Thermoelectric Properties of K$_2$Bi$_{8-x}$Sb$_x$Se$_{13}$ Solid Solutions and Se Doping

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ABSTRACT

Our efforts to improve the thermoelectric properties of β-K$_2$Bi$_8$Se$_{13}$, led to systematic studies of solid solutions of the type β-K$_2$Bi$_{8-x}$Sb$_x$Se$_{13}$. 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 as a 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, β-K$_2$Bi$_8$Se$_{13}$ [2], possesses low thermal conductivity (~1.4 W/m·K) and high power factor. The room temperature ZT value is 0.22 [2] and can be substantially improved on doped β-K$_2$Bi$_8$Se$_{13}$ mainly by raising the power factor [3]. A solid solution series of β-K$_2$Bi$_8$Se$_{13}$ was prepared in order to study the effects on the general properties such as electrical transport and the lattice thermal conductivity. β-K$_2$Bi$_8$Se$_{13}$ was alloyed with its isostructural K$_2$Sb$_8$Se$_{13}$ analog in order to generate extensive mass fluctuations in the lattice with the mixed occupation of Sb and Bi atoms. Se excess as a dopant was found to increase the figure-of-merit of the solid solutions.

RESULTS AND DISCUSSION

β-K$_2$Bi$_8$Se$_{13}$ and its isostructural Sb solid solutions are anisotropic three-dimensional monoclinic structures that propagate along the b-axis [2,4]. In the structure, Bi$_2$Te$_3$-type rods form layers perpendicular to the c-axis. The NaCl-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 $\text{K}_2\text{Bi}_{8-x}\text{Sb}_x\text{Se}_{13}$ ($x=0.8$ and 1.6) solid solutions $\beta$-$\text{K}_2\text{Bi}_8\text{Se}_{13}$ and $\text{K}_2\text{Sb}_8\text{Se}_{13}$ were mixed in various proportions at 850 °C. To prepare the doped $\text{K}_2\text{Bi}_{8-x}\text{Sb}_x\text{Se}_{13}$ with Se excess K, Bi, Sb and Se were mixed at 850°C. A modified vertical Bridgman technique [6] was applied on all samples to obtain well-oriented ingots for charge transport and thermal conductivity measurements.

**Charge Transport of $\text{K}_2\text{Bi}_{8-x}\text{Sb}_x\text{Se}_{13}$**

Charge transport measurements were carried out along the needle direction (i.e. crystallographic b-axis) on well-oriented ingots of $\text{K}_2\text{Bi}_{8-x}\text{Sb}_x\text{Se}_{13}$ 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 S/cm for the member $x = 0.8$ to 292 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 coefficients (see below). The carrier concentration was calculated ($R_H = 1/(n\cdot e))$ to be $\approx 1.6 \cdot 10^{20}$ cm$^{-3}$ for $x = 0.8$ and $\approx 1.1 \cdot 10^{20}$ cm$^{-3}$ for $x = 1.6$ at room temperature, Figure 2. These values and the weak temperature dependence indicate that the samples were in a relatively high doping state (degenerate) as prepared. The Hall mobility ($\mu_H = R_H \cdot \sigma$) at room temperature was greater for the $x = 1.6$ sample ($\approx 16$ cm$^2$/Vs) than for $x = 0.8$ ($\approx 2$ cm$^2$/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 $\text{K}_2\text{Bi}_{8-x}\text{Sb}_x\text{Se}_{13}$ solid solutions with $x=0.8$ and 1.6.

**Figure 2**: Temperature dependence of carrier concentration for ingot samples of $\text{K}_2\text{Bi}_{8-x}\text{Sb}_x\text{Se}_{13}$ solid solutions with $x=0.8$ and 1.6.
Thermoelectric power measurements on K$_2$Bi$_{8-x}$Sb$_x$Se$_{13}$ solid solutions were also carried out along the needle direction for the members $x=0.8$ and $x=1.6$. The Seebeck coefficients are negative in value and become less negative as the temperature is decreased below room temperature down to 4 K, consistent with heavily doped n-type semiconductor, see Figure 4. The Seebeck coefficients at room temperature were changed from -127 µV/K for member $x=0.8$ to -100 µV/K for member $x=1.6$.

