Effect of K/Bi ordering on the electronic structure of K$_2$Bi$_8$Se$_{13}$

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ABSTRACT

K$_2$Bi$_8$Se$_{13}$ belongs to a class of complex chalcogenides which show potential for superior thermoelectric performance. This compound forms in two distinct phases, $\alpha$ and $\beta$. The $\beta$-phase, which has several sites with mixed K/Bi occupancy is a better thermoelectric. To understand the origin of this difference we have carried out electronic structure calculations within ab initio density functional theory using full potential linearized augmented plane wave (FLAPW) method. The generalized gradient approximation was used to treat the exchange and correlation potential. Spin-orbit interaction (SOI) was incorporated using a second variational procedure. The $\alpha$-phase is found to be a semiconductor with an indirect band gap of 0.47eV compared to 0.76eV for the observed direct optical gap. For the $\beta$-phase we have chosen two different ordered structures with full occupancies of K and Bi atoms at the "mixed sites". The system is a semi-metal for both the ordered structures. To incorporate the effect of mixed occupancy we have chosen a 1x1x2 supercell with an alternative K/Bi occupancy at the "mixed sites". The superlattice ordering gives a semiconductor with an indirect gap of 0.38eV. Mixed occupancy is crucial for the system to be a semiconductor because the Bi atoms at the "mixed sites" stabilize the p orbitals of the neighboring Se atoms by lowering their energy, and opening up a gap at the chemical potential.

INTRODUCTION

Since the best bulk materials for thermoelectric applications are simple chalcogenides, specifically PbTe and Bi$_2$Te$_3$ alloys, complex chalcogenides provide a promising avenue for searching for new thermoelectric materials. Complex chalcogenides with large unit cells containing weakly bonded atoms or molecules, called "rattlers", have been studied to reduce the phonon thermal conductivity without affecting the thermopower S and electrical conductivity $\sigma$, thereby enhancing their thermoelectric efficiency.

$\alpha$-K$_2$Bi$_8$Se$_{13}$ and $\beta$-K$_2$Bi$_8$Se$_{13}$ represent an example where similar building blocks combine to give compounds with the same stoichiometry but different architecture at the atomic level. $\alpha$-K$_2$Bi$_8$Se$_{13}$ consist of Bi$_2$Te$_3$, CdI$_2$, and Sb$_2$Se$_3$-type rod fragments parallel to the z-axis (Figure 1) whereas $\beta$-K$_2$Bi$_8$Se$_{13}$ possesses an architecture made up of Bi$_2$Te$_3$, CdI$_2$, NaCl-type of rod fragments (Figure 2). These different types of fragments are common in other bismuth
chalcogenides such as Cs$_3$Bi$_7$Se$_{12}$ [1] and KBi$_{6.33}$S$_{10}$ [2]. The CdI$_2$-type and Bi$_2$Te$_3$-type rods in α and β-phase are arranged side by side to form layers perpendicular to the y-axis with tunnels filled with K$^+$ cations along the c-axis. Whereas in the β-phase the NaCl-type rod fragments connect the layers to build a 3-D framework, in the α-phase the small Sb$_2$Se$_3$-type rod fragments make a weak connection between layers. The inclusion of alkali atoms stabilizes the covalent bonding in the Bi-chalcogen framework. The width of the Bi$_2$Te$_3$ and NaCl-type rods in β-phase is three Bi polyhedra, while the width of CdI$_2$-type rod is only two Bi polyhedra. The dimensions of these building blocks define the structural characteristics of each structure type in these materials.

The α-phase has no structural disorder but the β-phase has two sites with very similar coordination environment, which have K/Bi disorder. Earlier studies indicate that the Bi8/K3 site contains 62% Bi and 38% K while the K1/Bi9 site contains 62% K and 38% Bi [3]. However a recent better refinement of these sites gives 50%/50% occupancy for Bi8/K3 and 57%/43% for K1/Bi9 [4].

Electronic structure calculations can serve to determine which materials are useful for thermoelectric applications. Since the best thermoelectrics are narrow band gap semiconductors, a detailed analysis of the electronic structure of these compound gives information about the gap, degeneracies of the conduction and valence band extrema, and carrier effective mass, all of which play an important role in determining the power factor $ZT=S^2\sigma T/\kappa$ (where $\kappa$ is the thermal conductivity). Therefore, to gain a deeper understanding of the electronic structure of the promising thermoelectric β-phase, to see how the difference in the crystal structures of α and β-phases shows up in their electronic structures, and the role of K/Bi mixing we have carried out detailed electronic structure calculations in these two systems.

