

# Lattice thermal conductivity of $K_2(Bi_{1-z}Sb_z)_8Se_{13}$ solid solutions

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(Received 12 December 2003; accepted 20 January 2004)

The family of solid solutions of the type  $\beta$ - $K_2(Bi_{1-z}Sb_z)_8Se_{13}$  ( $0 < z \leq 1$ ) was studied with respect to thermal conductivity as a function of temperature and stoichiometry. At low temperature, the variation of lattice thermal conductivity with composition shows a transition from a typical crystalline to glasslike behavior. Analysis of the high-temperature data shows a contribution due to the mixed occupation of Bi/Sb crystallographic sites as well as an additional contribution due to point defects. © 2004 American Institute of Physics. [DOI: 10.1063/1.1682674]

## I. INTRODUCTION

Our investigations of ternary and quaternary compounds of bismuth chalcogenides<sup>1</sup> have shown that several multinary compounds containing alkali metals present promising thermoelectric properties. Alkali metals contribute to the structural complexity of these compounds and therefore, indirectly, to their electronic complexity which in turn can lead to a high Seebeck coefficient according to the Mott equation.<sup>2</sup> The complex low symmetry structure and the presence of alkali metals result in very low thermal conductivity. The alkali metals interact ionically with the metal chalcogenide framework and tend to rattle, as revealed by their high thermal displacement parameters<sup>3</sup> (“rattling” atoms—“phonon glass electron crystal”).<sup>4</sup>

$\beta$ - $K_2Bi_8Se_{13}$  was found to be a promising material due to its low thermal conductivity (i.e.,  $\sim 1.3$  W/m K) and relatively high power factor.<sup>5</sup> Its structure is highly anisotropic, see Fig. 1, and presents several salient characteristics that include two different interconnected types of Bi/Se blocks, K ions positionally and compositionally disordered with Bi atoms over the same crystallographic sites, and loosely bound K atoms in tunnels. Crystals of the material grow as long needles with the needle direction being that of highest electrical conductivity.

All state-of-the-art thermoelectric materials (e.g.,  $Bi_{2-x}Sb_xTe_3$ ) are solid solutions because increased disorder in the structure leads to lower lattice thermal conductivity. For this reason, the formula  $K_2(Bi_{1-z}Sb_z)_8Se_{13}$  was produced when  $\beta$ - $K_2Bi_8Se_{13}$  was alloyed with its isostructural  $K_2Sb_8Se_{13}$  analog. The resulting Bi/Sb substitution in the structure generates extensive mass fluctuations in the lattice

of  $K_2Bi_8Se_{13}$ . These fluctuations have a strong effect on the thermal and charge transport properties of these materials.

In previous work, selected members of the  $K_2(Bi_{1-z}Sb_z)_8Se_{13}$  series were synthesized and characterized. Crystallographic studies showed that the Sb incorporation into this lattice is in fact nonuniform<sup>6</sup> and, for low Sb concentration, only certain crystallographic sites that connect the two different type blocks (Bi9/K1 and Bi8/K3) are affected (Fig. 1). More “true” solid solutions of  $K_2(Bi_{1-z}Sb_z)_8Se_{13}$  are formed only when  $z \geq 0.2$ . The band gaps of the various members vary systematically as a function of  $z$ , except for a slight anomalous behavior at low Sb concentration.<sup>7</sup> All materials were prepared with the Bridgman technique<sup>8</sup> in order to grow large highly oriented ingot samples and study the effects along the needle direction (i.e., crystallographic  $b$  axis). Charge transport studies on selected members showed that samples have a high carrier concentration ( $\sim 10^{20}$  cm<sup>-3</sup>) and exhibit semimetallic behavior as prepared. Doping studies on  $K_2(Bi_{1-z}Sb_z)_8Se_{13}$  and  $\beta$ - $K_2Bi_8Se_{13}$  have shown that its figure of merit  $ZT$  can be substantially improved, mainly by raising the power factor.<sup>9</sup> The materials showed strong anisotropy in their thermoelectric performance. Samples prepared with excess of Se on selected solid solution members had better thermoelectric properties and higher electron mobility.

In this work, the influence of the Bi/Sb partial substitution to the lattice thermal conductivity of the  $K_2(Bi_{1-z}Sb_z)_8Se_{13}$  ( $0 < z \leq 1$ ) solid solution series was investigated. We show that the variation of the lattice thermal conductivity with composition is impacted by two contributions, one from the disorder associated with the formation of solid solutions and another arising from point defects.

