

# Thermoelectric Properties of $K_2Bi_{8-x}Sb_xSe_3$ Solid Solutions and Se Doping

Theodora Kyratsi<sup>(1,2)</sup>, Jeffrey S. Dyck<sup>(3)</sup>, Wei Chen<sup>(3)</sup>, Duck-Young Chung<sup>(1)</sup>, Ctirad Uher<sup>(3)</sup>, Konstantinos M. Paraskevopoulos<sup>(2)</sup> and Mercouri G. Kanatzidis<sup>(1)</sup>

<sup>(1)</sup> Department of Chemistry, Michigan State University, East Lansing, MI 48824

<sup>(2)</sup> Department of Physics, Aristotle University of Thessaloniki, 54006 Thessaloniki, Greece

<sup>(3)</sup> Department of Physics, University of Michigan, Ann Arbor, MI 48109

## ABSTRACT

Our efforts to improve the thermoelectric properties of  $K_2Bi_8Se_3$ , led to systematic studies of solid solutions of the type  $K_2Bi_{8-x}Sb_xSe_3$ . The charge transport properties and thermal conductivities were studied for selected members of the series. Lattice thermal conductivity decreases due to the mass fluctuation generated in the lattice by the mixed occupation of Sb and Bi atoms. Se excess dopant was found to increase the figure-of merit of the solid solutions.

## INTRODUCTION

Our investigations of ternary and quaternary compounds of bismuth chalcogenides [1] have shown that several multinary compositions containing alkali metals show promising thermoelectric properties. One of these phases  $K_2Bi_8Se_3$  [2], possesses low thermal conductivity ( $\sim 1.4$  W/mK) and high power factor. The room temperature ZT value is 0.22 and can be substantially improved on doped  $K_2Bi_8Se_3$  mainly by raising the power factor [3]. A solid solution series of  $K_2Bi_8Se_3$  was prepared in order to study the effects on the general properties such as electrical transport and the lattice thermal conductivity.  $K_2Bi_8Se_3$  was alloyed with its isostructural  $K_2Sb_8Se_3$  analog in order to generate extensive mass fluctuations in the lattice with the Sb/Bi substitution. The Bi/Sb distribution in the structure was also studied by single crystal X-ray diffraction analysis of selected crystals of  $K_2Bi_{8-x}Sb_xSe_3$  [4]. The Sb is not uniformly distributed as would be expected from a true solid solution but it affects disproportionately the various metal sites in the structure. We find that the band gaps and the melting points vary systematically as a function of  $x$  [5]. Various  $K_2Bi_{8-x}Sb_xSe_3$  solid solutions were prepared with the Bridgman technique [6] in order to grow large oriented ingots samples. In this work, charge transport properties and thermal conductivity measurements of selected members of  $K_2Bi_{8-x}Sb_xSe_3$  solid solutions are presented. Dopant studies using excess of Se were also performed in order to study its influence on the thermoelectric properties.

## RESULTS AND DISCUSSION

$K_2Bi_8Se_3$  and its isostructural Sb solid solutions are anisotropic three-dimensional monoclinic structures that propagate along the b-axis [2,4]. In the structure,  $2Bi_3$ -type rods form layers perpendicular to the c-axis. The  $2K_2$ -type rods connect the layers to build a 3-D framework, which creates the needle-like crystal morphology along the b-axis, with tunnels filled with  $K^+$  cations. The anisotropic structure of these materials also causes strong anisotropy in their thermoelectric properties [6].

To prepare the  $\text{K}_2\text{Bi}_{8-x}\text{Sb}_x\text{Se}_3$  ( $x=0.8$  and  $1.6$ ) solid solutions,  $\text{K}_2\text{Bi}_8\text{Se}_3$  and  $\text{K}_2\text{Sb}_8\text{Se}_3$  were mixed in various proportions at  $850^\circ\text{C}$ . To prepare the doped  $\text{K}_2\text{Bi}_{8-x}\text{Sb}_x\text{Se}_3$  with Se excess K, Bi, Sb and Se were added at  $850^\circ\text{C}$ . A modified vertical Bridgman technique [6] was applied on all samples to obtain well-oriented ingots for charge transport and thermoelectric measurements.

