Bonding nature in tellurite glasses

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We show that the variation of the structural unit in tellurite glasses is due to the charge transfer from modifier atoms to TeO_6 octahedra with use of first-principles molecular-orbital calculations. Mulliken overlap populations indicate that the oxygen coordination number of a Te atom reduces as the charge transfer progresses. This is consistent with the trend found in metal tellurite structures. Orbital-overlap population analysis reveals that the transferred electrons to the Te-O antibonding orbital cause breaking in the Te-O bonds and lead to reducing the coordination number of the Te atom. The bond ionicity and charge states of a Te atom and an O atom in α-TeO_2 are also presented.

INTRODUCTION

Tellurite glasses are of technical interest because of their high refractive indices, dielectric constants, good infrared transmissions, and high thermal-expansion coefficients.[1,2] While intense studies have been made for applications, fundamental questions still remain unanswered because of the structural ambiguity of the disordered materials. Since the interesting physical properties of disordered materials which lack the structural periodicy are frequently associated with short-range structural effects, the electronic structure and the character of chemical bonding in the structural units are significant questions.

In the normal glass system, modifier atoms are usually added to enhance glass formation, as a result of network breaking (breaking the chains of structural units) and increment of entropy (decreasing liquidus temperature). In tellurite glasses, however, the modifier atoms play one more important role: causing the variation of the structural unit itself. Structural units of tellurite glasses are reported to be TeO_x ($x = 3-6$) polyhedra.[3-8] It is in contrast with the structural unit of silicate glasses (an SiO_4 tetrahedron) which is not affected by modifier atoms. Some researchers have discussed the mechanism of this variation of the structural unit based on the information from diffraction methods and Raman spectroscopies. Their proposed mechanisms, however, have never taken into account the electronic structure.[8,9]

In order to elucidate the variation of the structural unit induced by the modifier atoms, we have investigated the electronic structure and the nature of chemical bonding in tellurite glasses with use of first-principles calculations.

METHOD OF CALCULATION

In the random network model, glass has a structural unit similar to the short-range order (SRO) in the analogous crystalline compound. Examples of SRO for the crystalline compounds are TeO_{4+2} (α-TeO_2), TeO_4 ($Zn_2Te_3O_8$, $CuTeO_3$), TeO_{3+1} ($BaTeO_3$), and TeO_3 (Li_2TeO_3).[3-8,10] On the analogy of these structures, the structural units of the tellurite glasses should be TeO_x ($x = 3-6$) polyhedra as derived forms of the TeO_6 distorted octahedron found in α-TeO_2. In tellurite glasses, since the electronegativity of M (metal modifier atoms such as Zn, Cu, Ba, Li, etc.) is smaller than those of Te and O (0.8–1.9, 2.1, and 3.5 for M, Te, and O on the Pauling scale, respectively[11]), the charge should transfer from M to TeO_6.

In general, a bond in a compound is partly covalent and partly ionic. In α-TeO_2, the charge states of a Te atom and an O atom are $Te^{4\delta+}$ and $O^{2\delta-}$ using the parameter δ ($0 \le \delta \le 1$) which represents the fractional ionic character in a Te-O bond. Thus, the initial charge state for the TeO_6 octahedron should be $(TeO_6)^{8\delta-}$. The parameter δ cannot be easily determined. Despite considerable research effort, ionicity even of simple alkaline-earth oxides is still controversial.[12] The ionicity δ in α-TeO_2 will be estimated later in the next section. In tellurite glasses, the net charge n for $(TeO_6)^{n-}$ cluster can be defined by $8\delta + n_{CT}$, where n_{CT} is the amount of the charge transferred from M to TeO_6. We reveal how the parameter n affect the electronic structure and Te-O bonding in the TeO_6 octahedron.