![Figure 1](image1.png)  
**Figure 1.** Projection of the crystal structure of α-K$_2$Bi$_8$Se$_{13}$ viewed down to the c-axis. Different blocks are highlighted by the shaded areas.

![Figure 2](image2.png)  
**Figure 2.** Projection of the crystal structure of β-K$_2$Bi$_8$Se$_{13}$ viewed down to the c-axis.
METHOD OF CALCULATION

Electronic structure calculations were performed using the self-consistent full-potential linearized augmented plane wave method [5] (LAPW) within density functional theory [6] (DFT), using the generalized gradient approximation (GGA) of Perdew, Burke and Ernzerhof [7] for the exchange and correlation potential. The values of the atomic radii were taken to be: 2.2 a.u. for K, 2.4 a.u. for Se and 2.7 a.u. for Bi, where a.u. is the atomic unit (0.529 Å). Convergence of the self-consistent iterations was performed for 18 k points inside the reduced Brillouin zone to within 0.0001 Ry with a cutoff of -6.0 Ry between the valence and the core states. Scalar relativistic corrections were added for both systems and spin-orbit interaction was incorporated using a second variational procedure [8]. Similar calculations have been carried out in several ternary Bi-Te systems such as CsBi₄Te₆ [9] and BaBiTe₃ [10].

RESULTS

\( \alpha-K_2\text{Bi}_8\text{Se}_{13} \)

The unit cell parameters of \( \alpha-K_2\text{Bi}_8\text{Se}_{13} \) (triclinic with space group P-1) are: \( a=26.108 \) a.u., \( b=22.858 \) a.u., \( c=7.872 \) a.u., \( \alpha=89.98^{\circ} \), \( \beta=98.64^{\circ} \), \( \gamma=87.96^{\circ} \) [11] and the corresponding Brillouin zone is shown in Figure 3 (a). The band structures along different symmetry directions are shown in figure Figure 4. The effect of SOI on the band structure is to shift the conduction band down relative to the valence band and thereby decrease the indirect gap from 0.8eV to 0.47eV. There are however direct gaps at the X point (0.74eV) and at the V point (0.72eV) in the Brillouin zone, which compare quite well with the measured direct gap of 0.76eV [11]. The room temperature low electrical conductivity \( \sigma \) (2 S/cm) and high thermopower \( S \) (-200 \( \mu \)V/K) [11] are consistent with a wide-gap semiconductor as found from our electronic structure calculations.

Orbital character analysis reveals that all Se and Bi4, have a large contribution to the higher valence band (HVB) states. On the other hand, the lower conduction band (LCB) states have contributions from the atoms in the Bi₂Te₃ and CdI₂ fragments (Figure 1) and not from the

\[ \text{Figure 3.} \text{ Brillouin zone of (a) } \alpha-K_2\text{Bi}_8\text{Se}_{13} \text{ and (b) } \beta-K_2\text{Bi}_8\text{Se}_{13}. \]
Figure 4. Band Structure of $\alpha$-K$_2$Bi$_8$Se$_{13}$ (a) without SOI and (b) with SOI

This leads to a more 2D character of the electrons in the Bi$_2$Te$_3$ and CdI$_2$ layers suggesting better thermoelectric properties for the electron-doped systems [9].

$\beta$-K$_2$Bi$_8$Se$_{13}$

The unit cell parameters of $\beta$-K$_2$Bi$_8$Se$_{13}$ (monoclinic with space group P 2$_1$/m) are: a=33.055 a.u., b=34.886 a.u., c=7.946 a.u., and $\gamma$=90.49° with the corresponding Brillouin zone shown in Figure 3 (b). It is difficult to treat disorder in ab initio electronic structure calculations. We have however chosen two ordered configurations with full occupancy of Bi8/K3 and K1/Bi9 sites: Configuration I contains Bi 8 atom at the Bi8/K3 site and K1 atom at the K1/Bi9 site, whereas Configuration II contains K3 atom at the Bi8/K3 site and Bi9 atom at the K1/Bi9 site.

