THERMOELECTRIC PROPERTIES OF β-$K_2Bi_{8-x}Sb_xSe_{13}$ SOLID SOLUTIONS. A PROMISING SERIES FOR HIGH TEMPERATURE APPLICATIONS.

Th. Kyratsi[1,2], D-Y Chung[1], J.S. Dyck[3], C. Uher[3], E. Hatzikraniotis[4], K.M. Paraskevopoulos[4] and M.G. Kanatzidis[1]
[1] Department of Chemistry, Michigan State University, East Lansing, MI 48824, USA
[2] Department of Mechanical & Manufacturing Engineering, University of Cyprus, 1678 Nicosia, Cyprus
[3] Department of Physics, University of Michigan, Ann Arbor, MI 48109, USA
[4] Department of Physics, Aristotle University of Thessaloniki, 54124 Thessaloniki, Greece

Abstract

Our research in new thermoelectric materials has identified several ternary and quaternary bismuth chalcogenide compounds with alkali metals to have promising properties for thermoelectric applications. β-$K_2Bi_8Se_{13}$ and its solid solutions β-$K_2Bi_{8-x}Sb_xSe_{13}$ are found to be an interesting series for thermoelectric investigations mainly due to their low thermal conductivity and highly anisotropic electric properties. In this work, the Seebeck coefficient, the electrical and thermal conductivity of the β-$K_2Bi_{8-x}Sb_xSe_{13}$ ($0<x\leq8$) series as a function of temperature and composition will be presented. Transport properties show the transition from n-type to p-type character with increasing incorporation of Sb in the lattice. The Bi/Sb atomic disorder dramatically affects the lattice thermal conductivity where the Umklapp peak is suppressed. The thermoelectric performance is estimated up to high temperatures where the potential for applications of these materials appears to be.

Introduction

Research on ternary and multinary bismuth chalcogenide compounds [1] showed that β-$K_2Bi_8Se_{13}$ [2] has many of these features that make a material promising for thermoelectric applications such as complex structure that can lead [3] to high Seebeck coefficient based on Mott formula [4] as well as to low thermal conductivity due to large unit cell, weakly bound ions in cages ("phonon glass-electron crystal theory") [5] etc.

The formation of solid solutions is a common way to succeed low thermal conductivity and improve the thermoelectric performance of the materials. Solid solutions formation based on the β-$K_2Bi_8Se_{13}$ structure was attempted via substitution on the heavy metal sites (i.e. $K_2Bi_{8-x}Sb_xSe_{13}$) [6], on the chalcogenide sites (i.e. $K_2Bi_8Se_{13-x}S_x$) [7] as well as on the alkali metal site ($K_{2-x}Rb_xBi_8Se_{13}$) [8]. Crystallographic studies shows that the Bi/Sb [9] as well as K/Rb [8] distribution in the structure was non-uniform, while Se/S distribution[7] was more even and indicated the formation of more homogenous solid solutions.

$K_2Bi_{8-x}Sb_xSe_{13}$ series showed very low thermal conductivity [10] and this is encouraging for their thermoelectric performance. Transport measurements of $K_2Bi_{8-x}Sb_xSe_{13}$ members with low Sb concentration were carried out showing highly doped materials (carrier concentration ~$10^{20}cm^{-3}$) [6]. Samples prepared with excess of Se performed better thermoelectric properties due to their higher mobility [6].

In this work, charge transport measurements on $K_2Bi_{8-x}Sb_xSe_{13}$ series are studied. The Seebeck coefficient, electrical and thermal conductivity as a function of temperature and composition are discussed. The potential use of these materials appears at high temperature applications based on preliminary measurements up to 700K.