The electronic structure of $(TeO_6)^{n-}$ clusters are calculated with use of the self-consistent-charge discrete variational $X\alpha$ (SCC-DV-$X\alpha$) method.[13] An approach by using the molecular-orbital theory is suitable for analyzing the electronic structure of the structural unit which is easily cluster modeled. The SCC-DV-$X\alpha$ method has been successfully applied to the interpretation of x-ray-photoemission spectra for crystalline paratellurite.[10] In this method, the Hartree-Fock-Slater (HFS) equation for a cluster is self-consistently solved with use of a localized exchange potential ($X\alpha$ potential). The exchange parameter α was taken to be 0.7 as usual. Numerical tellurium $1s-5p$ and oxygen $1s-2p$ atomic orbitals, obtained as solutions of the atomic HFS equations, were used for basis sets.

In order to shed light on what occurs in the chemical bonding of the TeO_6 cluster due to the charge transfer, we assumed the same structure as the TeO_6 octahedron found in α-TeO_2. The $(TeO_6)^{n-}$ cluster is made of one central Te atom and three kinds of octahedral O atoms;
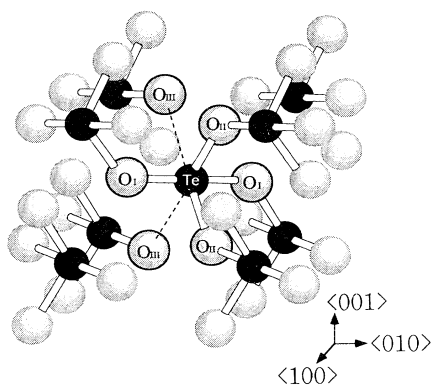
FIG. 1. Schematic illustration of a TeO_6 cluster in paratellurite. The TeO_6 cluster is made of one central Te atom and six octahedral O atoms which can be divided into following three types: The first is axial type (O_I) found at a distance of 3.84 a.u. from the central Te atom; The second is equatorial type (O_{II}) at a distance of 3.84 a.u. The third is also equatorial type (O_{III}) found at a distance of 5.05 a.u. (Ref. 18).

axial type O_I, equatorial types O_{II} and O_{III} as shown in Fig. 1. The calculations on this cluster were performed with C_2 point-group symmetry.

RESULTS AND DISCUSSION

Results for Mulliken overlap populations, which scale bond order in simple meaning, versus net charge n for the $(TeO_6)^{n-}$ clusters are shown in Fig. 2.[14] While the overlap population of Te-O_{II} bond increases slightly as n increases, those of bonds Te-O_{III} and Te-O_I decrease drastically to negative values at $n=7$ and 8, respectively. As no bonding is expected in the regions of the negative overlap population, the bonds Te-O_{III} and Te-O_I should break, and consequently the coordination number of the Te atom reduces from 6 via 4 to 2 as n increases from 6 to 8. While odd coordination numbers do not appear essentially in our present calculations because of C_2 point-group symmetry, the trend that the bonds Te-O_{III} break first and secondly the Te-O_I break as the coordination number reduces, is consistent with the experiments. For example, the structural unit TeO_6 (more strictly, TeO_{4+2})
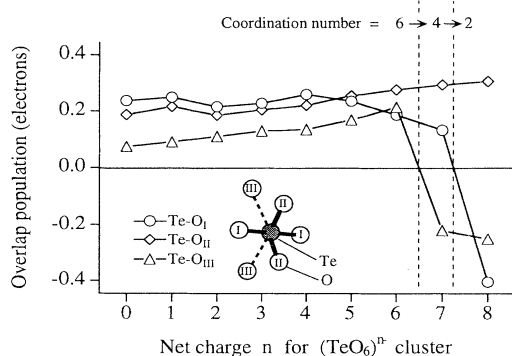
in α-TeO_2 changes to TeO_4 in $Zn_2Te_3O_8$ and $CuTeO_3$ due to the modifier atoms with bond breaking of Te-O_{III}.[3-7,10] The reduction in the coordination number from 4 to 2 is consistent with Raman investigation of alkali tellurite glasses which indicated that the coordination state of tellurium atom changes from TeO_4 through TeO_{3+1} to TeO_3 with the bond breaking between Te and axial O, which corresponds to O_I in present calculation, as increasing alkali oxide.[8] Actual tellurite glasses are made up of not one structural unit but the mixture of TeO_4, TeO_{3+1}, and/or TeO_3.[8,9] This is due to local inhomogenuity: The electrons do not transfer from the modifier atoms to all the structural units, and consequently two or more states of the structural unit exist in the actual tellurite glasses.

