

COMPOSITIONAL DEPENDENCE OF REFRACTIVE INDEX IN TELLURITE GLASSES

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ABSTRACT

The influence of molar volume, polarizability of oxide ion, and O1s binding energy on the refractive index was investigated for the various binary tellurite glasses. In the combination with P_2O_5 , B_2O_3 , and Al_2O_3 , the refractive index was linearly correlated to molar volume, polarizability, and O1s binding energy. In alkali tellurite systems, the refractive index was weakly related to molar volume and polarizability. A linear correlation was found between the refractive index and O1s binding energy, but the correlation was opposite to the case for P_2O_5 , B_2O_3 , and Al_2O_3 . It was commonly confirmed in the tellurite glasses that the refractive index was dominantly dependent on the optical band gap. Ab-initio molecular orbital calculations revealed that the LUMO levels were characterized by the structural units in tellurite glasses. In TeO_4 tbp unit, the LUMO levels were formed by the anti-bonding overlaps of Te5p and O2p orbitals in the axial Te-O bonds, resulting in the narrow HOMO-LUMO gap. In TeO_{3+1} unit, larger contribution of Te5p orbital was confirmed in the LUMO levels, resulting in the wider gap. It was finally concluded that the structural change from TeO_4 tbp to TeO_3 tp via TeO_{3+1} units widened the energy gap, resulting in the decrease in the refractive index.

INTRODUCTION

Refractive index is one of the most important properties in optical glasses. Therefore, a large number of researches have been done as for the relation between refractive index and glass composition. Among the theoretical expressions, the Lorentz-Lorenz equation^{1,2} relates the polarizability α to the refractive index n as follows.

$$\frac{n^2 - 1}{n^2 + 2} V_m = \frac{4}{3} \pi N \alpha_m = \frac{4}{3} \pi N \sum_i x_i \alpha_i \quad (1)$$

where V_m is the molar volume, N is Avogadro's number, α_m is the molar polarizability, x_i is the ionic ratio, α_i is the polarizability of the constituent i in a material. In Eq. 1, $(n^2 - 1)/(n^2 + 2)$ is almost proportional to n at $n < 2.2$, and hence larger n is achieved in the materials with smaller V_m and larger α_i . In the conventional oxide glasses, such as silicate and borate glasses, oxide ion possesses much larger polarizability than the other glass constituents.³ In such glasses, therefore, refractive index is largely dependent on the polarizability of oxide ion, $\alpha_{O^{2-}} = 1.3 - 1.8 \text{ \AA}^3$.⁴

However, the polarizability of tellurium ion ($\alpha_{\text{Te}^{4+}} = 1.595 \text{ \AA}^3$) is larger than the other cations,³ and is almost comparable to $\alpha_{\text{O}^{2-}}$. Therefore, the contribution of Te ions is not negligible in investigating the compositional dependence of refractive index in tellurite glasses.

On the other hand, basicity of oxide glass is also associated with the polarizability of oxide ion. In general, basicity of oxide glass is interpreted as the ability in electron donation of oxide ions. Electrons excessively localized on oxide ions are donated to the neighbors. Oxide ions with excess electrons are easily polarized, and hence they should have higher polarizability. Moreover, it has been proposed that oxygen 1s binding energy determined by X-ray photoelectron spectroscopy (XPS) is a measure of the basicity of oxide glass.⁵ It is therefore interesting to examine the correlation among O1s binding energy, polarizability, and refractive index of tellurite glasses.

In the tellurite glasses the network consists of TeO_4 trigonal bipyramid (tbp), TeO_{3+1} polyhedra, and TeO_3 trigonal pyramids (tp), and the structural change of $\text{TeO}_4 \rightarrow \text{TeO}_{3+1} \rightarrow \text{TeO}_3$ takes place along with the addition of modifier oxides. According to the conventional notation, TeO_4 tbp unit is formed by Te sp^2 hybrid orbitals in the equatorial positions and Te pd hybrid in the axial sites. Lone pair electrons occupy an equatorial site, and the unit is hence asymmetric, resulting in the different Te-O bonding distances between the axial and equatorial directions. TeO_3 tp unit is formed by Te sp^3 hybrid orbitals, and one of them is occupied by a lone pair of electrons. TeO_{3+1} unit is the structural intermediate. These structural units coexist in tellurite glasses, bringing about anomalous behaviors in various properties.⁶

In this study, refractive index was measured for some binary tellurite glasses, and the compositional dependence of refractive index was discussed based on the electronic states determined from XPS measurements. Ab-initio molecular orbital calculations were also performed using the Gaussian03 program⁷ to obtain theoretical interpretations for the compositional dependence.