## II. EXPERIMENTAL SECTION

### A. Reagents

The chemicals used in this work were generously provided by Tellurex Inc. (Traverse City, MI) as obtained: Bis-

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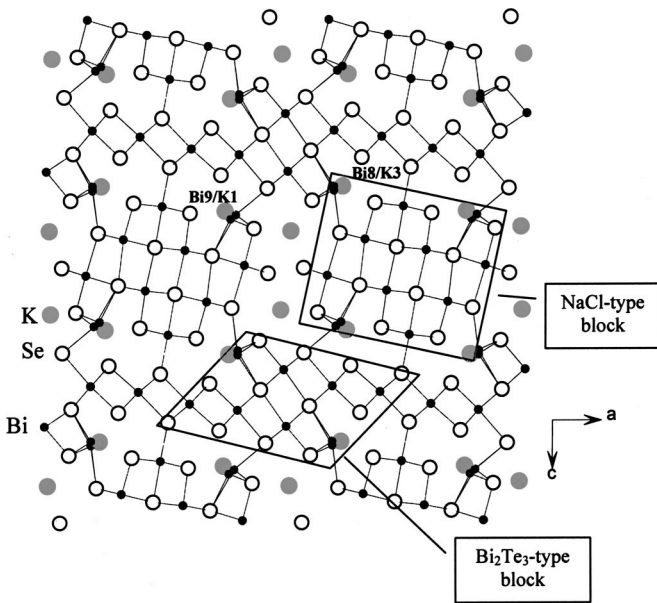


FIG. 1. Structure of  $\beta$ - $K_2Bi_8Se_{13}$  and  $K_2(Bi_{1-z}Sb_z)_8Se_{13}$  series.

muth chunks (99.999%), antimony chunks (99.999%), selenium shots (99.999%), and potassium chunks (98% Aldrich Chemical Co., Inc., Milwaukee, WI).

**B. Synthesis and crystal growth**

Selected compositions of  $K_2(Bi_{1-z}Sb_z)_8Se_{13}$  with 0.2% Se excess and  $z=0.1, 0.2, 0.3, 0.5, 0.7, 0.9$ , and 1.0 were synthesized. All manipulations of the starting materials were carried out under a dry nitrogen atmosphere in a Vacuum Atmospheres Dri-Lab glovebox. A mixture of potassium metal, bismuth, antimony, and selenium in various proportions was loaded into a silica tube and subsequently flame sealed at a residual pressure of  $<10^{-4}$  Torr. For example,  $K_2(Bi_{1-z}Sb_z)_8Se_{13}$  ( $z=0.2$ ) with 0.2% Se excess was prepared by mixing 0.271 g K (6.9 mmol), 5.086 g Bi (24.3 mmol), 0.741 g Sb (6.1 mmol), and 3.911 g Se (49.5 mmol). The mixtures were heated to 850 °C over 12 h and kept there for 1 h, followed by cooling to 50 °C at a rate of  $\sim 15$  °C/h.

Highly oriented crystal ingots of selected composition of  $K_2(Bi_{1-z}Sb_z)_8Se_{13}$  with Se excess were grown with a modified Bridgman technique. They were obtained by recrystallizing  $K_2(Bi_{1-z}Sb_z)_8Se_{13}$  in a vertical single-zone furnace, with a temperature gradient of  $\sim 15$  °C/cm. The material was placed in a rounded bottom silica tube and 13 mm outer diameter and flame sealed under a vacuum ( $<10^{-4}$  Torr). The tube was lowered through the temperature gradient profile with a dropping rate of  $\sim 0.3$  cm/h. The ingots consisted of needlelike crystals well-oriented parallel to the sample translation axis.

**C. Thermal conductivity measurements**

Thermal conductivity was determined using a longitudinal steady-state method over the temperature range of 4–300 K. In this case, samples were attached (using either a low melting point solder or silver-loaded epoxy) to the cold tip of the cryostat, while the other end of the sample was provided

with a small strain gauge resistor (thin film), which serves as a heater. Temperature difference across the sample was measured using a differential chromel-constantan thermocouple. The samples for the thermal conductivity measurements were cut in about  $3\times 3\times 5$  mm<sup>3</sup> dimensions. Measurements were carried out along the needle direction. There was inevitable radiation loss during the thermal conductivity measurements at high temperatures, therefore, the data were corrected based on  $T^3$  law.<sup>10</sup>

**III. RESULTS AND DISCUSSION**

Thermal conductivity measurements on the  $K_2(Bi_{1-z}Sb_z)_8Se_{13}$  solid solutions series were carried out along the needle direction (i.e., crystallographic  $b$  axis) for the members of  $z=0.1, 0.2, 0.3, 0.5, 0.7, 0.9$ , and the end member  $K_2Sb_8Se_{13}$ , i.e.,  $z=1.0$ .

The lattice thermal conductivity ( $\kappa_L$ ) values for the six members of the  $K_2Bi_{8-x}Sb_xSe_{13}$  series as well as the end-member  $K_2Sb_8Se_{13}$  (see Fig. 2) were extracted from the total thermal conductivity data by subtracting the electronic contribution ( $\kappa_e$ ) as described by the Wiedemann–Franz law:<sup>11</sup>

$$\kappa_e = \sigma \cdot L \cdot T, \tag{1}$$

where  $\sigma$  is the electrical conductivity,  $L$  is the Lorenz number, and  $T$  is the temperature. The Lorenz number in Eq. (1) was taken to be equal to  $2.45 \times 10^{-8}$  V<sup>2</sup>/K<sup>2</sup> as that appears to be valid for highly degenerate semiconductors.<sup>12</sup>