**Figure 3**: Temperature dependence of mobility for ingot samples of K$_2$Bi$_{8-x}$Sb$_x$Se$_{13}$ solid solutions with $x=0.8$ and 1.6.

**Figure 4**: Temperature dependence of Seebeck coefficient for ingot samples of K$_2$Bi$_{8-x}$Sb$_x$Se$_{13}$ solid solutions with $x=0.8$ and 1.6.

**Charge transport properties of K$_2$Bi$_{8-x}$Sb$_x$Se$_{13}$ with Se excess**

The Hall effect measurements presented above indicated that the K$_2$Bi$_{8-x}$Sb$_x$Se$_{13}$ samples are in a highly doped state. We speculated that a possible source of the high carrier concentration of the ingots might be defects related to Se vacancies created via Se vaporization during the sample preparation. To explore this possibility, ingots of K$_2$Bi$_{8-x}$Sb$_x$Se$_{13}$ solid solutions with 0.2 wt % Se excess were prepared. As shown below, Se excess improved the thermoelectric properties of members $x=0.8$ and 1.6, though not by lowering the number of carriers. Nevertheless this improvement caused us to examine other members of the series ($x=2.4$ and 4) also prepared with Se excess.

The electrical conductivity measurements along the needle direction for $x=1.6$ gave a significantly higher value of 746 S/cm at room temperature compared to 292 S/cm for the same member with no Se added, see Figure 5. Hall effect measurements for samples with 0.2 wt % Se excess gave a carrier concentration of about $1.7\times10^{20}$ cm$^{-3}$ and Hall mobility of ~30 cm$^2$/Vs. The Seebeck coefficient decreased with the addition of 0.2 wt % Se from ~100 to ~74 µV/K, see Figure 6. However, the power factor increased by factor of ~1.4. It is interesting that we were able to change the properties of the $x=1.6$ material but apparently not for the reasons we expected. The carrier concentration after excess Se actually increased (not decreased as expected) and the Seebeck coefficient decreased. Therefore, the origin of the high concentration of the K$_2$Bi$_{8-x}$Sb$_x$Se$_{13}$ samples is not well understood. Nevertheless a surprising finding is the substantial increase in carrier mobility upon adding excess Se suggesting an improved crystal
quality in the oriented ingot. It is possible that the increased mobility is due to improvement in external factors such as ingot morphology quality.

Similarly, preliminary measurements at higher temperature [7] show that this increasing trend was prepared and corresponding measurements were carried out. Solid solutions with x=2.4 and 4 were prepared and carrier concentration is only slightly higher (∼1.7⋅10^{20} \text{ cm}^{-3}). Although the Seebeck coefficient decreased from −127 \mu V/K to −92 \mu V/K, the power factor increased significantly by a factor of ∼5.

Because samples prepared with Se excess gave improved power factors further studies on other members of the solid solution series were carried out. Solid solutions with x=2.4 and 4 were prepared and corresponding measurements were carried out.

![Figure 5: Electrical conductivity of K_{2}Bi_{8-x}Sb_{x}Se_{13} prepared with Se excess for x=0.8, 1.6, 2.4 and 4.](image)

![Figure 6: Seebeck coefficient of K_{2}Bi_{8-x}Sb_{x}Se_{13} prepared with Se excess for x=0.8, 1.6, 2.4 and 4.](image)

Room temperature electrical conductivity of members with x=2.4 and 4 was 380 and 56 S/cm, respectively, see Figure 5. The Seebeck coefficients in room temperature increased from −100 \mu V/K for x=2.4 to −160 \mu V/K for x=4, see Figure 6.

The Seebeck coefficient increases with temperature for all members of the series. Interestingly, preliminary measurements at higher temperature [7] show that this increasing trend of Seebeck coefficient persists at least up to 700 K and probably even higher temperatures. This causes the power factor to increase at higher temperatures and actually makes these materials interesting for high temperature applications.

**Thermal conductivity**

The mass fluctuation generated in the lattice of K_{2}Bi_{8}Se_{13} by the mixed occupation of Sb and Bi atoms is expected to reduce the lattice thermal conductivity of K_{2}Bi_{8-x}Sb_{x}Se_{13} solid solutions when x increases at least up to 4.