EXPERIMENTAL PROCEDURES

Sample preparation and Measurements

The compositions of the glasses investigated were $x\text{P}_2\text{O}_5 \cdot (100-x)\text{TeO}_2$ ($x=10-30$ mol%), $x\text{B}_2\text{O}_3 \cdot (100-x)\text{TeO}_2$ ($x=15-20$ mol%), $x\text{Al}_2\text{O}_3 \cdot (100-x)\text{TeO}_2$ ($x=5-15$ mol%), $x\text{Li}_2\text{O} \cdot (100-x)\text{TeO}_2$ ($x=15-28$ mol%), $x\text{Na}_2\text{O} \cdot (100-x)\text{TeO}_2$ ($x=10-25$ mol%), $x\text{K}_2\text{O} \cdot (100-x)\text{TeO}_2$ ($x=7.5-22.5$ mol%), $x\text{Rb}_2\text{O} \cdot (100-x)\text{TeO}_2$ ($x=10-20$ mol%), $x\text{Cs}_2\text{O} \cdot (100-x)\text{TeO}_2$ ($x=7.5-12.5$ mol%). 10 g batch of well mixed oxides was melted in an Au or Pt crucible at 750 - 800 °C. After annealing at T_g-20 °C (T_g : glass transition temperature) for an hour, both glass surfaces were optically polished with kerosene.

The refractive index at the wavelength of 632.8 nm was measured by a prism coupler method (Metricon, Model 2010). O1s binding energy was measured by X-ray photoelectron spectrometry (Fisons Instruments, S-Probe ESCA SSX-100S). Density was measured by the Archimedes method using kerosene as an immersion liquid. Optical absorption spectrum was measured in the wavelength range from 190 to 2500 nm (JASCO, V-570).

Computational methods

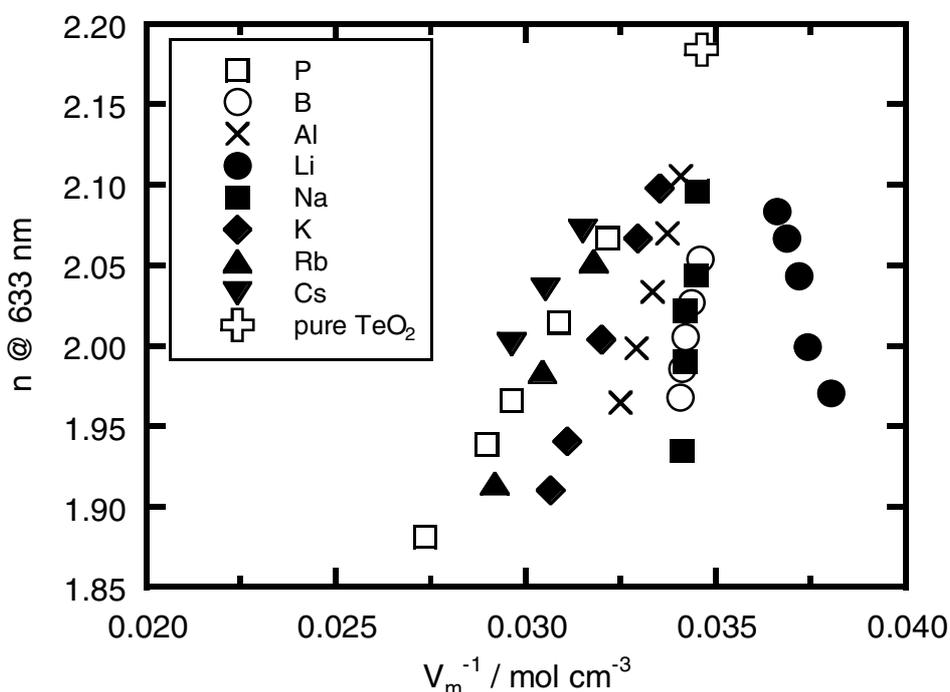
Two cluster models of $\text{Te}_5\text{O}_{16}\text{H}_{12}$ and $\text{Li}_4\text{Te}_3\text{O}_9\text{H}_2$ containing TeO_4 tbp and TeO_{3+1} units, respectively, were constructed from the structures of $\alpha\text{-TeO}_2$ and $\alpha\text{-Li}_2\text{Te}_2\text{O}_5$ crystals,^{8,9} where the dangling bonds were terminated by hydrogen atoms. Geometrical optimization and molecular orbital calculations were performed in the ab initio restricted B3LYP combination of functionals,

using the Gaussian 03 program.⁷ Density functional theory was used to calculate the atomic and electronic structures. O, Li and H atoms were described with the 6-31G* basis set, while Te was described with the CRENL ECP and basis set.^{10, 11, 12}