Thermal conduction is usually treated using the Debye approximation. In this model, the lattice thermal conductivity can be written as<sup>13</sup>

$$\kappa_L = \frac{k_B}{2\pi^2\nu} \left( \frac{k_B}{\hbar} \right)^3 T^3 \int_0^{\Theta_D/T} \tau_c \frac{x^4 e^x}{(e^x - 1)^2} dx, \tag{2}$$

where  $x = \hbar\omega/k_B T$  is dimensionless,  $\omega$  is the phonon frequency,  $k_B$  is the Boltzmann constant,  $\hbar$  is the Planck constant,  $\Theta_D$  is the Debye temperature,  $\nu$  is the velocity of sound, and  $\tau_c$  is the relaxation time. The  $\tau_c$  is determined by the various phonon–scattering processes, which limit the thermal conductivity. In the simplest model to consider, thermal conductivity is limited by the sample grain size ( $L$ ) and defect scattering at low temperatures, and Umklapp processes at higher temperatures. Using the Rayleigh rate for point defects, and the relaxation rate proposed by Glassbrenner and Slack<sup>14</sup> for the Umklapp processes, the overall relaxation rate  $\tau_c^{-1}$  can be determined as

$$\tau_c^{-1} = \nu/L + A\omega^4 + B\omega^2 T \cdot \exp\left(\frac{-\Theta_D}{3T}\right), \tag{3}$$

where the first term in Eq. (3) refers to the relaxation time for boundary scattering, the second to the defect scattering, and the third one to the Umklapp processes. The parameters  $A$  and  $B$  are both independent of temperature. In Fig. 3(a), the estimated thermal conductivity according to this simple model is shown. The parameters  $A$  and  $B$  were suitably selected to match the shape and the size of the experimentally observed peak for the thermal conductivity in the  $K_2(Bi_{1-z}Sb_z)_8Se_{13}$  series of solid solutions. As the Debye temperature ( $\Theta_D$ ) is not known for the series of the solid

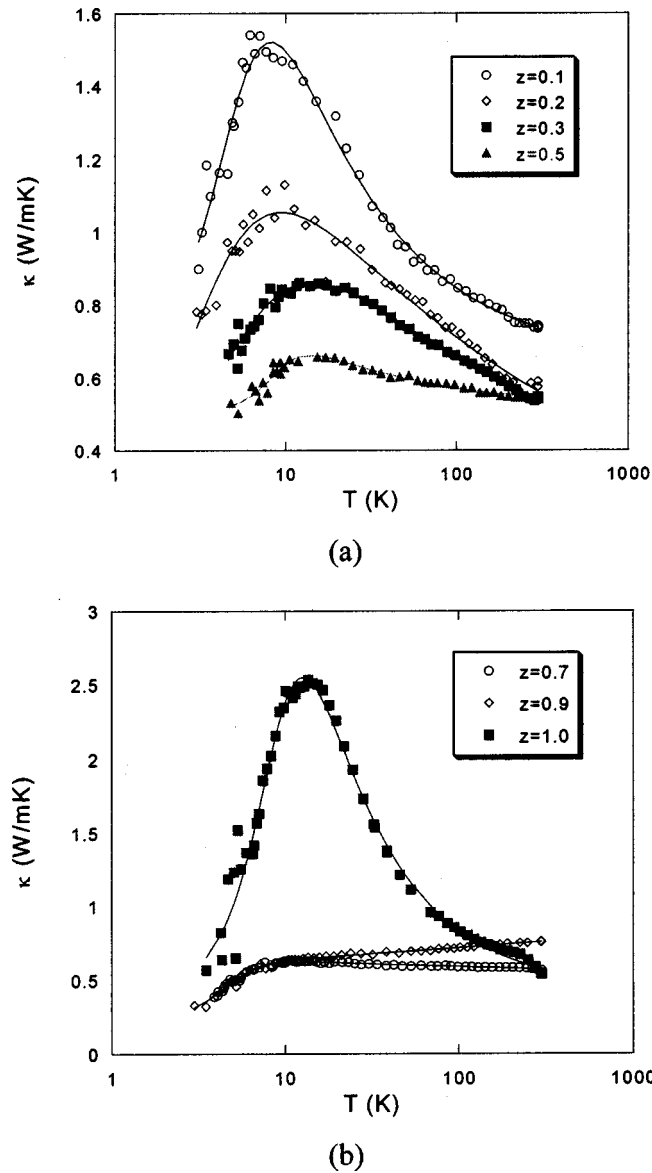


FIG. 2. Lattice thermal conductivity ( $\kappa_L$ ) of (a) Bi-rich members ( $z=0.1, 0.2, 0.3,$  and  $0.5$ ) and (b) Sb-rich members ( $z=0.7, 0.9,$  and  $1.0$ ) of  $K_2(Bi_{1-z}Sb_z)_8Se_{13}$  solid solutions series at temperature range 4–300 K. [Dashed lines follow phenomenological relation (4)].

solutions, the graph in Fig. 3 is plotted against the dimensionless  $T/\Theta_D$ . Two plots are given, increasing the concentration of defects by almost one order of magnitude (A and 5A, respectively). The calculated thermal conductivity is in good qualitative agreement with the measured data. Thermal conductivity decreases, as expected by increasing the concentration of defects, the peak becomes broader and shifts to slightly higher temperatures and the temperature dependence of the thermal conductivity becomes weaker. The  $(T/\Theta_D)^3$  curve is also presented in Fig. 3(a) to demonstrate the deviation of the thermal conductivity as expected from the ideal  $T^3$  law at low temperatures, with an increasing concentration of defects.

