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Cluster calculational approach to tellurite glasses

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Ab initio self-consistent-charge discrete variational $X\alpha$ molecular-orbital calculations on the TeO_4 cluster modeling tellurite glasses are presented. By taking into account the net charge in the cluster calculation, the change of the structural unit in tellurite glasses is consistently interpreted. The difference charge density of the cluster shows the charge accumulation on the Te atom, corresponding to a lone pair of electrons predicted by stereochemical analysis. [S0163-1829(98)01145-X]

An oxide glass is not a simple and straightforward material for theoretical study because its structures are very complicated and the nature of the electronic interactions in the system is rather complex. However, since the interesting physical and/or chemical properties of such an oxide glass are frequently associated with short-range structural effects, it should be useful to consider the structural unit that can be characterized in terms of well-defined coordination polyhedra by x-ray structural analysis.

For example, vitreous silica and SiO_2-based glasses are built up from the well-defined and rigid structural unit, the SiO_4 tetrahedron. In these structures, each Si atom is bound to four O atoms in SiO_4 tetrahedral coordination, while each O atom is bound to two Si atoms that link the tetrahedra in a continuous random network. Since the high symmetry of the SiO_4 structural unit is convenient for theoretical calculations and the essential feature of these materials is twofold-fourfold coordination of the O and Si atoms that can be generalized to all other mixed tetrahedral solids, most of the fundamental theoretical studies are of SiO_2.[1,2]

On the other hand, tellurite glasses (M_xO_y-TeO_2, where M is a modifier atom such as Li, Na, K, Ba, Cu, etc.) are typical ones of the complex oxide glasses and much different from the SiO_2-based glasses in the viewpoint of the structural unit. The tellurite glasses are built up from asymmetrical network formers, which are TeO_4, TeO_{3+1}, and/or TeO_3 structural units as shown in Fig. 1.[3] Because of these asymmetrical structural units, the theoretical studies on the tellurite glasses seem to be not many, while intense studies have been done on applications of their good infrared transmissions, high refractive indices, high thermal-expansion coefficients, and thermochromic properties.[4,5]

The *ab initio* molecular-orbital (MO) method is a useful scheme for investigating electronic structure and chemical bonding of complex systems such as oxide glasses and crystalline solids containing substituent ions and defects.[6,7] With use of the *ab initio* MO method, we have studied the bonding nature of the tellurite glasses. In previous work, 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 the MO calculations on the TeO_6 cluster that is found in paratellurite (α-TeO_2).[8] However, this leaves room for further investigation, since it was concluded only based on the calculation of the TeO_6 cluster modeling the crystalline paratellurite. In this Brief Report, we present the *ab initio* MO calculation of the TeO_4 structural unit found in various tellurite glasses, discuss the chemical bonding in the structural unit, and show the formation of the electron lone pair on a Te atom predicted by stereochemical analysis using the valence-shell electron-pair repulsion (VSEPR) model.[9,10]

We have performed the *ab initio* self-consistent-charge discrete variational $X\alpha$ (SCC-DV-$X\alpha$) MO calculations on the clusters modeling the structural units of the tellurite glasses. 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. The minimum basis sets of $1s$-$5s,5p$ for the Te atom and $1s$-$2p$ for O atoms, which were numerical atomic orbitals by solving the atomic HFS equations, were used in present calculations.[11] Although quantitative results from cluster calculations should be looked at carefully, the analysis of such calculations, i.e., Mulliken orbital-population analysis, gives a simple intuitive picture of the electronic structure in terms of local chemical bonds.[12] Such a picture helps one to understand results from experimental facts.[8,13]

The structural unit was modeled with the smallest representative unit, i.e., the $(TeO_4)^{4-}$ cluster as shown in Fig. 1(a). It consists of one central Te atom, two axial O (O_{ax}) atoms at a distance of 0.190 nm, and two equatorial O (O_{eq})

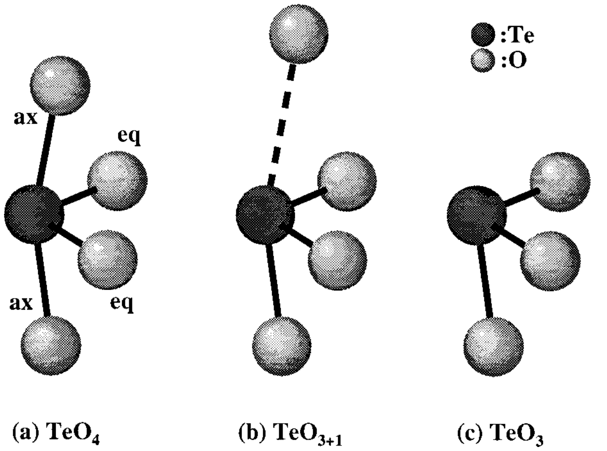

FIG. 1. Typical structural units found in tellurite glasses: (a) TeO_4 trigonal bipyramid, (b) TeO_{3+1} polyhedron, and (c) TeO_3 trigonal pyramid (Ref. 3).