RESULTS AND DISCUSSION

Polarizability of oxide ion

As mentioned, it is expected from the Lorentz-Lorenz equation (Eq. 1) that the refractive index n is inversely related to the molar volume V_m^{-1} and is proportionally related to the polarizability α . Then, the relation between n and V_m^{-1} was examined. As shown in Fig. 1, when the network forming and intermediate oxides, such as P_2O_5 , B_2O_3 and Al_2O_3 , are added to TeO_2 , both n and V_m^{-1} decrease, that is, n is proportional to V_m^{-1} . In case of the addition of the network modifying alkali oxides, the proportional relations were also observed, except for Li_2O addition.



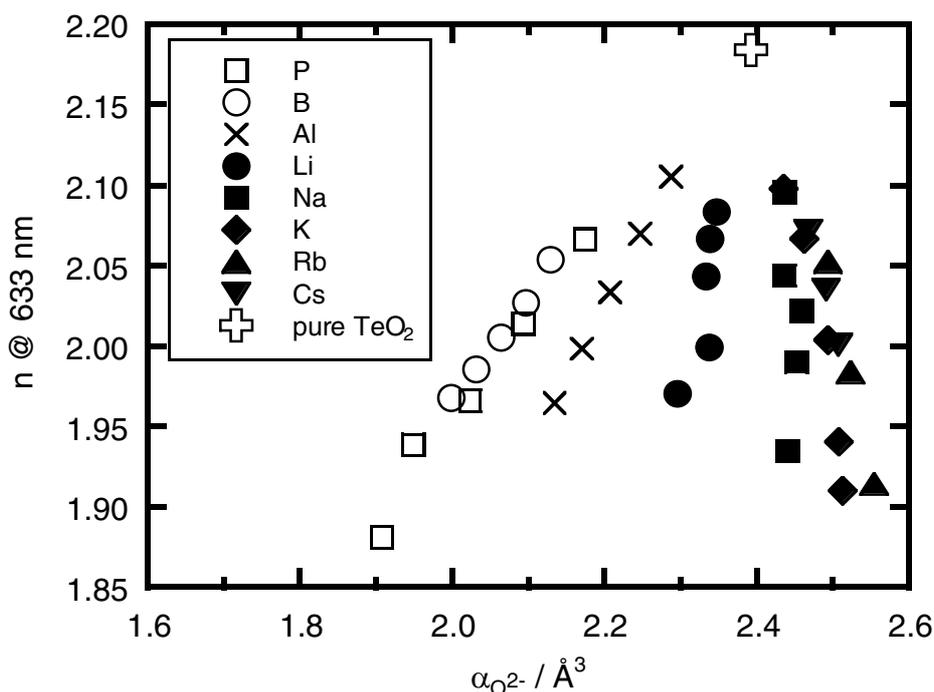


Fig. 2. Relation between refractive index n and polarizability of oxide ion $\alpha_{O^{2-}}$. The refractive index of pure TeO_2 was referred from S. Kim.¹³

It is consequently concluded that the refractive index n is proportional to $\alpha_{O^{2-}}$ and V_m^{-1} in the combination with the network forming and intermediate oxides. In the case of the network modifying oxides, however, no predominant factor is seen in the compositional dependence of n .

O1s binding energy

Fig. 3 shows the relation between O1s binding energy and refractive index. O1s binding energy is a measure of basicity of oxide ion; with increasing the electron density in the valence region, that is, with increasing the basicity, the binding energies of core orbitals such as O1s shift to lower energy side. When the network forming and intermediate oxides are added to TeO_2 , O1s binding energy increases, and in the case of alkali addition, the binding energy decreases. It is expected that the electron density in the valence region is related to the polarizability.