The lattice thermal conductivity (\kappa_{l}) can be obtained, by subtracting the electronic contribution (\kappa_{e}) from the total thermal conductivity (corrected measured thermal conductivity from radiation losses based on ∼T^3 law [8]). The latter can be estimated by applying the

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Weidemann-Franz Law, $\kappa_e = \sigma \cdot L \cdot T$, where $L$ is the Lorentz number taken$^9$ to be $\approx 2.44 \times 10^{-8}$ $V^2/K^2$, $\sigma$ the electrical conductivity, and $T$ the temperature.

![Figure 7](image)

**Figure 7**: Temperature dependence of lattice thermal conductivity of the $K_2Bi_{8-x}Sb_xSe_{13}$ solid solutions for $x=0.8$ and 1.6.

Thermal conductivity measurements were carried out along the needle direction (i.e., crystallographic b-axis) on well-oriented ingots of $K_2Bi_{8-x}Sb_xSe_{13}$ members $x=0.8$ and 1.6. The measured thermal conductivity of $K_2Bi_{8-x}Sb_xSe_{13}$ solid solutions was 1.4 and 1.2 W/m-K for $x=0.8$ and 1.6 at room temperature, respectively. The lattice thermal conductivities decreased from 1.1 W/m-K for $x = 0.8$ to 0.6 W/m-K for $x = 1.6$, see Figure 7. Therefore, mass fluctuation due to Sb incorporation decreases the lattice thermal conductivity by a factor of $\approx 2$ when $x$ increases from 0.8 to 1.6.

The lattice thermal conductivity of the four members of the solid solutions ($x=0.8, 1.6, 2.4$ and 4) with Se excess, decreases when Sb concentration increases and the low temperature Umklapp peak is suppressed due to the increase of the disorder in the lattice, see Figure 8. The room temperature value decreases from $\approx 0.6$ to $\approx 0.5$ W/m-K when $x$ increases from 0.8 to 1.6. However, for higher Sb concentration the room temperature lattice thermal conductivity is not decreased further and tends to a value of $\approx 0.5$ W/m-K.

**Thermoelectric performance**

Figure 9 shows the ZT for the four members of $K_2Bi_{8-x}Sb_xSe_{13}$ solid solutions prepared with Se excess. At room temperature, ZT reaches almost

![Figure 8](image)

**Figure 8**: Thermal conductivity of $K_2Bi_{8-x}Sb_xSe_{13}$ with 0.2% Se excess for $x=0.8, 1.6, 2.4$ and 4.

![Figure 9](image)

**Figure 9**: ZT of the $K_2Bi_{8-x}Sb_xSe_{13}$ solid solutions with Se excess for $x=0.8, 1.6, 2.4$ and 4.
The temperature dependence of ZT shows a strong trend upwards at higher temperatures. 
This derives from the increasing Seebeck coefficient at higher temperature. Therefore, the 
optimum performance of these materials will be achieved at higher temperature perhaps around 
700K. ZT as high as 0.8 is predicted at 700K from extrapolation of the data at higher temperature 
for x=2.4. Extrapolation was performed based on a quadratic fitting of electrical resistivity and 
linear fitting of Seebeck coefficient. For x=0.8 and 1.6, ZT of 0.5 and 0.7 at 700K is predicted, 
respectively. These trends suggest that these materials are promising and suitable for high temperature applications, especially if addition improvements are achieved through doping. However, measurements at higher temperatures (i.e. 300-700K) need to be performed.

CONCLUSIONS

In this work, the thermoelectric properties of K$_2$Bi$_{8-x}$Sb$_x$Se$_{13}$ solid solutions were studied. 
The mass fluctuation generated in the lattice of K$_2$Bi$_{8}$Se$_{13}$ by the mixed occupation of Sb and Bi 
atoms in K$_2$Bi$_{8-x}$Sb$_x$Se$_{13}$ solid solutions leads to lower lattice thermal conductivity. It seems that 
for 20% Sb substitution of Bi, lattice thermal conductivity already reaches a minimum plateau, 
thus this is an interesting member for further doping studies.

Doping studies performed with Se excess on selected members of the solid solutions series showed the figure-of-merit was improved. Temperature dependence of ZT and extrapolation at higher temperatures show that these full potential of these materials will be realized at high temperature possibly for power generation applications.

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