by LiF, which was also observed in the system LiCl-Li$_2$O-TeO$_2$.[1)] In this sense, LiF plays the same role as LiCl in tellurite glasses.

In Figs. 4 and 5 IR spectra are shown for the

binary $x$LiBr·$(100-x)$TeO$_2$ and ternary $y$LiBr·$(40-y)$Li$_2$O·60 TeO$_2$ systems, respectively. The peak at 720cm$^{-1}$ due to TeO$_3$ trigonal bipyramid first appears at 50mol% LiBr in the binary $x$LiBr·$(100-x)$TeO$_2$ glasses. For the ternary $y$LiBr·$(40-y)$Li$_2$O·60 TeO$_2$, it also rapidly decreases by substituting Li$_2$O by LiBr and completely disappears on addition of 30mol% LiBr.

The peak position assigned to Te-O$_{ax}$ symmetric vibration $\nu^s$(TeO$_2$(ax)) is plotted as a function of Li$_2$O and LiX (X=F and Br) in **Fig. 6** together with the data for the LiCl and Li$_2$O containing systems.[2] As seen from Fig. 6, the peak is observed at 628 cm$^{-1}$, when the content of LiX is 20mol% LiX, independent of the kinds of halides and is shifted towards lower wave numbers with increasing content of LiX. The degree of a decrease in $\nu^s$(TeO$_2$(ax)) increases in the order : Br$<$Cl$\ll$F$<$O. This indicates that the bond strength of Te-O$_{ax}$ decreases in this order, assuming that the shift towards lower wave numbers results from the weakening of a bond.

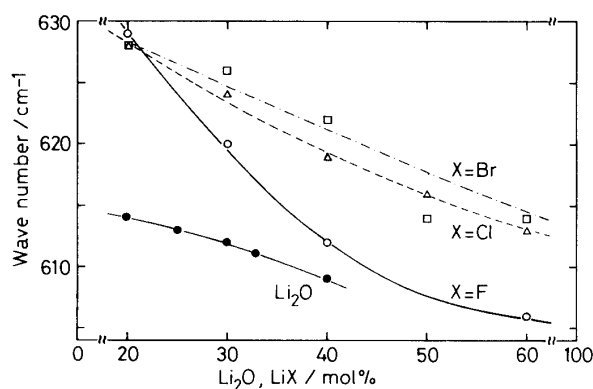**Figure 7** depicts the variations of $\nu^s$(TeO$_2$(ax)) with the fraction of LiX, [LiX]/[LiX] + [Li$_2$O],



**Fig. 6.** Variations of the wave number of IR peak due to Te-O$_{ax}$ bond with LiX content in the LiX-TeO$_2$ binary systems (open marks) and Li$_2$O content in the Li$_2$O-TeO$_2$ binary system (closed mark).
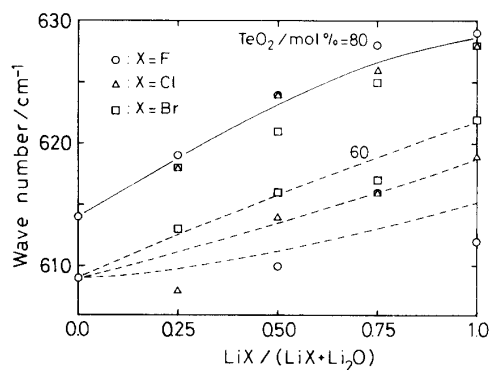


**Fig. 7.** Variations of the wave number of IR peak due to Te-O$_{ax}$ bond with LiX/(LiX+Li$_2$O) ratio in the LiX-Li$_2$O-TeO$_2$ ternary systems : solid line, $y$LiX·(20$-y$)Li$_2$O·80TeO$_2$; broken line, $y$LiX·(40$-y$)Li$_2$O·60TeO$_2$.

for the ternary $y$LiX · (20$-y$)Li$_2$O·80 TeO$_2$ and $y$LiX·(40$-y$)Li$_2$O·60 TeO$_2$(X=F, Cl and Br) glasses. When the total alkali content is small ( = 20mol%), $\nu^s$(TeO$_2$(ax)) increases with increasing fraction of LiX, and independent of the kinds of LiX. On the other hand, when it is as large as 40mol%, the degree of an increase in $\nu^s$(TeO$_2$ (ax)) increases in the order : F$<$Cl$<$Br.

