Feature Article

Complex Chalcogenides as Thermoelectric Materials: A Solid State Chemistry Approach

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Received October 1, 1998

A solid state chemical approach to discover new mateials with enhanced thermoelectric properties is described. The aim is to construct three-dimensional bismuth chalcogenide framework structures which contain ionically interacting alkali or alkaline earth atoms. The alkali atoms tend to have soft "rattling" type phonon modes which result in very low thermal conductivity in these materials. Another desirable feature in this class of compounds is the low crystal symmetry and narrow band-gaps. Several promising materials such as $BaBiTe_3$, $KBi_{6.33}S_{10}$, $K_2Bi_8S_{13}$, β-$K_2Bi_8Se_{13}$, $K_{2.5}Bi_{8.5}Se_{14}$, $Ba_4Bi_6Se_{13}$, $Eu_2Pb_2Bi_6Se_{13}$, $A_{1+x}Pb_{4-2x}Sb_{7+x}Se_{15}$ (A=K, Rb), and $CsBi_4Te_6$ are described.

Despite spectacular advances in many areas of materials research and technology during the last 40 years, the efficiency of thermoelectric materials has not improved to any significant extent during the same period. The efficiency of thermoelectric coolers operating near room temperature is only about 10% of Carnot efficiency; yet the thermodynamics of thermoelectric cooling suggests that achieving close to 100% of Carnot efficiency may be possible.

An efficient thermoelectric device is fabricated from two materials, one n-type and the other a p-type conductor. Each material is separately chosen to optimize the figure of merit, ZT, where $Z=S^2\sigma/\kappa$; T is the temperature, S the thermopower, σ the electrical conductivity, and κ the thermal conductivity. All three of these properties are determined by the details of the electronic structure and scattering of charge carriers (electrons or holes) and thus are not independently controllable parameters.[1] κ has a contribution from lattice vibrations, κ_{ph}, the phonon thermal conductivity as well as the carrier thermal conductivity κ_{el}. In order to carry a heat flux of reasonable magnitude, moderate to high carrier densities are needed (small band gap semiconductors with carrier densities of 10^{18}-10^{19}/cm^3 to metals at 10^{23}/cm^3). When the carrier densities approach 10^{23}/cm^3, κ_{el} usually is much larger than κ_{ph}. In that case, the ratio κ/σ is given approximately by the Wiedemann-Franz law, $\kappa/\sigma=L_oT$, where L_o has the value 2.45×10^{-8} watt-Ω/K^2.[2] Because cancellation in thermoelectric power can occur when both electrons and holes are dominant (*i.e.* $S=S_e+S_h$) one needs materials with preferably one type of carrier. The used in commercial devices is $Bi_{2-x}Sb_xTe_{3-y}Se_y$ alloy, and its ZT value at room temperature is about 0.9. As ZT increases, the cooling efficiency increases. Thus improving device performance means improving ZT or increasing S while keeping moderate to large carrier densities of one carrier type. Since the thermopower of optimally n or p doped $Bi_{2-x}Sb_xTe_{3-y}Se_y$ is on the order of ±220 μV/K,[3] significant improvements in thermoelectric cooling efficiencies could occur if materials of reasonable carrier density with thermopowers of 300 to 400 μV/K can be found.

Our efforts aim to synthesize bulk materials with higher figures of merit than those attainable with Bi_2Te_3. A desirable feature for these materials is a higher compositional and structural complexity than Bi_2Te_3. Along with chemical and structural complexity comes the ability to produce and control more complex electronic structures. This is certainly evident in the field of high temperature superconductors,

where the structures and six or more element compositions of the materials are well adapted to chemical control and modification of the properties. Boltzmann transport theory describes both electrical and thermal transport in the vast majority of solids. This theory provides a general understanding of the thermopower that is expressed in the Mott equation:

$$S = \frac{\pi^2}{3} \cdot \frac{k^2 T}{e} \cdot \frac{d\ln \sigma(E)}{dE} \bigg|_{E=E_F} \tag{1}$$

$\sigma(E)$ is the electrical conductivity determined as a function of band filling or Fermi energy, E_F. If the electronic scattering is independent of energy, then $\sigma(E)$ is just proportional to the density of states at E. In the general case, S is a measure of the difference in $\sigma(E)$ above and below the Fermi surface, specifically through the logarithmic derivative of σ with E. Since the thermopower of a material is a measure of the asymmetry in electronic structure and scattering rates near the Fermi level, we desire to produce complexities in either or both in a small energy interval (a few kT) near E_F.