Results and Discussion

$K_2Bi_{8-x}Sb_xSe_{13}$ series, isostructural to β-$K_2Bi_8Se_{13}$, have complex monoclinic structure [2] that include two different interconnected types of Bi/Se building blocks (the so-called $NaCl^{100}$- and Bi_2Te_3-type) and K^+ atoms in tunnels, see Figure 1. The two different Bi/Se blocks are connected to each other at special mixed-occupancy K/Bi sites. These sites seem to be crucial in the electronic properties [3,11].

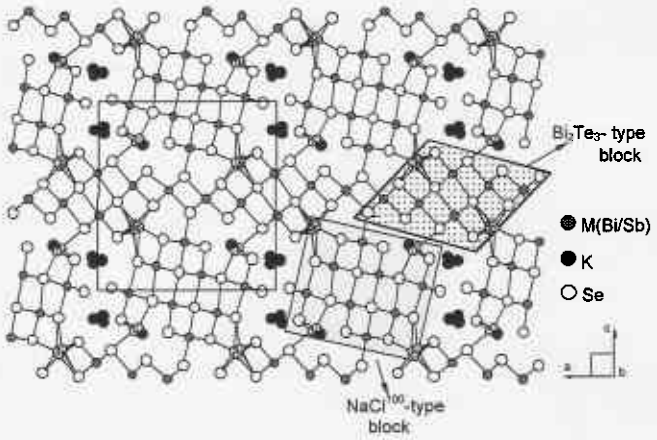


Figure 1. Crystal Structure of β-$K_2Bi_8Se_{13}$ and $K_2Bi_{8-x}Sb_xSe_{13}$ series.

$K_2Bi_{8-x}Sb_xSe_{13}$ samples were prepared by mixing potassium metal, bismuth, antimony and selenium with 0.2wt% Se excess as described elsewhere [6]. The samples for measurement were cut from well-oriented ingots grown with modified Bridgman technique [12], see Figure 2.

Figure 2. Ingot of $K_2Bi_{8-x}Sb_xSe_{13}$, x=1.6.

Charge transport and thermal conductivity measurements were carried out on $K_2Bi_{8-x}Sb_xSe_{13}$ series for the members x=0.8, 1.6, 2.4, 4.0, 5.6 and 8.0, along the needle direction (i.e. crystallographic b-axis). The room temperature values are shown in Table 1.

Thermoelectric power

The Seebeck coefficients of Bi-rich members of the series are negative in value and this indicates electrons as main carriers. The n-type character is common in most of the bismuth selenide based compounds [1], while rarely p-type material is reported [13]. For members with x≤2.4, the Seebeck coefficients are negative and become less negative as the temperature is decreased. This is consistent with heavily doped semiconducting behavior, see Figure 3a, while transition to the intrinsic region is not observed. The smooth variation of Seebeck coefficient at low temperatures can be attribute to the high carrier concentration (see also Hall effect measurements). This behavior of Seebeck coefficient is typical to that of almost all ternary and quaternary alkali bismuth chalcogenides compounds [5].

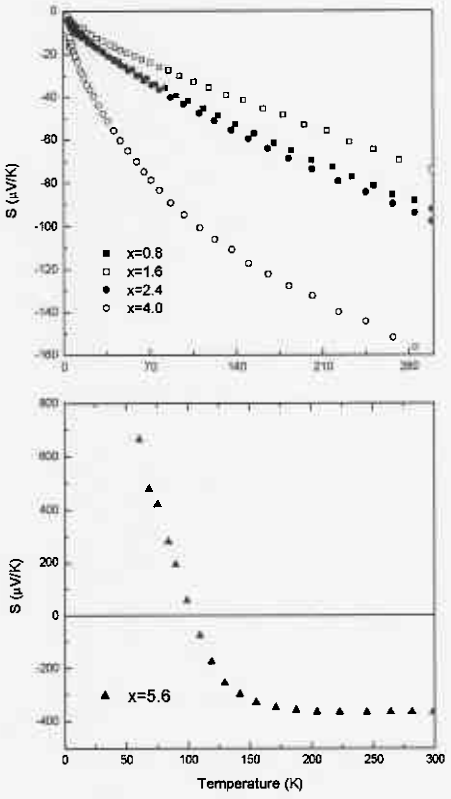


Figure 3. Temperature dependence of Seebeck coefficient of $K_2Bi_{8-x}Sb_xSe_{13}$ series with Se excess for (a) Bi-rich samples, x=0.8, 1.6, 2.4 and 4.0 and (b) Sb rich sample, x=5.6.