Both with and without the inclusion of the SI, Configuration I yields a semi-metallic behavior with several very flat bands along the $\Gamma Y$ and $\Gamma A B\Gamma$, (see Figure 5) i.e. in the plane perpendicular to the z-axis also called the needle axis. Single crystal conductivity measurements show either a semi-metallic or a narrow-gap semi-conducting behavior[3]. However the measured optical gap of 0.59eV does not appear to be consistent with the band structure results. An orbital analysis shows that the top of the "valence band" consists of Se9 p and Se10 p bands (Figure 5 (a),(b)) while the lowest two conduction bands have Bi8 p and Se4 p hybridized orbital character (Figure 5 (c),(d)). Se9 lies at the edge of the NaCl- fragment next to the K1 atom occupying K1/Bi9 site whereas the Se4 lies at the edge of the Bi$_2$Te$_3$- fragment next the Bi8 atom at the Bi8/K3 site. In this configuration Se9 atom has two K1 atoms as nearest neighbors whereas Se4 atom has two Bi8 atoms as nearest neighbors. As a result the Se9 p orbitals are not very well stabilized in energy and they float to the Fermi energy to give a semi-metallic behavior.

In the case of Configuration II, before the inclusion of SOI, there is a direct gap of 0.38eV. But after its inclusion, the gap disappears and the band structure looks very similar to that of the Configuration I. Orbital character analysis shows that in this case the top of the "valence band has" Se4 p orbital character (instead of Se9 in Configuration I) (Figure 6 (a)), while the lowest two conduction bands have Bi9 p and Se9 p (instead of Bi8 p and Se4 p) hybridized character (Figure 6 (b)). In this configuration Se4 atom has two K3 atoms as nearest neighbors. As a result Se4 p orbitals float up to the Fermi energy giving rise to a semi-metallic character.
Figure 5. Band structure of $\beta$-K$_2$Bi$_8$Se$_{13}$-Configuration I with SOI
Orbital character of (a) Se9 p, (b) Se10 p, (c) Bi8 p, (d) Se4 p
The size of the circles is directly proportional to the strength of the orbital character.

Since both configurations I and II with the extreme occupancy of the atoms at the mixed sites show semi-metallic behavior, the observed semiconducting behavior of the $\beta$-phase has to originate from the mixed site occupancy. In order to incorporate mixed occupancy, we have chosen a 1x1x2 supercell (92 atoms/cell) with an alternative occupancy of K and Bi atoms at the mixed sites. Such a supercell ordering along the c-axis has been observed recently in the Sb analog $\beta$-K$_2$Sb$_8$Se$_{13}$ compound [4]. In this ordered model both Se9 and Se4 atoms have one K and one Bi atoms as nearest neighbors. Band structure results show that without SOI the system is a semiconductor with an indirect gap of 0.63eV while incorporating the SOI the gap reduce to 0.39eV (Figure 7 (a),(b)). The VBM occurs at the A point (located at (0.5, 0.5, 0) in fractions of the primitive reciprocal lattice vector lengths) whereas the CBM is located at (0.4, 0.6, 0) in the Brillouin zone. Also, at A point, the system has a direct gap of 0.42eV.

Orbital character analysis reveals that the states near the bottom of the CBM consist of Bi9 and Bi8 p orbitals highly hybridized with the Se and Bi p orbitals of atoms close to the mixed sites whereas the states near the VBM have mostly hybridized Se10 and Bi3 p orbital character. Furthermore the states near the VBM have small contribution from Se9 and Se4 p orbitals because the Bi atoms at the mixed sites stabilize these p orbitals by lowering their energies and removing these states from the neighborhood of the Fermi energy leading to the opening of a
gap. Therefore, this alternative K/Bi order at mixed sites along the c-axis (needle axis) appears to be crucial for the gap formation.

CONCLUSION

In summary, *ab initio* electronic structure calculations show that the $\alpha$-phase is an indirect gap semiconductor with a band gap of 0.47eV and direct band gaps of 0.72-0.74eV, in good agreement with the observed optical gap of 0.76eV [11]. On the other hand for the $\beta$-phase, the type of atoms at the mixed sites is found to be very important in determining the electronic properties of this material. When the mixed sites are treated as fully occupied by K or Bi atoms (Configurations I and II), the system is a semimetal. Incorporation of mixed occupancy using a supercell model results in an indirect gap semiconductor with a gap of 0.39eV. Although the indirect gap (relevant in transport) has not been measured experimentally, we find two rather flat bands along $\Gamma Y$ direction separated by ~0.55eV, which may explain the observed direct gap of 0.59eV (optical) [3].

ACKNOWLEDGMENTS

This work was supported by the Office of Naval Research and DARPA (Contract No. N00014-01-1-0728 and N00014-02-1-0867).

REFERENCES

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