In Fig. 3(b), we present the thermal resistivity ( $1/\kappa$ ), as predicted by the simple three-phonon process model. We kept the term  $B$  constant in Eq. (3), and increased the concentration of defects by five-fold (curves A and 5A, respec-

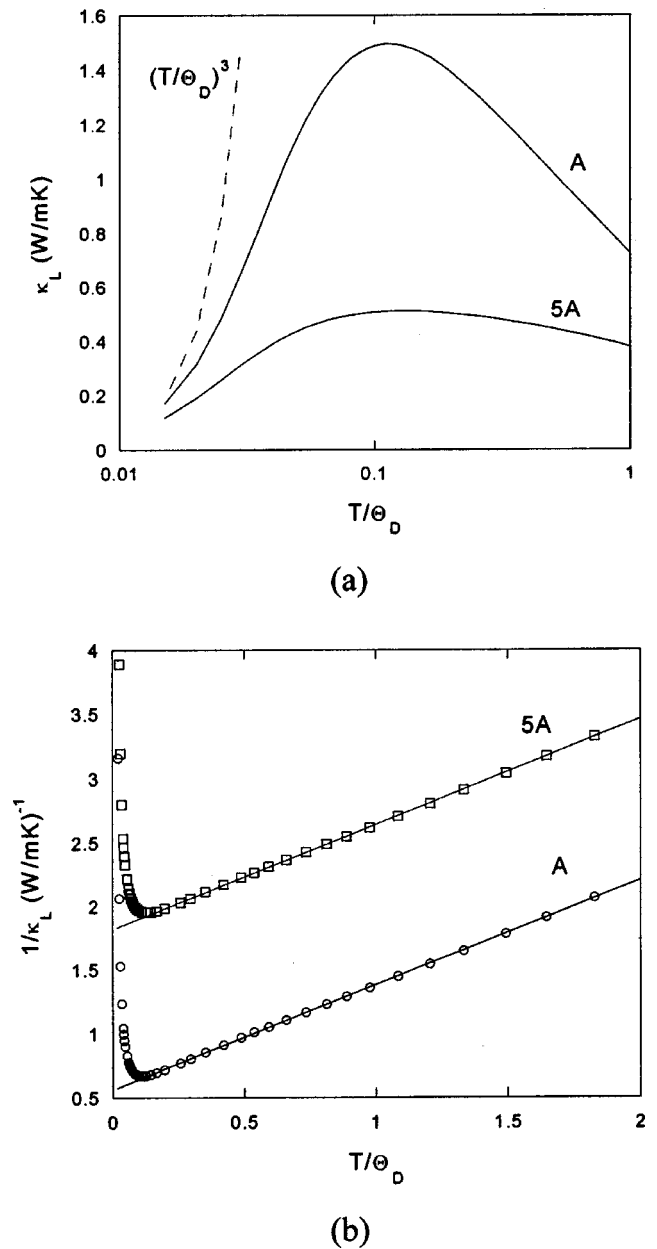


FIG. 3. (a) Calculated lattice thermal conductivity for two different concentrations of point defects (A and 5A, respectively). (b) Calculated lattice thermal resistivity for two different concentrations of point defects (A and 5A, respectively).

tively). As can be seen in Fig. 3(b), the calculated thermal resistivity exhibits a good linear relation with temperature, and the constant term in the linear trend is strongly related to the concentration of defects. The change in the slope is negligible, and this can be attributed to the constant value of the term  $B$ .

The lattice thermal conductivity of  $K_2(Bi_{1-z}Sb_z)_8Se_{13}$  series presents the expected peak at low temperatures that is caused by the competition between the phonon–boundary scattering and Umklapp phonon–phonon interactions and it is characteristic of crystalline materials,<sup>15</sup> see Fig. 2. The peak decreases with the incorporation of Sb in the lattice due to the increased disorder that is caused mainly by the Bi/Sb mass fluctuation in the structure. With the increase of Sb

concentration, this peak shifts to higher temperatures and becomes broader. The member with  $z=0.1$  possesses the strongest peak in the series, which becomes weaker for higher  $z$  values while for  $z \geq 0.5$ , there is practically no peak. These features agree with the theoretical curves of Fig. 3(a).