### Charge Transport of $\text{K}_2\text{Bi}_{8-x}\text{Sb}_x\text{Se}_3$

Charge transport measurements were carried out along the needle direction (i.e. crystallographic b-axis) on well-oriented ingots of  $\text{K}_2\text{Bi}_{8-x}\text{Sb}_x\text{Se}_3$  members  $x=0.8$  and  $1.6$ . The electrical conductivity has a weak negative temperature dependence, which is consistent with a semi-metal or a narrow-gap semiconductor, see Figure 1. The room temperature values increase from  $55 \text{ S/cm}$  for the member  $x = 0.8$  to  $292 \text{ S/cm}$  for the member  $x = 1.6$ .

Hall effect measurements as a function of temperature showed a negative Hall coefficient ( $R_H$ ) for both members, indicating electrons as the major charge carrier (n-type) in agreement with the observed negative Seebeck coefficient (see below). The carrier concentration was calculated ( $n = 1/(R_H \cdot e)$ ) to be  $\sim 1.6 \cdot 10^{20} \text{ cm}^{-3}$  for  $x = 0.8$  and  $\sim 1.1 \cdot 10^{20} \text{ cm}^{-3}$  for  $x = 1.6$  at room temperature, Figure 2. These values and their weak temperature dependence indicate that the samples were in a relatively high doping state (degenerate) as prepared. The Hall mobility ( $\mu_H \sim R_H \cdot \sigma$ ) at room temperature was great for the  $x = 1.6$  sample ( $\sim 16 \text{ cm}^2/\text{Vs}$ ) than for  $x = 0.8$  ( $\sim 2 \text{ cm}^2/\text{Vs}$ ), Figure 3. The relatively low Hall mobilities most certainly indicate the existence of many defects and other carrier scattering centers in these ingots. For example, a major source of such scattering centers is the microcracks in the ingots due to their polycrystalline nature. We believe the true intrinsic mobilities in the crystal is much higher and improved ingot quality in the future will help raise the observed mobility closer to it.

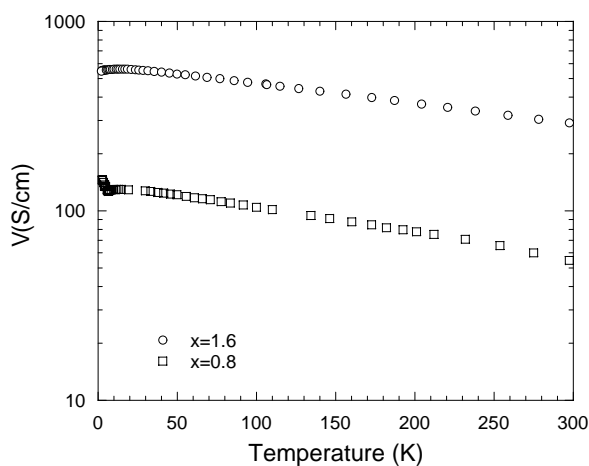


Figure 1: Temperature dependence of the electrical conductivity for ingot samples of  $\text{K}_2\text{Bi}_{8-x}\text{Sb}_x\text{Se}_3$  solid solutions with  $x=0.8$  and  $1.6$ .

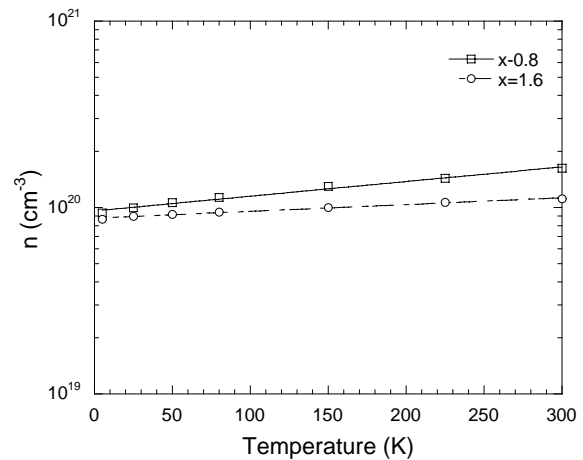


Figure 2: Temperature dependence of carrier concentration for ingot samples of  $\text{K}_2\text{Bi}_{8-x}\text{Sb}_x\text{Se}_3$  solid solutions with  $x=0.8$  and  $1.6$ .







