Electronic Structure of ZnSb_2O_6 with Trirutile-Type Structure*

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Electronic structure of ZnSb_2O_6 was investigated using the discrete variational (DV)- $X\alpha$ method on the model cluster $[\text{Zn}_5\text{Sb}_{10}\text{O}_{56}]^{52-}$. In the calculation, the band gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied MO (LUMO) was 3.80 eV. In the valence band, Sb - O and Zn - O bondings are considered to be not perfectly ionic but partially covalent because of the hybridization of O 2p orbitals with Sb 5s and Zn 3d orbitals. Furthermore, ZnSb_2O_6 crystal is expected to have a large electron mobility because Sb 5s orbitals are dominant at the bottom of the conduction band. The calculated net charges are +1.48e for Zn, -1.20e for O and +3.02e for Sb. The bond overlap populations are calculated to be 0.09 and 0.29 for Zn - O and Sb - O bondings, respectively. These results show that Sb - O bonding is more covalent than Zn - O bonding in ZnSb_2O_6 crystal.

KEY WORDS : Molecular Orbital Calculation, ZnSb_2O_6 , DV- $X\alpha$ Method, Electronic Structure

1. Introduction

Mineralogically, ZnSb_2O_6 is called ordonezite and crystallizes trirutile-type structure, which has the space group of D_{4h}^{14} ($P4_2/mnm$) and contains two chemical formulas in the unit cell (Bystrom et al., 1941). ZnSb_2O_6 is expected to show the high electric conductivity by doping carriers. The reasons are as follows: (1) Sb 5s orbitals are dominant at the bottom of the conduction band, (2) the edge-shared MO_6 octahedron (M:metal) continues it regularly in the trirutile-type structure.

Up to now, ZnSb_2O_6 has been examined as a thermoelectric conversion material (Nishiyama and Hattori, 2000). The thermoelectric phenomenon is related with the electrons lying near the Fermi level. Therefore, the clarification of the electronic structure from the valence band to the conduction band is very important to understand the properties of ZnSb_2O_6 . However, no report is so far available about the electronic structure of trirutile-type structure. In the present study, we have performed a molecular orbital (MO) cluster calculation for ZnSb_2O_6 by discrete-variational (DV)- $X\alpha$ method (Adachi et al., 1978) and have elucidated the electronic structure of this compound.

2. Calculation Method

MO calculation has been carried out by the non-relativistic DV- $X\alpha$ method. Electronic structure of a model cluster has been self-consistently calculated using numerical atomic basis functions. The lattice parameters used are the same values as in bulk, $a = 0.466$, $c = 0.924$ nm for ZnSb_2O_6 (Bystrom et al., 1941). Each Zn and Sb atom is octahedrally coordinated by six O atoms. The alternation of edge-shared one ZnO_6 and two SbO_6 octahedra forms linear chains along the z direction.

Figure 1 shows the cluster model composed of 71 atoms $[\text{Zn}_5\text{Sb}_{10}\text{O}_{56}]^{52-}$ which is employed in the MO calculation. The cluster was embedded in a Madelung potential generated by point charges outside the cluster. The total charge of the cluster -52e was obtained by counting the formal charges of Zn^{2+} , Sb^{5+} and O^{2-} . The atomic orbitals used in the calculation are 1s-4p orbitals for Zn, 1s-5p for Sb and 1s-2p for O, respectively.

3. Results and Discussion

Figure 2 shows total density of states (TDOS) and partial DOS (PDOS) for $[\text{Zn}_5\text{Sb}_{10}\text{O}_{56}]^{52-}$ cluster. All of DOS curves are made by broadening the discrete energy eigenvalues by Gaussian functions with 0.3 eV full width at half maximum. MO energies are aligned so as to make the highest occupied molecular orbital (HOMO) zero. The band gap between HOMO and the lowest unoccupied MO (LUMO) was 3.80 eV for $[\text{Zn}_5\text{Sb}_{10}\text{O}_{56}]^{52-}$ cluster. The valence band in the energy range from about -10.0 to 0 eV is mainly constructed from O 2p orbitals, and they hybridize with Sb 5s and Zn 3d orbitals. The presence of Sb 5s and Zn 3d components in O 2p band region means that Sb-O and Zn-O bondings are not perfectly

Fig. 1 $[\text{Zn}_5\text{Sb}_{10}\text{O}_{56}]^{52-}$ cluster.