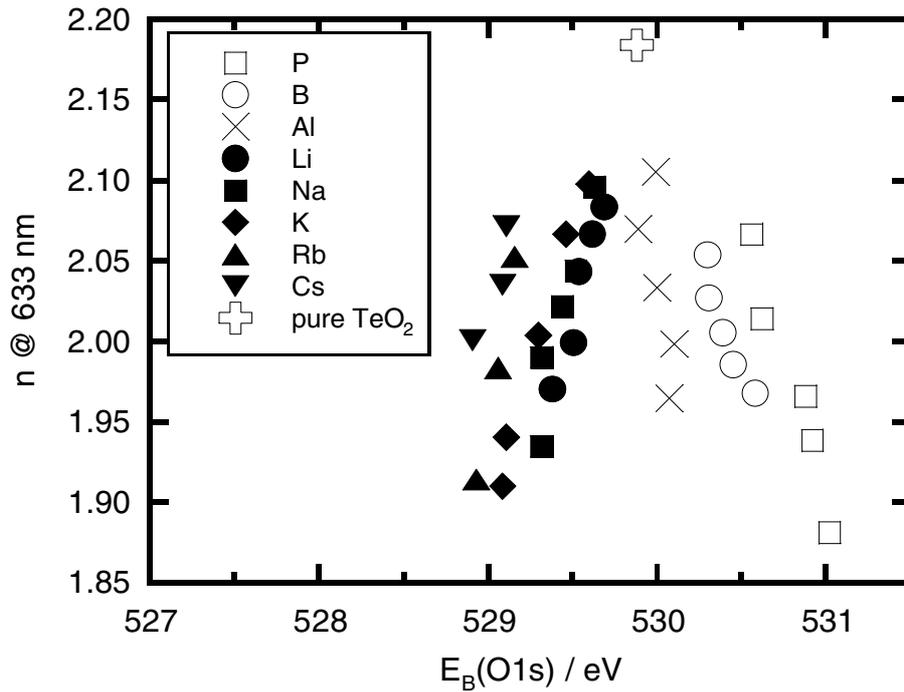


Fig. 3. Relation between refractive index n and O1s binding energy $E_B(\text{O1s})$. The refractive index of pure TeO_2 was referred from S. Kim.¹³

Comparing Fig. 3 with Fig. 2, when O1s binding energy decreases, the polarizability of oxide ion increases, being confirmed the rough correlation between O1s binding energy and polarizability. Between the binding energy and refractive index, however, no linear correlation was observed. As for K, Rb, and Cs tellurite glasses, the polarizability of oxide ion increases but the refractive index decreases along with the alkali addition. It is quite anomalous phenomenon.

Optical band gap E_g

Dimitrov et al.¹⁴ showed the relationship between the refractive index n and the energy band gap E_g .

$$\frac{n^2 - 1}{n^2 + 2} = 1 - \sqrt{E_g/20} \quad (2)$$

Then, the relation between the refractive index n and the optical band gap E_g was examined. As shown in Fig. 4, a rough correlation is observed between n and E_g , that is, the refractive index decreases with increasing the optical band gap. In the conventional binary glasses, such as alkali silicate and alkali borate systems, the optical band gap decreases along with the alkali addition. In the alkali tellurite glasses, however, the gap increases oppositely due to the alkali addition. It is noted that the chemical shifts of O1s binding energy due to the alkali addition are the same between tellurite and the other conventional oxide glasses. It is therefore expected that the tellurite glasses have a quite different electronic structure from the conventional glasses.

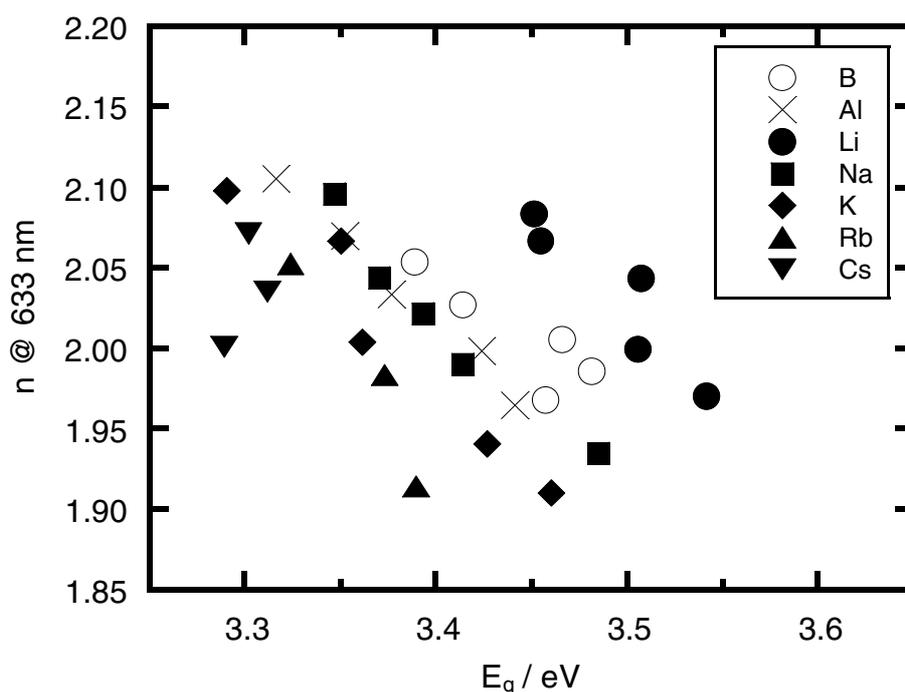


Fig. 4. Relation between refractive index n and optical band gap E_g .