In order to understand the bond breaking, orbital overlap populations (OOP's) for each Te-O bond in the neutral $(TeO_6)^{0-}$ cluster are shown in Fig. 3 with the energy-level structure. Positive (negative) OOP means bonding (antibonding) feature of that orbital. An electron in bonding (antibonding) state contributes to making (breaking) the bonds, hence the integral of the OOP below the highest occupied molecular orbital (HOMO) gives bond order, namely, the Mulliken overlap population.[15] In Fig. 3, there are five well-separated bands in the occupied state region. The bands A and B are mainly composed of O $2s$ with small amount of Te $5s$ and $5p$ bonding characters, respectively. The band C is made up of the Te $5s$ orbital admixed with O $2s$ antibonding states. The band D is bonding orbitals between Te $5p$ and O $2p$ containing a small amount of the O $2s$ antibonding character. The band E originates from the O $2p$ states.[10] In

FIG. 2. Mulliken overlap populations for bonds Te-O_I, Te-O_{II}, and Te-O_{III} versus net charge n for the $(TeO_6)^{n-}$ cluster.
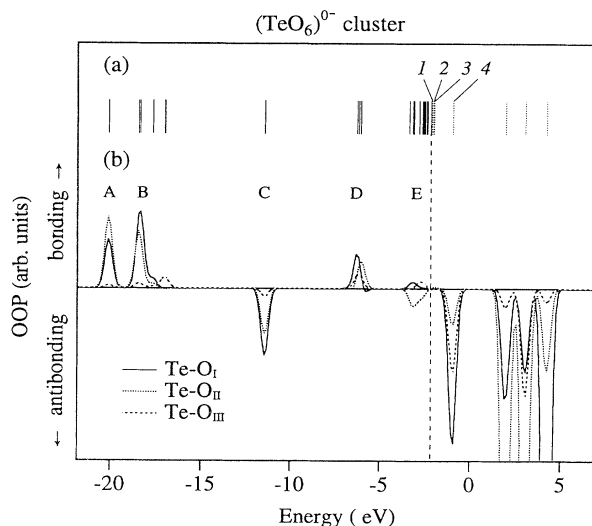

FIG. 3. (a) Energy-level structure of $(TeO_6)^{0-}$ cluster. Solid and dotted lines show occupied and unoccupied levels, respectively. Levels marked 1, 2, and 3 are of O $2p$ character and marked level 4 is of Te $5s$ and $5p$, and O $2p$ characters. (b) Orbital overlap populations (OOP's) for bonds Te-O_I, Te-O_{II}, and Te-O_{III} in the $(TeO_6)^{0-}$ cluster. The OOP curves are obtained by convolution of the OOP and a Gaussian function with 0.5 eV full width at half maximum. The vertical dashed line separates the occupied states in the left-hand side from the unoccupied states in the right-hand side.
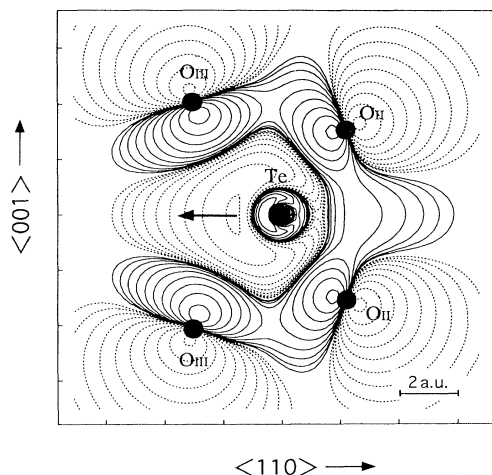
FIG. 4. Contour map of the marked level 4 in Fig. 3 for the $(TeO_6)^{0-}$ cluster. The contours are drawn for the equatorial plane including atoms Te, O_{II}, and O_{III} in Fig. 1. The lobe of Te $5s$ and $5p$ orbital components can be clearly seen to point away from Te along the arrow, showing antibonding characteristic against O $2p$ orbitals.

