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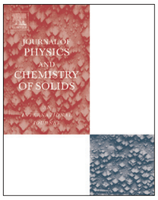

Transport properties of mixed CuAl($S_{1-x}Se_x$)$_2$ as promising thermoelectric crystalline materials

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ABSTRACT

The semi-classical Boltzmann theory as implemented in the BoltzTraP code is used to study the influence of substituting S by Se in the mixed CuAl($S_{1-x}Se_x$)$_2$ crystalline materials on the transport properties. The carrier concentration (n), electrical conductivity (σ/τ), Seebeck coefficient (S), electronic thermal conductivity (κ_e/τ), the electronic power factor ($S^2\sigma/\tau$), and the figure of merit (ZT) as a function of temperature at certain value of chemical potential are calculated. The carrier concentration, electrical conductivity, electronic thermal conductivity and the electronic power factor increase exponentially with increasing temperature. CuAl($S_{0.75}Se_{0.25}$)$_2$ exhibits the highest n, σ/τ, κ_e/τ and $S^2\sigma/\tau$ among these compounds along the whole temperature scale. We should emphasize that S is positive for all compounds which represents p-type concentration. At room temperature CuAl($S_{0.25}Se_{0.75}$)$_2$ and CuAl($S_{0.5}Se_{0.5}$)$_2$ exhibit ZT very close to unity, which implies that these materials could be good candidates for thermoelectric applications. The state-of-the-art full potential linear augmented plane wave (FPLAPW) method is used to calculate the electronic band structure, density of states and energy gaps for CuAl($S_{1-x}Se_x$)$_2$. The electron effective mass ratio (m_e^*/m_e) and effective mass of the heavy holes (m_{hh}^*/m_e) and light holes (m_{lh}^*/m_e) around Γ point, the center of the BZ, for CuAlS$_2$ and CuAlSe$_2$ are calculated.

1. Introduction

The conversion of sun's energy into electricity using photovoltaic cells open a new direction for the ecologically friendly production of electrical energy. Several materials have been tested for such photovoltaic applications. As a result, a notable progress in the photovoltaic field has been reported [1–4]. The ternary $A^{I}B^{III}C_2^{VI}$ semiconducting compounds which crystallize in the chalcopyrite structure have received much attention in recent years [5–7]. They form a large group of semiconducting materials with diverse optical, electrical, and structural properties [8–15]. Ternary chalcopyrite appears to be promising candidate for solar-cell applications [16] and thermoelectric applications [17].

The specific $A^{XI}B^{XIII}C_2^{XVI}$ chalcopyrites studied in this work used copper as the group *XI* element, aluminum as the group *XIII* element, and sulphur or selenium as the group *XVI* element. Since these compounds display large birefringence [18], they are potentially interesting as optical materials as well as semiconductors. We should emphasize that for the Cu containing chalcogenide crystal, strong electron–phonon anharmonicity interacting with the highly polarizable cations a principal role begins to play [19]. So far, however, the trends of the coupling coefficients in these materials are not well understood. Here the first-principle calculations are used to predict enhancement of thermoelectric properties by substitution of S by Se. The band structure of $A^{XI}B^{XIII}C_2^{XVI}$ chalcopyrites is influenced by intrinsic defects which exhibit additional trapping levels within the band gap of host materials, which leads to enhanced thermoelectric properties, as a consequence these materials turn to be suitable for optoelectronics, thermoelectric and photovoltaic applications. We would like to mention that we are not aware of calculations or experimental data for the thermoelectric properties for CuAl($S_{1-x}Se_x$)$_2$. Therefore we thought it would be worthwhile to calculate the thermoelectric properties using the semi-classical Boltzmann theory as incorporated in BoltzTraP code [20].

2. Details of calculations

CuAl($S_{1-x}Se_x$)$_2$ belongs to the group of ternary semiconducting compounds which are of great interest as solar cell materials [16] and nonlinear optical materials [21,22]. The state-of-the-art full potential linear augmented plane wave (FPLAPW) method in a

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scalar relativistic version as embodied in the WIEN2k code [23] is used. This is an implementation of the density functional theory (DFT). Exchange and correlation potential is described in the generalized gradient approximation (GGA) of Perdew–Becke–Ernzerhof (PBE) [24], which is based on exchange-correlation energy optimization to calculate the total energy. The Kohn–Sham equations are solved using a basis of linear APWs. To achieve the total energy convergence, the basic functions in the interstitial regions are expanded up to $R_{mt} \times K_{max}=7.0$ and inside the atomic spheres for the wave function. The potential and charge density in the muffin-tin (MT) spheres are expanded in spherical harmonics with $l_{max}=8$ and nonspherical components up to $l_{max}=6$. In the interstitial region the potential and the charge density are represented by Fourier series up to $G_{max}=20$ $(\text{a.u})^{-1}$. Self-consistency is obtained using 400 $\vec{k}$ points in the irreducible Brillouin zone (IBZ) for $x=0.0$ and 1.0, while for $x=0.25$, 0.5 and 0.75 a mesh of 600 $\vec{k}$ points was used. We have calculated the transport properties using 5000 $\vec{k}$ points in the IBZ. The self-consistent calculations are convergence since the total energy of the system is stable within 10^{-5} Ry.