For  $z=1.0$  ( $K_2Sb_8Se_{13}$ ), the low-temperature lattice thermal conductivity peak is the strongest of any member of the  $K_2(Bi_{1-z}Sb_z)_8Se_{13}$  series since it lacks the Bi/Sb disorder. On the other hand, it is weaker compared to compounds, such as  $Bi_2Te_3$ ,  $Sb_2Te_3$ , etc. For example, the maximum value of this peak in  $K_2Sb_8Se_{13}$  at a low temperature is at  $\sim 2.5$  W/m K while that of  $Sb_2Te_3$  is at  $\sim 20$  W/m K.<sup>16</sup> We attribute this to the more complex structure of  $K_2Sb_8Se_{13}$  compared to  $Sb_2Te_3$ , the larger unit cell, the presence of weakly bound K atoms and the mixed occupied crystallographic sites (K/Sb).<sup>5,17</sup>

At sufficiently low temperatures (below the Umklapp peak), the lattice thermal conductivity increases following  $T^n$  dependence. Since grain-boundary scattering dominates at this temperature region, the exponent  $n$  for an ideal crystalline solid should be equal to 3.<sup>15</sup> Due to scattering in the data in the low-temperature range and the lack of data below 4 K, an accurate evaluation of the exponent  $n$  in the  $T^n$  trend was not possible. We assume that both low- (LT) and high-temperature (HT) regions,  $\kappa_{LT}$  and  $\kappa_{HT}$ , respectively, can be approximated by a power-law dependence, i.e.,  $\kappa_{LT} \sim T^n$  and  $\kappa_{HT} \sim T^m$ , and the lattice thermal conductivity  $\kappa_L$  can be expressed using the phenomenological relation:

$$\frac{1}{\kappa_L} = \frac{1}{\kappa_{LT}} + \frac{1}{\kappa_{HT}}. \quad (4)$$

Expression (4) seems to describe quite well the thermal conductivity  $\kappa_L$  for all members of  $K_2(Bi_{1-z}Sb_z)_8Se_{13}$  in the entire temperature range, as shown by the dashed lines in Figs. 2(a) and 2(b).

The exponent  $n$  in the low-temperature region, as calculated from expression (4) is found to be  $n=2.3$  for  $z=0.1$ . For the Bi-rich members, the exponent  $n$  is gradually decreased as Sb increasingly substitutes Bi ( $n=1.6$  and  $n=1.5$  for  $z=0.2$  and  $0.3$ , respectively). However, there is no clear trend for  $n$  with Sb substitution for the entire range of stoichiometry. The deviation from the expected  $T^3$  law at low temperatures indicates an additional mechanism that involves scattering of phonons by point defects at these temperatures.<sup>18</sup> Additionally, scattering due to electron-phonon interactions cannot be excluded as the Bi-rich members can exhibit a substantially high free electron concentration. The free carrier concentration is drastically decreased in the Sb-rich members<sup>19</sup> which changes the electron-phonon scattering term, which is an independent parameter and thus could be responsible for the observed lack of trend of the exponent  $n$  on Sb substitution.

In the high-temperature region,  $T > 80$  K, the exponent  $m$  ( $\kappa_{HT} \sim T^m$ ) is  $-0.27$  for  $z=0.1$  and smoothly decreases to practically zero ( $m = -0.03$ ) for the  $z=0.7$  and  $z=0.9$  members. For a crystalline and almost defect-free solid, scattering in this temperature region is mainly dominated by the three-phonon Umklapp process, and the thermal conductivity is

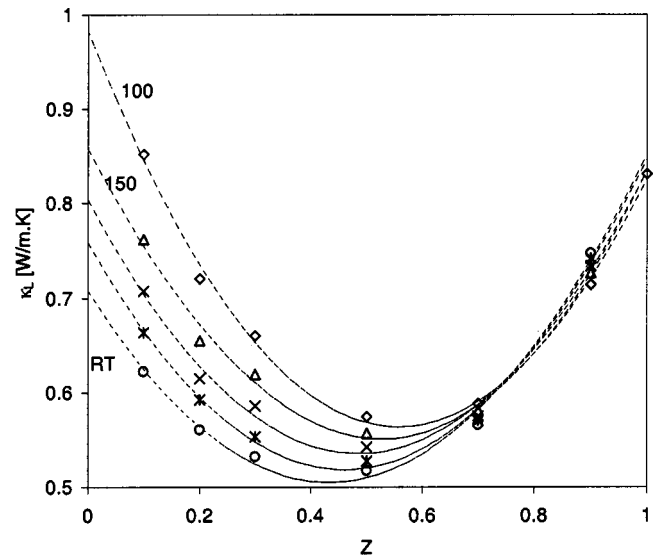


FIG. 4. Lattice thermal conductivity of  $K_2(Bi_{1-z}Sb_z)_8Se_{13}$  solid solutions series vs stoichiometry at different temperatures. Dashed lines are from a second-order polynomial fit.

expected to exhibit the usual  $1/T$  dependence. For an amorphous material, or an “electron crystal-phonon glass” (ECPG) material,<sup>4</sup> the thermal conductivity is limited by the minimum value  $\kappa_{MIN}$ , as predicted by Slack and, in this temperature region, does not show a significant temperature dependence.<sup>20</sup> The exponent  $m$  is thus expected to be zero for an ECPG-like material. In our case, the smooth decrease of the exponent  $m$  on Sb substitution is consistent with a transition from crystalline to glasslike thermal transport behavior. The relatively low value ( $m = -0.27$ ) for the  $z=0.1$  member is indicative of the presence of defects in the structure, such as mass fluctuation (Bi/Sb/K mixed occupation) and point defects. Similar behavior, with low  $m$  values, has been observed in other materials.<sup>21</sup>