The member with x=5.6 has different behavior compare to the other members. Seebeck coefficient is positive at low temperatures and becomes negative at higher temperatures, see Figure 3b. This indicates the transition of the material from p-type to n-type with the temperature. The p-to-n type transition temperature appears at ~100K. At temperatures higher than 150K the Seebeck coefficient is constant and equal to –370 μV/K up to room temperature. These features are characteristic for intrinsic behavior.

For the Sb-member (x=8.0) Seebeck coefficient is positive and equal to +750 μV/K at room temperature. The positive value indicate its p-type character and suggests that its transition temperature is >300K. Experimental data at lower temperatures for this member are not available.

In Table 1 the increase of absolute value of Seebeck coefficient with composition x suggesting the decrease of the electron concentration is clear. For x<1.5, Seebeck coefficient does not follow the increasing trend with composition x and this could be attributed to the preferential substitution that Sb shows on special crystallographic sites of the structure [9].

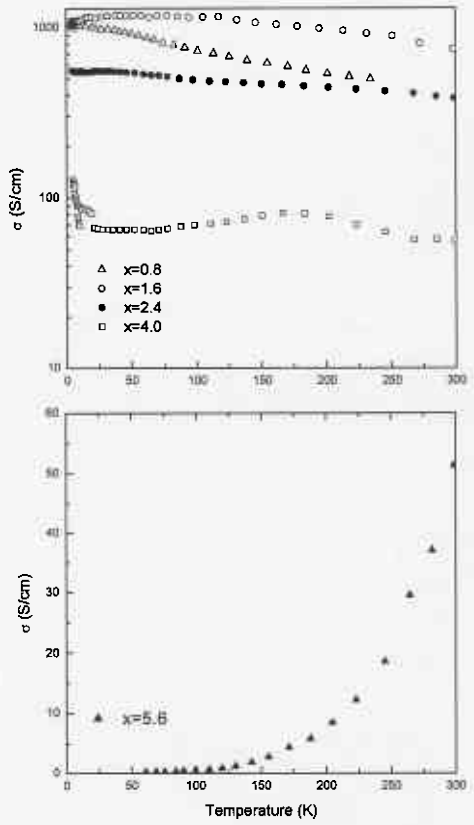


Figure 4. Temperature dependence of electrical conductivity of $K_2Bi_{8-x}Sb_xSe_{13}$ series with Se excess for (a) Bi-rich samples, x=0.8, 1.6, 2.4 and 4.0 and (b) Sb rich sample, x=5.6.

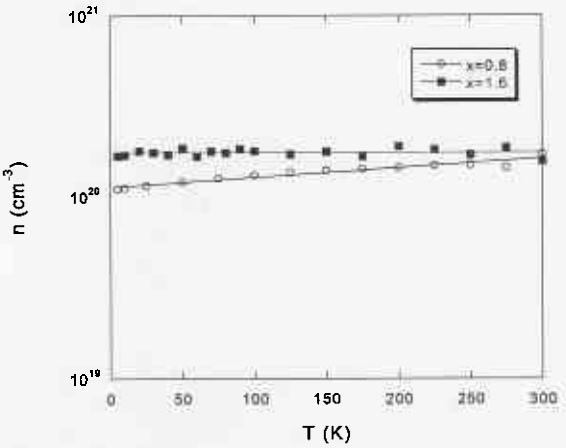
Electrical conductivity

The electrical conductivity of members x=0.8, 1.6 and 2.4 has a weak negative temperature dependence, consistent with the extrinsic behavior of semiconductor, see Figure 4a. For the member x=5.6, the intrinsic behavior appears, see Figure 4b. This behavior agrees with the increase of p-type character that Sb causes. For the Sb-member (x=8.0) electrical conductivity