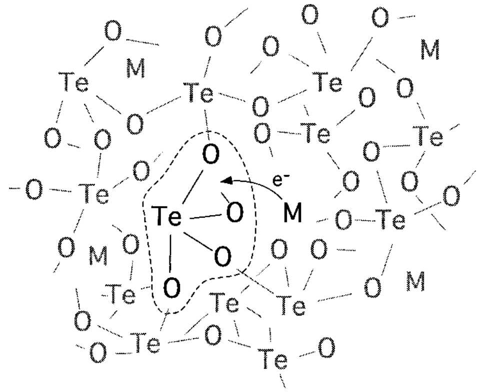

FIG. 2. Schematic view of the electron charge transfer within an M_xO_y-TeO_2 glass. A modifier atom donates the electron to the network former nearby.

atoms at a distance of 0.208 nm with the bond angles of 102° and 169° for O_{eq}-Te-O_{eq} and O_{ax}-Te-O_{ax}, respectively.[3] The calculations were performed with C_2 point-group symmetry.

Usually atomic charges in cluster modeling an oxide are of nominal valences.[14] In this way, the net charge n of the $(TeO_4)^{n-}$ cluster would be 4. However, the net charge 4 derived from the nominal valences is inappropriate for the TeO_4 cluster calculation because any chemical bonding between heterogeneous atoms is not of perfect ionic character. For taking into account of the ionicity, we start by considering the Te-O bonding in pure TeO_2 (for example, paratellurite). Here, the atomic charge states of Te and O are $Te^{4\delta+}$ and $O^{2\delta-}$ with use of the parameter $\delta\,(0<\delta<1)$ representing the ionic character of a Te-O bond. Thus, the charge state for the TeO_4 cluster model should be $(TeO_4)^{4\delta-}$. Next, we consider the effect of a modifier atom M added to pure TeO_2 for making a tellurite glass. Since the electronegativity of an M is smaller than that of Te and O atoms (0.8–1.9, 2.1, and 3.5 on the Pauling scale for M, Te, and O, respectively[15]), the electron should transfer from M to $(TeO_4)^{4\delta-}$. Figure 2 shows the schematic illustration of the charge transfer where an M donates the electron to the network former nearby. Accordingly, the net charge n for the $(TeO_4)^{n-}$ cluster can be defined by $4\delta+\tau$, where τ is the amount of the electron transferred. It must be noted that δ would be a constant derived from the Te-O bonds in pure TeO_2; however, the appropriate δ cannot be easily determined because ionicity even of simple alkaline-earth oxides is still controversial,[16] and the charge-transfer amount τ depends on both the kind and the amount of the added modifier atom. We therefore performed the calculations on the $(TeO_4)^{n-}$ cluster, varying the net charge n from 0 to 4.

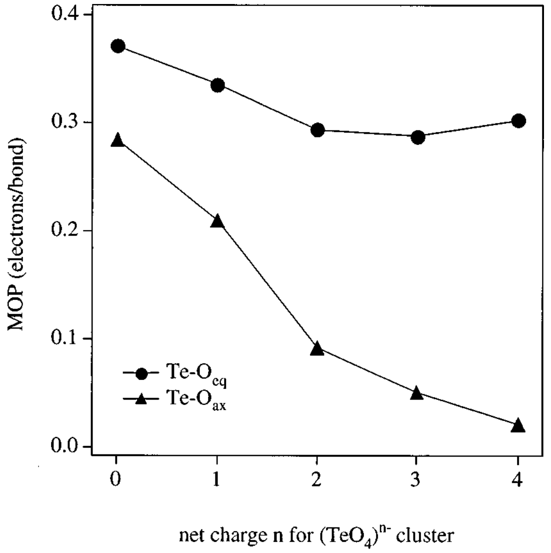

FIG. 3. Mulliken overlap populations (MOP) for Te-O_{eq} and Te-O_{ax} bonds vs the net charge n for the $(TeO_4)^{n-}$ cluster. The MOP of the Te-O_{ax} bond decreases from ~0.3 toward zero as n increases, while the MOP of the Te-O_{eq} bond gradually declines and is steady at ~0.3.