The above discussion is summarized in Fig. 4, where the lattice thermal conductivity is presented versus Sb stoichiometry at different temperatures. The observed dependence is typical for solid solutions,<sup>22</sup> where a minimum in the thermal conductivity is expected for the substitution of Bi to Sb. The dependence is stronger at lower temperatures, and at 100 K, the minimum of thermal conductivity is at  $z \sim 0.6$ . As the temperature increases, the dependence becomes weaker and broader and the minimum is shifted to lower  $z$  values  $\sim 0.4$ . The weaker dependence is expected due to the smooth decrease of the exponent  $m$  upon increasing substitution. At low  $z$  values, the higher value of  $m$  causes well-separated equitemperature curves in Fig. 3. As  $z$  increases, the temperature dependence becomes weaker, and for the member  $z \approx 0.75$ , no temperature dependence is observed ( $m=0$ ).

Usually, the composition dependence of thermal conductivity  $\kappa(z)$  in solid solutions series  $A_{1-z}B_z$  can be modeled using the harmonic mean<sup>23</sup> of the two end members  $\kappa_A$  and  $\kappa_B$ , respectively, plus an additional “bowing” term



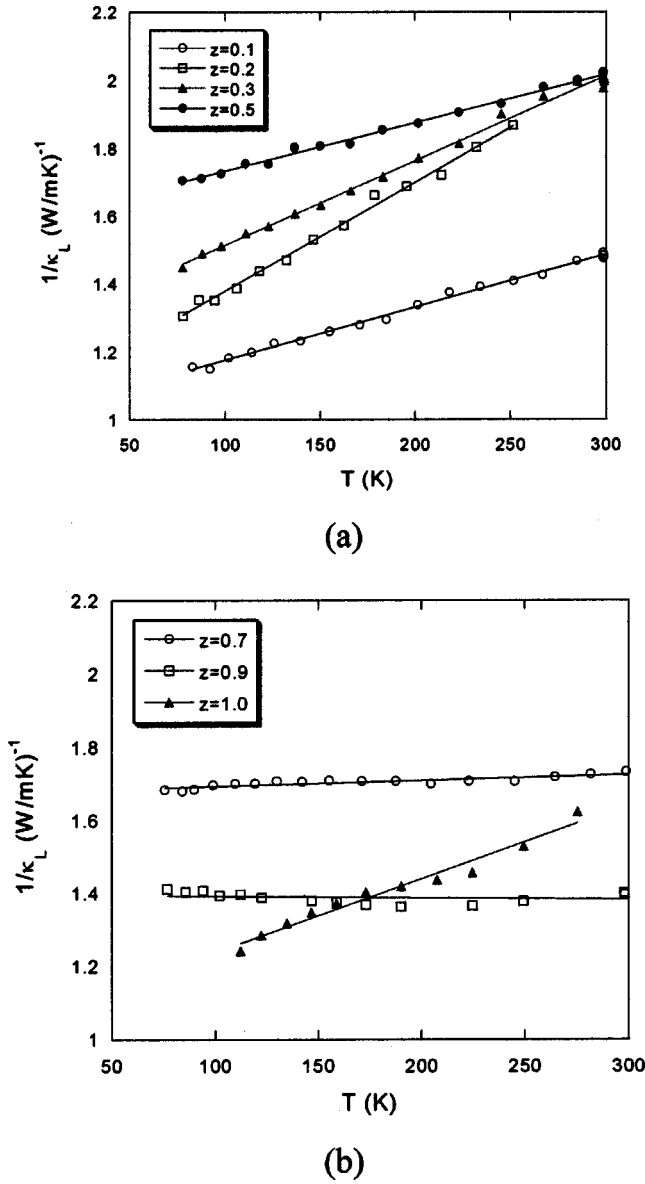


FIG. 5. Reciprocal lattice thermal conductivity of (a) Bi-rich members ( $z = 0.1, 0.2, 0.3,$  and  $0.5$ ) and (b) Sb-rich members ( $z = 0.7, 0.9,$  and  $1.0$ ) of  $\text{K}_2(\text{Bi}_{1-z}\text{Sb}_z)_8\text{Se}_{13}$  solid solutions series at temperature range of 80–300 K.

$$\begin{aligned}
 w &= \frac{1}{\kappa(z)} \\
 &= \frac{1-z}{\kappa_A} + \frac{z}{\kappa_B} + \frac{z(1-z)}{C} \\
 \Rightarrow w &= (1-z)w_A + zw_B + \frac{z(1-z)}{C}. \quad (5)
 \end{aligned}$$

The bowing term in Eq. (5) is introduced to account for the reduction of lattice thermal conductivity with the increase of Sb incorporation. In order to investigate the effect of Bi/Sb substitution quantitatively, we adopted the simple linear expression [see Fig. 3(b)] that the reciprocal lattice thermal conductivity ( $1/\kappa_L$ ) obeys in the high-temperature region (80–300 K) for all members of the  $\text{K}_2(\text{Bi}_{1-z}\text{Sb}_z)_8\text{Se}_{13}$  family, see Fig. 5. This linear dependence has been observed in other materials as well.<sup>24–26</sup> The observed linear dependence