## 4. Discussion

As seen from Fig. 1 ( c ), TeO$_2$ is hardly vitrified by itself, while it easily forms a glass on the addition of modifiers such as oxides and halides except LiF. The minimum amount of a modifier required for glass formation was found to be about 13-15mol% regardless of the kind of modifiers. This means that lithium halides except LiF added to TeO$_2$ in effect act as a modifier just like lithium oxide.[1],[2],[7],[10] This is also confirmed from the IR spectra (Fig. 6) showing that the $\nu^s$ (TeO$_2$(ax)) of tellurite glasses is shifted towards low wave numbers with increasing content of a modifier added to TeO$_2$.

In the previous study on the ternary LiCl-Li$_2$O-TeO$_2$ system,[2] the authors proposed a mechanism that LiCl incorporated into TeO$_2$ modifies the network structure as follows,

Te-$_{ax}$O$_{eq}$-Te+LiCl----→Te-O$_{ax}$-Li···Cl$_{eq}$-Te

where the Cl atom occupies an equatorial position of TeO$_4$ trigonal bipyramid(tbp). According to the Bent rule a substitutional group with lower electronegativity (EN) favors a position rich in s-character, while that with higher EN favors a position poor in s-character when two kinds of atoms with different EN's form bonds with the Te (IV) atom in a form of tbp. Since Cl atom has EN lower than O atom, the former preferentially takes an equatorial position consisting of the sp$^2$ hybrid orbital and the latter takes an axial one consisting of the p$_z$d$_z^2$ hybrid orbital. This mechanism was supported by the IR measurements.[2]

LiBr is considered to behave just like LiCl, because Br has EN less than Cl, and the glass-forming region and the variation of IR spectrum with composition in the system LiBr-Li$_2$O-TeO$_2$ are very similar to those in the system containing LiCl.[1],[2]

In the binary Li$_2$O-TeO$_2$ system, the glass formation is restricted by the formation of Li$_2$TeO$_3$ as elucidated in the previous studies.[1],[2],[7] The mechanism ( I ) of the formation of TeO$_3$ trigonal pyramid (tp) is illustrated in **Fig. 8**. When Li$_2$O added to TeO$_2$ breaks Te-$_{ax}$O$_{eq}$-Te bridging bond, the electron-donating ability of the non-bridging oxygen formed in an equatorial position may increase, leading to the
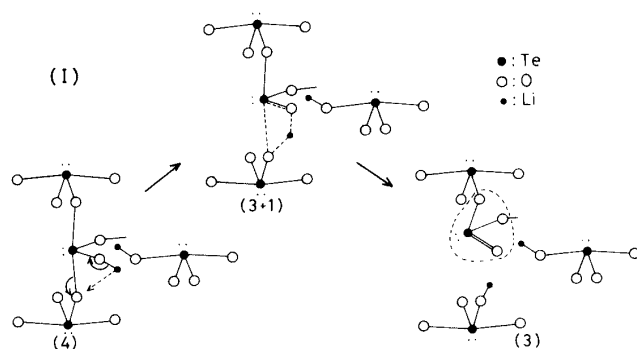
**Fig. 8.** Mechanism ( I ) of a change in the coordination number of $Te^{4+}$ from $4\rightarrow3+1\rightarrow3(Li_2O/TeO_2\leqq0.5)$ : broken and solid arrows stand for $Li^+$ ion and electron transfer, respectively.

strengthening of $Te-O_{eq}$ bond. As a result, either of the two $Te-O_{ax}$ bonds is weakened due to the excess negative charge around $Te$ atom and increases in the bond length (3+1 coordination state). Then, the oxygen in an axial position turns out to be compensated by $Li^+$ ion which is originally associated with the non-bridging oxygen in an equatorial position. Consequently, $TeO_3$ tp group surrounded by the dotted line is formed. In the $TeO_3$ tp the spatial occupation probability of a lone pair of electrons further increases compared to the $TeO_4$ tbp. This causes a mutual repulsion between the $TeO_3$ and $TeO_4$ and/or another $TeO_3$ in addition to a decrease in the number of bridging bonds, which severely restricts the spatial arrangement of structural units and deteriorates glass formation. In the case that every $TeO_4$ group has one non-bridging bond (mechanism II ), the formation of $TeO_3$ tp takes place more easily by further addition of $Li_2O$, as expected from **Fig. 9.**

