First-Principles Energy Band Calculation for $ZnSb_2O_6$ with Trirutile-Type Structure

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(Received June 12, 2001; CL-010550)

The electronic structure of $ZnSb_2O_6$ is calculated by using the FLAPW method and the DV-Xα method. The valence band with the width of ca. 10.5 eV is roughly classified into the two bands, where O 2p orbitals are dominant and hybridize with Zn 3d and Sb 5s orbitals. On the other hand, the lower conduction band is mainly constructed from Sb 5s orbitals which have large spatial extent. Therefore, $ZnSb_2O_6$ crystal is expected to have large electron mobility with doping carriers.

Generally, a thermoelectric conversion material must possess high thermoelectricity and high electrical conductivity to transform the heat energy into the electricity energy efficiently. $ZnSb_2O_6$ is called ordonezite and crystallizes trirutile-type structure, which contains two chemical formulas in the unit cell and each Zn and Sb atom is octahedrally coordinated by six O atoms.[1] Until now, $ZnSb_2O_6$ has been examined as a promising thermoelectric conversion material with n-type carriers.[2] The reasons are as follows: (1) the edge-shared MO_6 (M: metal) octahedrons are aligned regularly in the trirutile-type structure, (2) M ns (n: principal quantum number) orbitals spread largely spatially and overlaps mutually. Needless to say, the thermoelectric phenomenon is deeply 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 first-principles band calculation based on the local density-functional approximation (LDA) and have elucidated the electronic structure of $ZnSb_2O_6$. Furthermore, a molecular orbital (MO) cluster calculation has been carried out to analyze the chemical properties.

$ZnSb_2O_6$ has space group D^{14}_{4h} ($P4_2/mnm$), with unit-cell parameters: a = 0.466, c = 0.924 nm.[1] In this structure, Zn atoms occupy Wyckoff positions 2a, Sb 4e (z = 0.333), four oxygens O(1) 4f (x = 0.303), and eight oxygens O(2) 8j (x = 0.303, z = 0.328), respectively.[1] The first-principles band calculation has performed with the scalar-relativistic full potential linearized augmented plane wave (FLAPW) method.[3] Exchange and correlation interactions were treated within the generalized gradient approximation (GGA).[4] In the calculation of the electronic structure approximately 2000 plane waves were used. The atomic spheres (radii) of the Zn, Sb and O atoms were 1.8, 1.8 and 1.6 au, respectively. The k point sampling was chosen to be 30 irreducible points within the Brillouin zone. For MO calculation, it has been carried out by the non-relativistic DV-Xα method.[5] Electronic structure of a model cluster has been self-consistently calculated using numerical atomic basis functions. $[Zn_5Sb_{10}O_{56}]^{52-}$ cluster was 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 were 1s–4p orbitals for Zn, 1s–5p for Sb and 1s–2p for O, respectively.

We have calculated the self-consistent band structure, shown in Figure 1, along the high-symmetry directions of the irreducible Brillouin zone (BZ) (see Figure 2). The energy zero has been taken as the valence band maximum. The valence band is roughly classified into the largely dispersed lower valence band and the upper one with the width of ca. 10.5 eV. A forbidden gap at Γ is ca. 0.9 eV, which would be smaller than the experimental optical band gap (ca. 3.1 eV),[6] since the local density approximation usually underestimates the band gap of the semiconductors and the insulators. Figure 3 represents the total density of states (TDOS) for each inequivalent atom of $ZnSb_2O_6$ crystal. The upper valence band from –2.0 to 0 eV is mainly constructed from O 2p orbitals, where Zn 3d slightly contributes and Sb does almost not appear. In the range from –6.4 to –2.5 eV, large state densities of Zn 3d are observed and they hybridize with O 2p orbitals. The lower valence band in

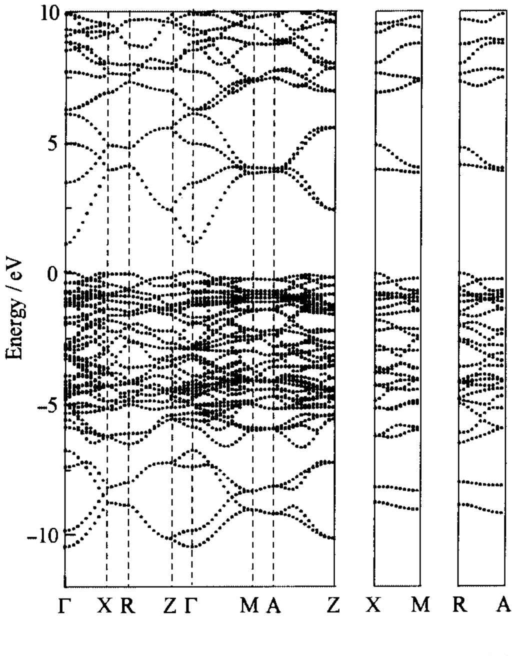

Figure 1. Band structure of $ZnSb_2O_6$ along the high symmetry lines of the first Brillouin zone.