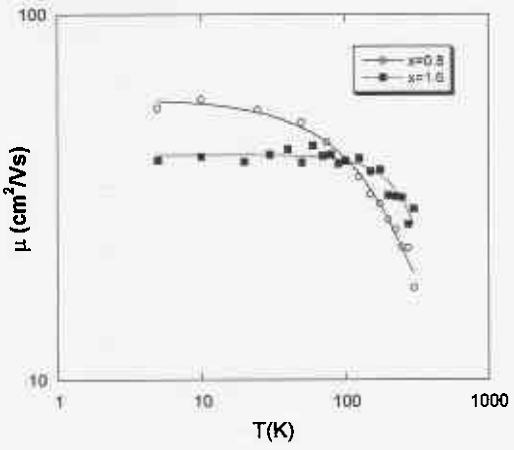
is 0.01 S/cm at room temperature while data at lower temperatures were not available.

Hall Effect

Hall effect measurements on the members of $K_2Bi_{8-x}Sb_xSe_{13}$ solid solutions and low Sb concentration ($x<2$) showed negative Hall coefficient suggesting n-type character that agrees with the Seebeck coefficient measurements. The carrier concentration is calculated (based on $R_H=1/n\cdot e$) to be ~10^{20} cm^{-3} with weak temperature dependence, see Figure 5a. They confirm the high doping state of these members. Mobility is also calculated and the temperature dependence for both samples (x=0.8 and x=1.6) is shown in Figure 5b. It is obvious that mixed scattering mechanisms are involved in mobility for this temperature region. These results are similar to these of pure members where no Se excess is added [9].



(a)



(b)

Figure 5. Temperature dependence of (a) carrier concentration and (b) mobility for the $K_2Bi_{8-x}Sb_xSe_{13}$ with Se excess, x=0.8 and 1.6.

Thermal conductivity

The mass fluctuation generated in the lattice of $K_2Bi_8Se_{13}$ by the mixed occupation of Sb and Bi atoms is expected to reduce the lattice thermal conductivity of $K_2Bi_{8-x}Sb_xSe_{13}$ series. The lattice thermal conductivity (κ_l) can be obtained, by subtracting the electronic contribution (κ_e) from the total thermal conductivity (corrected measured thermal conductivity from radiation losses based on ~T^3 law [14]). The latter can be estimated by applying the Weidemann-Franz Law, $\kappa_e = \sigma\cdot L\cdot T$, where L is the Lorentz number taken[15] to be ~$2.44\cdot10^{-8}$ V^2/K^2, σ the electrical conductivity, and T the temperature.

The lattice thermal conductivity 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 6. The room temperature lattice thermal conductivity is decreased and tends to a minimum value of ~0.5 W/m·K.

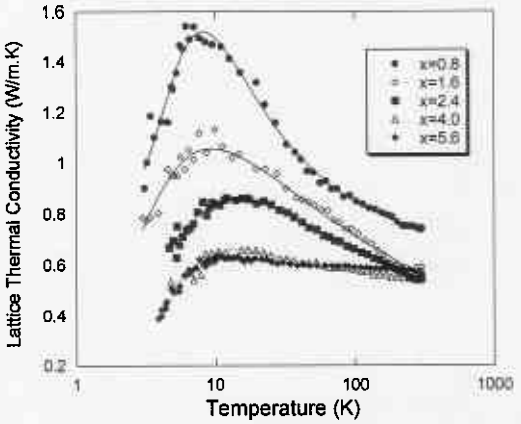


Figure 6. Lattice thermal conductivity of the $K_2Bi_{8-x}Sb_xSe_{13}$ series with Se excess.