The mechanisms of the introduction of LiX(X =Cl and Br) into $TeO_2$ are illustrated in **Fig. 10.** When $LiX/TeO_2\leqq0.5$ (mechanism III ), the average number of non-bridging bonds in the structural unit is less than unity. Since Cl or Br atom located at an equatorial position has less electron-donating ability than oxygen, the weakening of $Te-O_{ax}$ bond occurs to a much less extent com-
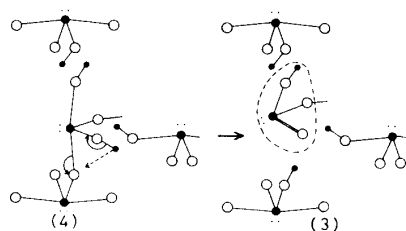


**Fig. 9.** Mechanism ( II ) of a change in the coordination number of $Te^{4+}$ from $4\rightarrow3(0.5<Li_2O/TeO_2\leqq1)$ : broken and solid arrows stand for $Li^+$ ion and electron transfer, respectively.



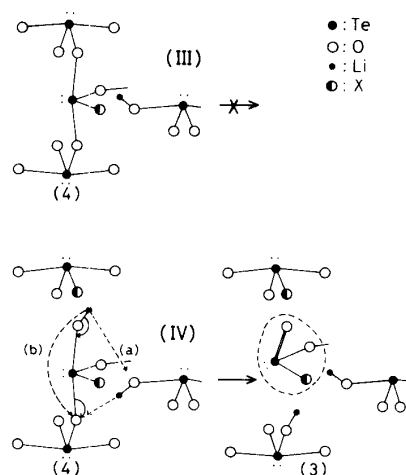**Fig. 10.** Mechanisms ( III and IV) of a change in the coordination number of $Te^{4+}$ from $4\rightarrow3($ III ;LiX/$TeO_2\leqq0.5$, IV ;$0.5<LiX/TeO_2\leqq1$) : broken and solid arrows stand for $Li^+$ ion and electron transfer, respectively.

pared to the $Li_2O$ addition, not resulting in the formation of $TeO_3$ tp. When the ratio $LiX/TeO_2$ exceeds 0.5 (mechanism IV ), every structural unit has at least one non-bridging bond. Therefore, further addition of LiX may lead to the formation of $TeO_3$ tp. In this case, two routes, ( a ) and ( b ), are possible for the $Li^+$ ion transfer, where route ( b ) is rather plausible compared with the route ( a ), because the route ( a ) involves two successive steps. Anyhow, the formation of $TeO_3$ tp via mechanism IV is expected hardly to occur unlike the mechanism II , which is evidenced by the results of IR measurements.

On the other hand, the glass-forming region in the $LiF-Li_2O-TeO_2$ system is very limited compared with the LiCl- and LiBr-containing systems. Also, no glass is formed by the slow cooling method in the binary $LiF-TeO_2$ system, although glass is formed when the rapid quenching method was employed. This difficulty in glass formation may be related to the highest EN among all the elements. That is, F atoms added to $TeO_2$ possibly take an axial position following the Bent rule,

$$Te-_{ax}O_{eq}-Te+LiF\text{----}Te-F_{ax}\cdots Li-O_{eq}-Te.$$
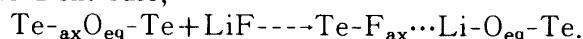
The absorption peaks due to the $Te-F$ stretching vibration in $TeF_4$ crystal[9] occur at 572, 587, 682 and 695$cm^{-1}$. These peaks are unfortunately superposed on the very strong $Te-O_{ax}$ vibration peak and can not be distinguished in the IR spectrum. However, the shift of $\nu^s(TeO_2(ax))$ towards low wave numbers with increasing content of LiF as observed in Fig. 6 might serve as an evidence for the formation of $Te-F$ bond in the glass.

As seen in Fig. 3, the addition of LiF also

suppresses the formation of $TeO_3$ tp, although the glass forming region is restricted to a considerable extent. Therefore, the difficulty in glass formation on the LiF rich side can not be attributed to the formation of $TeO_3$ tp. Taking into account the facts that $\alpha$-$TeO_2$ crystals are precipitated out of the glasses with the content more than 50mol% $TeO_2$ on the LiF rich side and glasses containing more than 10mol% LiF are opaque, it is very likely that the tellurite glasses containing LiF have a marked tendency towards phase separation.

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