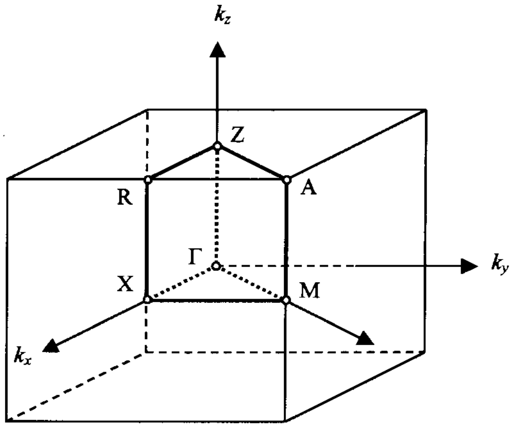

Figure 2. Symmetry labels for irreducible Brillouin zone of the tetragonal Bravais lattice.

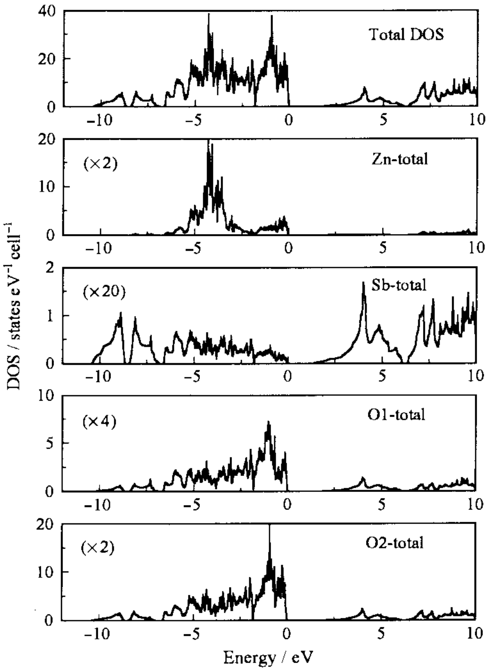

Figure 3. Calculated density of states of $ZnSb_2O_6$ crystal.

the energy range from –10.5 to –7.0 eV arises from the bonding states between Sb 5s orbitals and O 2p orbitals. Their antibonding states form the lower conduction band. As seen from Figure 1, a large curvature is observed in the lower conduction band; the mobility of electron is proportional to the reciprocal effective mass of electron that is in proportion to the curvature. This means that $ZnSb_2O_6$ crystal has the large electron mobility with doping carriers. The band structure is an important characteristic regarding the thermoelectric conversion material, because the electric power that is consumed in the inside of the thermoelectric conversion material must be made small.

In order to reveal the nature of Sb–O and Zn–O bonds, we also performed a MO calculation. Figure 4 shows the overlap population diagrams of Zn–O and Sb–O bonds obtained for the $[Zn_5Sb_{10}O_{56}]^{52-}$ cluster. A solid line shows a bonding contribution and a broken line an 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 –7.5 to –2.5 eV and an anti-bonding contribution from –2.5 to 0 eV. On the other hand, Sb–O is almost bonding in the energy range from –10.0 to –2.0 eV, non-bonding from –2.0 to 0 eV and anti-bonding in the lower conduction band. Therefore, the Sb–O interaction demonstrates an electronic structure typifying n-type oxide semiconductors such as SnO_2 and In_2O_3;[7,8] the upper valence band is mainly constructed from non-bonding O 2p orbitals and the lower conduction band from unoccupied s orbitals of metal ions. The net charges are +1.48e, –1.20e and +3.02e for Zn, O and Sb, respectively. The bond overlap populations defined as a sum of the overlap population of occupied orbitals are 0.09 for Zn–O and 0.29 for Sb–O. The results mean that Sb–O bonding is more covalent than Zn–O bonding.

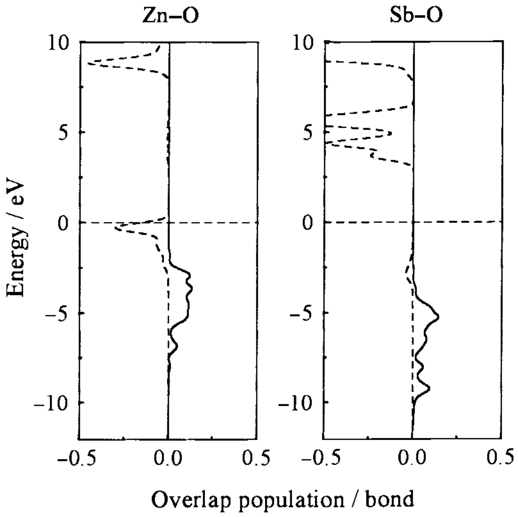

Figure 4. Overlap population diagrams of Zn–O and Sb–O bonds for $[Zn_5Sb_{10}O_{56}]^{52-}$ cluster. A solid line shows a bonding contribution and a broken line an anti-bonding contribution.

References and Notes

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