the rigid-band scheme, electrons occupy the levels marked 1, 2, 3, and 4 in order as n increases. Each level can contain two electrons. The occupation of levels 1, 2, and 3 hardly contribute to the Te-O bonding judging from the small OOP's. These levels are of O $2p$ character and merely make lone pairs. Therefore, the bonding nature does not change up to $n = 6$. When n exceeds 7, electrons occupy the marked level 4 and then the overlap populations of each bond decrease because of the large antibonding character of this level. In this case, Te-O_I bond is most weakened. However, Te-O_{III} bond is first broken since Te-O_{III} bond has smaller overlap population than Te-O_I from the beginning. The OOP at the marked level 4 for the Te-O_{II} bond is the smallest antibonding character, and therefore, this bond remains in bonding state. Thus, the variation of the structural unit in tellurite glasses is most likely caused by the electrons in the marked level 4. Figure 4 shows the contour map of the marked level 4 for the $(TeO_6)^{0-}$ cluster drawn for the equatorial plane, including atoms Te, O_{II}, and O_{III}. The corresponding orbital for the $(TeO_6)^{8-}$ cluster, which

refers to the HOMO, remains almost the same in spatial distribution. The lobe consisting of Te $5s$ and $5p$ orbital components can be clearly seen to point away from the Te atom along the arrow, showing antibonding characteristic against O $2p$ orbital components. From the contour map, electrons at this orbital seem to contribute to the formation of the lone pair on the Te atom which has been suggested by works on some tellurite compounds.[4,16,17]

Finally, we estimate the initial charge state and the bond ionicity of α-TeO_2. As discussed above, the variation of the structural unit is caused by two or less electrons in the marked level 4. This is consistent with the crystalline compounds: Even assuming that all modifier atoms are completely ionized, the transfer charge n_{CT} par one cluster is two or less; For example, $n_{CT} = 0$ for α-TeO_2, $n_{CT} = 2$ for Li_2TeO_3, $BaTeO_3$, $CuTeO_3$, and $n_{CT} = 4/3$ for $Zn_2Te_3O_8$. Thus, we may estimate n_{CT} to be 2 or less. It follows from this estimation that the initial net charge 8δ must be ~ 6, i.e., $\delta \approx 0.75$, for structural unit changing by n_{CT}. In α-TeO_2, therefore, the net charge of a Te atom and an O atom should be $\sim +3$ and ~ -1.5, respectively.

CONCLUSION

We have shown that the variation of the structural unit of tellurite glasses can be consistently interpreted within the charge-transfer picture with use of SCC-DV-Xα calculations on $(TeO_6)^{n-}$ clusters. Mulliken overlap populations indicate that the bonds Te-O_{III} and Te-O_I break in order and the coordination number of the Te atom reduces from 6 via 4 to 2 as n increases. This trend is consistent with the experimental facts that the bonds Te-O_{III} break first and secondly the Te-O_I break as the coordination number reduces. Orbital overlap population analysis reveals that the transferred electrons to the Te-O antibonding orbital cause breaking Te-$O_{I,III}$ bonds and lead to reducing the coordination number of the Te atom. The bond ionicity and the charge states of the Te atom and the O atom in α-TeO_2 are also estimated. The values are 0.75, +3, and -1.5, respectively.

ACKNOWLEDGMENT

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