Electronic structure of tellurite system

The calculated core electron O1s binding energies and band gaps corresponded to the experiment values well.

Table 1 shows the energies of HOMO, LUMO, and the energy gap between LUMO and HOMO calculated from $\text{Te}_5\text{O}_{16}\text{H}_{12}$ and $\text{Li}_4\text{Te}_3\text{O}_9\text{H}_2$ clusters, where only the results for TeO_4 and TeO_{3+1} units present in the clusters are evaluated. Between the clusters, the difference in HOMO is quite small (0.03 eV), but the difference in LUMO is obvious (0.46 eV); the energy gap increases due to the larger energy shift in the LUMO levels, which is consistent with the experimental results.

According to the molecular orbital calculations, in TeO_4 tbp unit in $\text{Te}_5\text{O}_{16}\text{H}_{12}$ cluster, the HOMO levels consists of the lone pair electrons in O2p and Te5s orbitals, and the LUMO levels are mainly composed of O2p and Te5p orbitals, and a small amount of Te5s orbitals are also seen. In TeO_{3+1} unit in $\text{Li}_4\text{Te}_3\text{O}_9\text{H}_2$ cluster, the HOMO levels also consists of the lone pair electrons in O2p and Te5s as well as TeO_4 unit, but the contribution of atomic orbitals in the LUMO levels are different; Te5p becomes larger, and Te5s becomes smaller. According to the conventional notation, the hybrid orbitals of Te changes from sp^2+pd in TeO_4 tbp unit to sp^3 in TeO_3 tp unit due to the decrease in the coordination number of Te. The LUMO levels in TeO_4 unit are assigned to anti-bonding orbitals of Te5p + O2p overlap in the weak Te-O bonds. Along with the structural change, $\text{TeO}_4 \rightarrow \text{TeO}_{3+1} \rightarrow \text{TeO}_3$, the contribution of the weak pd hybrid orbitals, of which energy gap between bonding and anti-bonding orbitals is narrow, disappears gradually from the LUMO levels, resulting in wider gap and smaller refractive index.

Table 1. Calculated energies of HOMO, LUMO, and the energy gap (LUMO-HOMO).

Cluster / tellurite unit	HOMO (eV)	LUMO (eV)	Gap (eV)
Te ₅ O ₁₆ H ₁₂ / TeO ₄	-6.82	-1.90	4.92
Li ₄ Te ₃ O ₉ H ₂ / TeO ₃₊₁	-6.79	-1.44	5.35

CONCLUSION

The compositional dependence on refractive index was discussed in the binary tellurite glasses. In the case of combination with the network forming oxides (P₂O₅, B₂O₃) and the intermediate oxide (Al₂O₃), the refractive index n was almost proportional to the polarizability of oxide ion $\alpha_{O^{2-}}$ and the reciprocal of molar volume V_m^{-1} . In the case of the network modifying alkali oxides (Li₂O, Na₂O, K₂O, Rb₂O, Cs₂O), the refractive index were weakly dependent on $\alpha_{O^{2-}}$ and V_m^{-1} . A correlation was confirmed between $\alpha_{O^{2-}}$ and O1s binding energy $E_B(O1s)$, and $E_B(O1s)$ was not the dominant factor on n . It was finally confirmed that n was mainly dependent on the optical band gap E_g . With increasing alkali content, E_g increased in tellurite glasses, even though E_g decreased in the conventional glasses such as silicate and borate. The compositional dependence on E_g was successfully reproduced by the theoretical molecular orbital calculations for the clusters containing TeO₄ tbp and TeO₃₊₁ units. The structural difference was clearly reflected on the LUMO levels. In TeO₄ tbp unit, the LUMO levels were formed by the anti-bonding overlaps of Te5p and O2p orbitals in the axial Te-O bonds, resulting in the narrow HOMO-LUMO gap. Along with the structural change from TeO₄ tbp to TeO₃ tp via TeO₃₊₁ units, the contribution of more stable sp³ hybrid orbitals increased to widen the energy gap, resulting in the decrease in the refractive index.

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