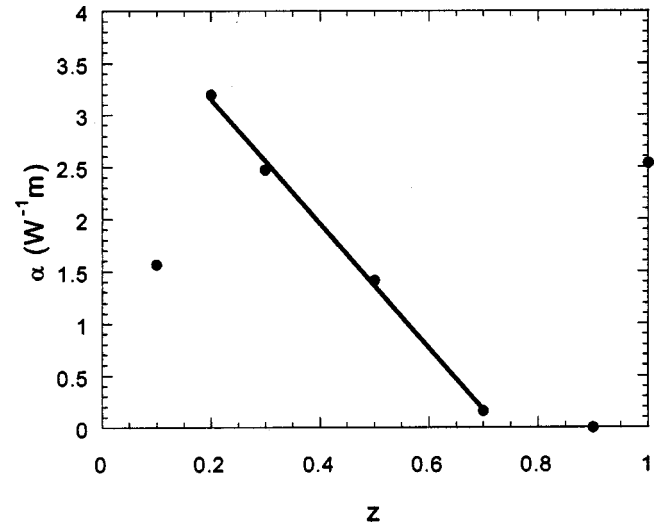


FIG. 6. Factor  $\alpha$  in lattice thermal conductivity of  $\text{K}_2(\text{Bi}_{1-z}\text{Sb}_z)_8\text{Se}_{13}$  solid solutions series vs stoichiometry.

can be understood as follows: The lattice thermal resistivity ( $w_L$ ) is considered to arise from two contributions according to

$$w_L = \frac{1}{\kappa_L} = w_0 + \Delta w = \alpha \cdot T + \beta, \quad (6)$$

where the term  $w_0$  is the lattice thermal resistivity of the ideal crystal and  $\Delta w$  represents a contribution due to the presence of defects. For the ideal defect-free crystal  $w_0 \sim T$  in the high-temperature range and  $\Delta w = 0$ . The simplicity of the empirical Eq. (6) enables us to draw some conclusions about the effect of Bi/Sb substitution, separating the expected ideal behavior of a defect-free crystal from that due to the presence of defects.

Combining Eqs. (6) and (5), we get

$$\begin{aligned}
 \frac{1}{\kappa_L} &= [\alpha_A(1-z) + z\alpha_B] \cdot T + \left[ (1-z)\beta_A + z\beta_B + \frac{z(1-z)}{C} \right] \\
 &= \alpha \cdot T + \beta. \quad (7)
 \end{aligned}$$

From Eq. (7), it follows that for  $\text{A}_{1-z}\text{B}_z$  solid solutions, the factor  $\alpha$  should vary linearly from  $\alpha_A$  to  $\alpha_B$  of the two end members, while factor  $\beta$  should vary from  $\beta_A$  to  $\beta_B$  with a bowing factor  $C$ .

In order to study how the Sb incorporation influences the terms  $\alpha$  and  $\beta$  in the lattice thermal conductivity [Eq. (7)], these parameters were extracted from fitting the data (in the region 80–300 K) for each member of the series. The two factors  $\alpha$  and  $\beta$  vary with stoichiometry.

The temperature slope (factor  $\alpha$ ) of the reciprocal lattice thermal conductivity versus stoichiometry is shown in Fig. 6. It follows a linear variation at the stoichiometric region  $0.2 \leq z \leq 0.7$ , as expected for a solid solution series according to Eq. (7). For  $z < 0.2$ , there is a preferential occupation of Sb atoms at special sites of the structure, thus only for  $z \geq 0.2$ , we have samples that are reasonably described as solid solutions. The factor  $\alpha$  tends to be zero at higher  $z$  values. This is actually related to the exponent  $m$  discussed above and expresses a transition from a typical crystalline-like lattice ther-

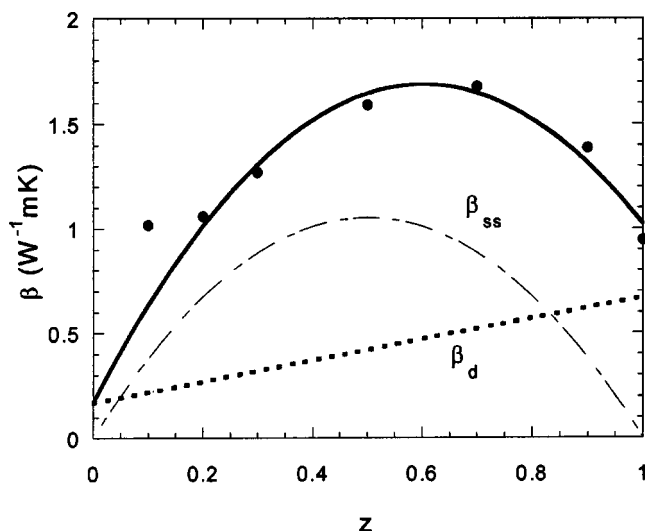


FIG. 7. Factor  $\beta$  and its contributions ( $\beta_1, \beta_2$ ) in lattice thermal conductivity of  $K_2(\text{Bi}_{1-z}\text{Sb}_z)_8\text{Se}_{13}$  solid solutions series vs stoichiometry.

mal conductivity behavior—where the Umklapp peak is well defined followed by a decrease at higher temperatures—to a behavior practically independent of temperature over a wide region with the absence of the Umklapp peak. This change in behavior seems to be completed in the stoichiometric region between  $z=0.75$  and  $0.95$  where the factor  $\alpha$  is practically zero, while  $\alpha$  becomes high again for the Sb-end member ( $z=1.0$ ) where no Bi/Sb disorder exists.