Figure 3 shows Mulliken overlap populations (MOP), which scale bond order in simple terms, versus net charge n for the $(TeO_4)^{n-}$ cluster. The MOP of the Te-O_{ax} bond decreases from ~0.3 toward zero as n increases while the MOP of the Te-O_{eq} bond is larger than ~0.3 and is not much affected by n. These results indicate that the increase of the net charge n weakens the Te-O_{ax} bond. Since the increment of n offers the increment of the charge-transfer amount τ (cf. δ is a constant), it is most likely that either of two Te-O_{ax} bonds is weakened; then its bond length increases ($TeO_4 \rightarrow TeO_{3+1}$), and, as a result, the reducing of the coordination number of Te ($TeO_{3+1} \rightarrow TeO_3$) occurs with increasing content of modifier atoms in tellurite glasses. This interpretation of the relationship between MOP and τ is fairly consistent with the proposed mechanisms of the structural changes in tellurite glasses based on the experimental facts to the point that the electron transferred from the modifier to the TeO_4 structural unit weakens the Te-O_{ax} bond, and leads to the structural change from TeO_4 through TeO_{3+1} to TeO_3.[17,18]

We show a contour plot of the difference charge density $\Delta\rho=\rho\{(TeO_4)^{4-}\}-\Sigma\rho(\text{atoms})$ drawn for the equatorial plane including the Te and O_{eq} atoms in Fig. 4. The formation of

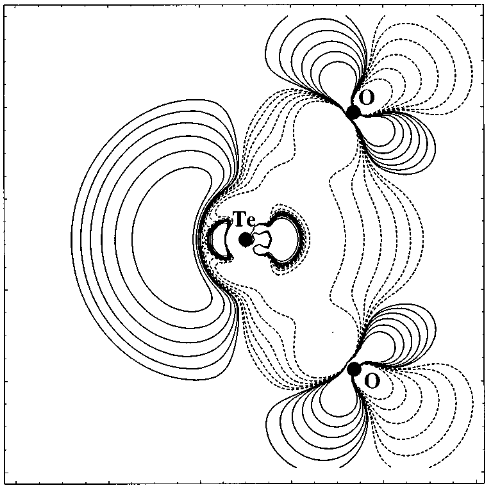

FIG. 4. A contour plot of the difference charge density $\Delta\rho=\rho\{(TeO_4)^{4-}\}-\Sigma\rho(\text{atoms})$ for the $(TeO_4)^{4-}$ cluster. It is drawn for the equatorial plane including Te and O_{eq} atoms. Solid and dotted lines show positive and negative contours, respectively. The charge accumulation sticking out to the left of the Te atom can be clearly seen. It should correspond to the lone pair of electrons that can be predicted by the VSEPR theory (Refs. 9 and 10) and has been widely believed (Refs. 17–21).

the electron lone pair on a Te atom is predicted by VSEPR theory[9,10] and has been widely believed.[17–21] VSEPR theory is the empirical one based on the mutual repulsion of the bonding and/or nonbonding electron pairs around an atom. This theory is very powerful for predicting structures of molecules; however, there has been some disagreement in some compounds.[10] In Fig. 4, the charge accumulation sticking out to the left of the Te atom is clearly seen, and it should correspond to the predicted lone pair of electrons. This result indicates that the VSEPR theory is applicable to the structural study of the tellurite glasses.

Finally, we compare the above results with our previous ones using the TeO_6 cluster model. Despite the different cluster model, the present results are almost all compatible with our previous calculations on the TeO_6 cluster model to the point that the electron charge transfer weakens the Te-O_{ax} bonds and leads to the change of the structural unit.[8] There are, however, some discrepancies between these results. First, the charge accumulation corresponding to the lone pair of electrons is also seen at a similar position in the difference charge contour map of the $(TeO_6)^{8-}$ cluster model; however, it is considerably shrunken.[22] This should be caused by the two nonbonding oxygen atoms at the equatorial positions on the lone-pair side that could not exist as the charge transfer progresses. Second, the MOP for the Te-O_{ax} bonds shows large negative value in the $(TeO_6)^{8-}$ cluster model (i.e., the two Te-O_{ax} bonds are completely broken), while it shows small positive value in the $(TeO_4)^{4-}$ cluster model (i.e., the Te-O_{ax} bonds are weak but in bonding state). Since an actual structural unit found in tellurite glasses has at least one Te-O_{ax} bond, it is most likely that the present TeO_4 cluster model is more suitable for representing the structural unit of tellurite glasses than the previous TeO_6 cluster model.

In conclusion, we presented the *ab initio* SCC-DV-$X\alpha$ MO calculations on the TeO_4 cluster modeling of the tellurite glasses. By taking into account of the net charge n for the $(TeO_4)^{n-}$ cluster in the cluster calculations, we obtained the result that the electron charge transfer from M to TeO_4 causes the Te-O_{ax} bond weakening, and then, should lead to reduction of the coordination number of a Te atom. This result was consistent with the proposed mechanisms based on the experimental facts. The contour plot of the difference charge density of the $(TeO_4)^{4-}$ cluster was also presented. In the contour plot, the charge accumulation on the Te atom was clearly seen, which should correspond to the lone pair of electrons predicted by the VSEPR theory. These results were compared with our previous work using the TeO_6 cluster model.

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