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Fig. 2
Total and partial DOS of
[Zn₅Sb₁₀O₅₆]⁵²⁻ cluster.

Fig. 3
Overlap population diagrams of
[Zn₅Sb₁₀O₅₆]⁵²⁻ cluster. Solid line
shows the bonding contribution and
the broken line the anti-bonding
contribution.

ionic but partially covalent. In particular, the hybridization of the filled Zn 3d orbitals with O 2sp orbitals is noteworthy. The conduction band is mainly constructed from the interaction between Sb 5s and O 2p orbitals. Sb 5s orbitals are dominant at the bottom of the conduction band. Therefore, ZnSb₂O₆ crystal is expected to have a large electron mobility.

Figure 3 shows the overlap population diagrams of Zn-O and Sb-O bondings obtained for the [Zn₅Sb₁₀O₅₆]⁵²⁻ cluster. The solid line shows the bonding contribution and the broken line the anti-bonding contribution. Each nearest-neighbor interaction in the cluster (Zn-O : 0.200 nm, Sb-O : 0.198 nm) was used in the overlap population analysis. Regarding the Zn-O interaction, a bonding contribution is observed in the energy range from about -8 to -2 eV and an anti-bonding contribution from about -2 to 0 eV. This result means that the lower peak is bonding contribution, the higher one being anti-bonding contribution in the partial DOS of Zn 3d in Figure 2. This is correlated with the general trend that fivefold d states of a transition metal split into threefold *t_{2g}* and twofold *e_g* states in an octahedral ligand field. On the other hand, Sb-O is almost bonding in the energy range from about -10 to 0 eV. Both 5s and 5p orbitals of Sb contribute the interaction. Here, the net

charges of the central Zn atom and the surrounding six O atoms are +1.48e and -1.20e, respectively. These values are larger than those of ZnO, +1.11e for Zn and -1.12e for O, calculated for [Zn₁₃O₂₉]³²⁻ cluster (Matsushima and Kobayashi, 2000). Accordingly, a Zn-O bonding in ZnSb₂O₆ crystal is more ionic, compared with the one in ZnO crystal. The net charge of Sb atom is +3.02e and is about 60 % of the corresponding formal charge. In addition, bond overlap populations defined as a sum of the overlap population of occupied orbitals at the Zn-O and Sb-O bondings are calculated to be 0.09 and 0.29, respectively. These results also show that Sb-O bonding is more covalent than Zn-O bonding in ZnSb₂O₆ crystal.

4. Conclusions

The electronic structure of ZnSb₂O₆ was investigated by DV-X α method on the [Zn₅Sb₁₀O₅₆]⁵²⁻ cluster. The results obtained in this study are summarized as follows;

- (1) The energy gap between HOMO and LUMO was 3.80 eV.
- (2) Sb-O and Zn-O bondings are not perfectly ionic but partially covalent because of the hybridization of O 2p orbitals with Sb 5sp and Zn 3d orbitals in the valence band.
- (3) ZnSb₂O₆ crystal is expected to have a large electron mobility because Sb 5s orbitals are dominant at the bottom of the conduction band.
- (4) Sb-O bonding is more covalent than Zn-O bonding in ZnSb₂O₆ crystal.

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三重ルチル構造を持つ ZnSb₂O₆ の電子構造

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ZnSb₂O₆ の電子構造が、[Zn₅Sb₁₀O₅₆]⁵²⁻モデルクラスターに関して DV-X α 法を用いて研究された。計算の結果、最高占有軌道 (HOMO) と最低非占有軌道 (LUMO) 間のエネルギーギャップは 3.80 eV であった。価電子帯において、O 2p 軌道が Sb 5sp と Zn 3d 軌道と混成することから、Sb-O および Zn-O 結合は完全にはイオン性ではなく部分的に共有結合性であることが分かった。さらに、伝導帯底において Sb 5s 軌道が支配的であることから、ZnSb₂O₆ 結晶は大きな電子移動度を持つことが考えられる。計算

によって得られた有効電荷は、Zn について +1.48 e、O について -1.20 e、Sb について +3.02 e であった。有効共有結合電荷は、Zn-O 結合について 0.09、Sb-O 結合について 0.29 であった。これらの結果は、ZnSb₂O₆ 結晶において Sb-O 結合が Zn-O 結合より共有結合的であることを示す。

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