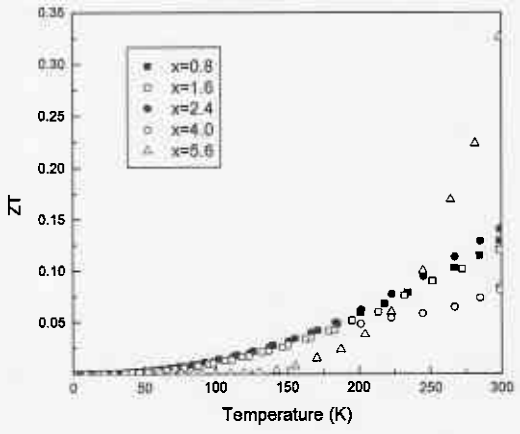


Figure 7. Thermoelectric performance ZT of the $K_2Bi_{8-x}Sb_xSe_{13}$ series with Se excess.

Thermoelectric Performance ZT

The thermoelectric performance of $K_2Bi_{8-x}Sb_xSe_{13}$ series was calculated ($ZT = \frac{S^2\sigma}{\kappa}T$) and the room temperature values

are shown in Table 1, while Figure 7 shows the increasing trend with the temperature for all members. For members with $x \leq 2.4$ there is similar increasing ZT with temperature while for the member with x=5.6 appears quite larger slope. This difference is due to the different behavior of this member with increasing electrical conductivity with temperature while Seebeck coefficient is almost constant.

The values of ZT as well as the increasing trend with temperature suggest the potential use of these materials at high temperature applications (i.e. power generation) and high temperature experimental data are needed. However, experimental data at high temperature region are necessary. Preliminary experimental data for member x=0.8 shows that Seebeck coefficient increases with temperature up to 700K, see Figure 8. The increasing trend is very encouraging since thermoelectric performance is affected strongly by Seebeck coefficient (eq. 1).

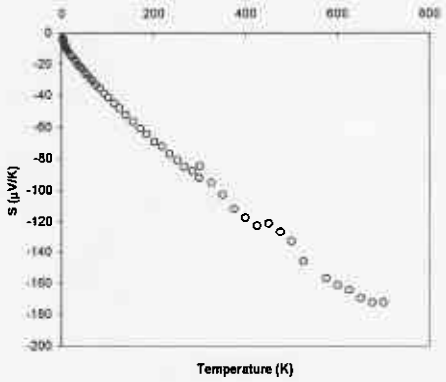


Figure 8. Temperature dependence of Seebeck coefficient of member x=0.8 of $K_2Bi_{8-x}Sb_xSe_{13}$ series from 4 to 700K.

Table 1: Room temperature values of Seebeck coefficient (S), electrical (σ) and thermal (κ) conductivity, power factor ($S^2\sigma$) and thermoelectric performance (ZT) of $K_2Bi_{8-x}Sb_xSe_{13}$ series with Se excess.

x	S (μV/K)	σ (S/cm)	κ (W/m·K)	$S^2\sigma$ (μW/cm·K^2)	ZT
0.8	-92	495	0.98	4.19	0.13
1.6	-74	746	1.07	4.09	0.11
2.4	-98	382	0.78	3.67	0.14
4.0	-161	56	0.54	1.45	0.08
5.6	-366	51	0.63	6.83	0.33
8	+730	0.01	0.75	0.05	0.00

Conclusions

In this work, $K_2Bi_{8-x}Sb_xSe_{13}$ series were studied with respect to Seebeck coefficient, electrical conductivity and Hall effect. Transport properties showed the change to semiconducting behavior with the Sb incorporation in the lattice. Seebeck coefficient measurements showed a transition from n-type to p-type of the $K_2Bi_{8-x}Sb_xSe_{13}$ series with composition. The thermoelectric performance of this series seems promising and suggests the potential of using these materials to high temperature thermoelectric applications.

Acknowledgments

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