The variation of factor  $\beta$  of lattice thermal conductivity with composition is shown in Fig. 7. The variation follows a quadratic dependence, as expected from Eq. (7). Fitting of the data gave  $\beta_{\text{Bi}}=0.17 \text{ W}^{-1} \text{ mK}$  (for  $z=0$ ),  $\beta_{\text{Sb}}=1.02 \text{ W}^{-1} \text{ mK}$  (for  $z=1$ ) with bowing factor  $C=0.24 \text{ W/mK}$ , where  $\beta_{\text{Bi}}$  and  $\beta_{\text{Sb}}$  correspond to the end members  $z=0$  and  $1.0$  according to Eq. (7). Note that fitting does not include the member with  $z=0.1$  but only the true solid solution members ( $z \geq 0.2$ ).<sup>8</sup>

The variation of factor  $\beta$  is attributed to the variation in the extent of defects in the structure predominantly due to the mass fluctuation that exists in a solid solutions environment. In an ideal solid solution series where only the Bi/Sb partial substitution is responsible for random mass fluctuations, the end members should have  $\beta_{\text{Bi}}=\beta_{\text{Sb}}=0$  and the factor  $\beta$  should have a maximum value at  $z=0.5$ . In our case, the factor  $\beta$  shows a maximum at  $z \approx 0.65$  and  $\beta_{\text{Bi}}$  ( $z=0$ ) and  $\beta_{\text{Sb}}$  ( $z=1$ ) are not zero. Thus, this factor is not only due to the Bi/Sb partial substitution in the structure but also to other types of disorder and defects such as atom vacancies, antisite defects, and K/Bi or K/Sb disorder which are common in these complex chalcogenide materials.

These types of contributions (Bi/Sb and other defects) have also been reported for the lattice thermal conductivity of other solid solution series.<sup>27</sup> It was found that isotopic point defects<sup>28</sup> cause an additional term in the reciprocal lattice thermal conductivity proportional to the defect concentration  $z$ ,<sup>29</sup> whereas the formation of solid solutions introduces yet another term depending<sup>30</sup> on  $z(1-z)$ . In Eq. (7), the contribution of the formation of solid solution on factor  $\beta$

is actually expressed by the term  $\beta_{\text{ss}}=z(1-z)/C$  while the defect contribution is expressed by  $\beta_d=(1-z)\beta_{\text{Bi}}+z\beta_{\text{Sb}}$ .

The two contributions  $\beta_{\text{ss}}$  and  $\beta_d$  are shown in Fig. 6:

- (1)  $\beta_{\text{ss}}$ , which arises from the solid solution nature (mass fluctuation) of the materials exhibits a maximum at  $z=0.5$ , as expected.
- (2)  $\beta_d$ , which is due to other types of defects, exhibits a linear dependence on stoichiometry and indicates an increase of such defects when Sb is introduced in the lattice. This could be attributed to a number of possible factors such as potassium atom disorder, growth conditions, and the fact that the more Sb present in the lattice leads to lower melting point and thus higher cooling rate during the growth of the oriented ingots.

The  $\beta_{\text{ss}}$  contribution is higher for members with  $z < 0.8$ . For the members with higher Sb concentration ( $z > 0.8$ ), the  $\beta_d$  contribution becomes more dominant and suggests that the low thermal conductivity of these members is mainly due to these other defects (mentioned above) rather than the mass fluctuation present in the solid solution.

#### IV. CONCLUSIONS

In this work, the influence of the Bi/Sb partial substitution in the lattice thermal conductivity, the  $K_2(\text{Bi}_{1-z}\text{Sb}_z)_8\text{Se}_{13}$  ( $0 < z \leq 1$ ), solid solution series was examined. The low-temperature Umklapp peak of lattice thermal conductivity is gradually suppressed when the Sb concentration increases due to the increase of the disorder that is caused mainly by the Bi/Sb partial substitution. There is a transition from a typical crystalline type behavior to one that is practically temperature independent over a wide region with no Umklapp peak at a low temperature. This transition seems to be completed in the region between  $z=0.75$  and  $0.95$ . The contribution from the formation of solid solutions varies with stoichiometry showing a maximum when Sb substitutes 50% of Bi. There is also a contribution due to point defects that increases with Sb concentration in the lattice. Given the strongly anisotropic nature of these materials, it would be interesting in the future to examine thermal transport in other crystallographic directions as a function of Sb substitution.

#### ACKNOWLEDGMENTS

Financial support from the Office of Naval Research (Contract No. N00014-02-1-0867) and DARPA is gratefully acknowledged.

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