3. Results and discussion

3.1. Salient features of the electronic band structures and density of states

We have used the semi-classical Boltzmann theory as implemented in the BoltzTraP code to study the influence of substituting S by Se in the mixed $\text{CuAl}(\text{S}_{1-x}\text{Se}_x)_2$ on the transport properties. The calculated electronic band structure (Fig. 1) illustrated that substituting S by Se introduces extra bands in the valence and the conduction bands. The extra bands in the conduction band cause to push the conduction band minimum (CBM) towards Fermi level resulting in significant reduction in the energy gaps with increasing the content of Se. The values of the energy gaps are about 2.2 eV (CuAlS_2), 1.9 eV ($\text{CuAl}(\text{S}_{0.75}\text{Se}_{0.25})_2$), 1.7 eV ($\text{CuAl}(\text{S}_{0.5}\text{Se}_{0.5})_2$), 1.5 eV ($\text{CuAl}(\text{S}_{0.25}\text{Se}_{0.75})_2$) and 1.4 eV ($\text{CuAlSe}_2$). In all cases the valence band maximum (VBM) and CBM are situated at Γ point, the center of the BZ. From the calculated electronic band structure one can obtain the values of the effective mass of electrons as well as heavy and light holes of CuAlS_2 and CuAlSe_2, which are very important quantities for transport properties.

For further deep insight into the electronic structure of $\text{CuAl}(\text{S}_{1-x}\text{Se}_x)_2$ we have calculated the partial density of states (PDOS). The calculated PDOS enables us to identify the angular momentum character of the various structures. The PDOS of CuAlS_2 is illustrated in Fig. 2(a) and (b); one can see that the VBM is mainly formed by Cu-d state with a small contribution from Cu-s/p, Al-s/p and S-p states. However the CBM is formed by Al-s/p and Cu-s/p states. The calculated energy gap is about 2.2 eV. Below Fermi level (E_F) there exists a strong hybridization between Cu-s/p and Al-s/p states and between Cu-d and S-p states, while above Fermi level the Al-s state strongly hybridizes with Al-p state; also Al-p hybridizes with Cu-p state. The strong hybridization may lead to covalent bonds between the atoms.

Replacing 25% of S by Se leads to introduction of more bands in the VB and the CB; these bands are belong to Se-d, which shift the CBM towards E_F, resulting in energy gap's reduction by around 0.3 eV with respect to CuAlS_2 (see Fig. 2(c)–(e)). The calculated energy band gap of $\text{CuAl}(\text{S}_{0.75}\text{Se}_{0.25})_2$ is about 1.9 eV. It is clear that there is a strong hybridization between the states below and above E_F, for instance around – 15.0 eV, Cu-s/p hybridized with Al-p and also Se-s with S-s. In the energy region between –7.0 eV and E_F, Cu-s hybridized with Al-p, Al-p with Cu-p and Se-p with S-p. Whereas above E_F, Cu-s/p hybridized with Se-d; also Cu-p hybridized with Al-p and Se-p states.

The PDOS of $\text{CuAl}(\text{S}_{0.5}\text{Se}_{0.5})_2$ is represented in Fig. 2(f)–(h); one can see that they are quite similar to those of $\text{CuAl}(\text{S}_{0.75}\text{Se}_{0.25})_2$ in the matter of peak positions and the hybridizations except that the CBM shifts towards E_F by around 0.2 eV with respect to $\text{CuAl}(\text{S}_{0.75}\text{Se}_{0.25})_2$ leading to reduction of the energy band gap to 1.7 eV.

Substituting 75% of S by Se led to pushing the CBM further towards E_F resulting in a band gap of about 1.5 eV; the PDOS of $\text{CuAl}(\text{S}_{0.25}\text{Se}_{0.75})_2$ is shown in Fig. 2(i)–(k). Finally substituting all S atoms by Se to form the end compound CuAlSe_2 causes to further shifts of the CBM towards E_F to yield a band gap of about 1.4 eV; the PDOS of CuAlSe_2 is represented in Fig. 2(l) and (m). These figures suggest that there exists a strong hybridization between the states below and above E_F.

3.2. Effective mass

It is further interesting to study the effective masses of electrons and holes, which are important for the excitonic compounds. To obtain accurate values of the effective mass one needs to calculate the curvature of the CBM and the VBM in the vicinity of Γ point. At Γ point, the effective mass can be obtained through a simple parabolic fitting using the definition of effective mass as a second derivative of energy band with respect to the wave vector, k:

$$\frac{1}{m^*} = \frac{\partial^2 E(k)}{\hbar^2 \partial k^2} \tag{1}$$

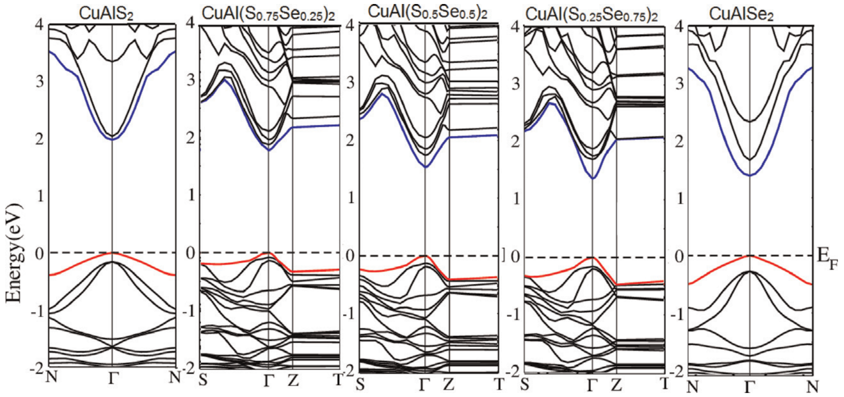

Fig. 1. Calculated electronic band structure for $\text{CuAl}(\text{S}_{1-x}\text{Se}_x)_2$ used to calculate the electron effective mass ratio (m_e^*/m_e), effective mass of the heavy holes (m_{hh}^*/m_e) and light holes (m_{lh}^*/m_e), around Γ point the center of the BZ. The larger the band curvature, the smaller the effective mass.