The subject of thermoelectric materials is a now a growing and active field not only because of the several new concepts but also because of a recognized technological need for better thermoelectrics for cooling applications.[4,5] Several new ideas and approaches to the design of improved thermoelectric materials have stimulated a resurgence of interest in this old field.[6-8] Although there are many different approaches and avenues taken by different groups around the world,[9-11] here we discuss our approach to new thermoelectric materials,[12] exploring complex chalcogenide materials using newly developed solid state synthetic techniques for these systems.[12,13]

Complex Materials From The Alkali-Metal Polychalcogenide Flux Method

Structural and compositional complexity can result in corresponding complexities in the electronic structure, which may produce the required asymmetry in $\sigma(E)$ (see eq. (1)) to obtain large thermopowers. The phonon contribution to the thermal conductivity can also be lowered by such structural complexity, by choosing heavy elements as components of the material and by choosing combinations of elements that normally make moderate to weak chemical bonds. Since the known materials that are used in thermoelectric devices are chalcogenide compounds, we are searching for more complex semiconducting compounds of this type.

A significant development is the concept and realization of materials that conduct electricity like a crystalline solid but heat like a glass. In these materials a weakly bound atom or molecule 'rattler' is used to lower the thermal conductivity of the solid without severely affecting electronic conduction, thus leading to improved thermoelectric efficiency.[14,15] The class of chalcogenide materials described here fall under this description because, as it will become apparent, they are made of three-dimensional or two-dimensional bismuth-chalcogenide frameworks, stabilized by weakly bonded alkali atoms which reside in cavities, tunnels or galleries of the framework. These electropositive atoms almost always possess the highest thermal displacement parameters in the

structure, which is evidence that a certain degree of "rattling" is going on. This feature is very important in the low observed thermal conductivities of these materials.

For chalcogenide materials discovery, the use of molten alkali metal polychalcogenides, of the type A_2Q_x (A=alkali metal, Q=chalcogen) as solvents is very appropriate as we and others have demonstrated already.[13,16,17] As solvents for intermediate temperature reactions, A_2Q_x salts are especially well-suited because the melting points range between the extremes of K_2S at about 850 °C to K_2S_4 at 145 °C, with the majority of compositions melting at <300 °C. The poly-telluride versions melt between 300-500 °C. Low melting A_2Q_x fluxes remain nonvolatile over a wide temperature range, and so once above the melting point, reaction temperatures can be varied considerably without concern for solvent loss. Polychalcogenide fluxes are highly reactive towards metals because they are very strong oxidants. Reactions between metals and molten A_2Q_x are performed *in situ*. The powdered reagents (polychalcogenide and metal or metal chalcogenide) are mixed under inert atmosphere and loaded into reaction vessels of either pyrex or quartz. Once evacuated, the tubes are flame sealed and subjected to the desired heating program in a computer controlled furnace.

To synthesize new compounds, one or more metals are added directly to the A_2Q/Q reaction mixture and heated in a sealed pyrex or quartz container. Crystalline products either precipitate from the melt or form on slow cooling of the melt, depending on the specific stoichiometric and processing conditions. Presumably, the nucleated species are in equilibrium with the soluble intermediates, especially if the flux is present in excess, and hence a solvation/reprecipitation effect (often referred to as the mineralizer effect) occurs. This aids in the growth of high quality single crystals because the flux can redissolve small or poorly formed crystallites and then reprecipitate the species onto larger, well-formed crystals. The advantage of the flux method is that one allows the system to end up where it wants in the kinetic or thermodynamic sense without attempting to force upon it a certain stoichiometry or structure. Provided the temperature and time are appropriate, the reaction systems has all the ingredients to form a new phase. The benefit of this becomes apparent from the unusual compositions often found for the new materials which most certainly could not have been predicted *a-priori*.

What are the empirical guidelines with which we have to design thermoelectric materials and how do we go about choosing a particular system for exploration? We know that heavy atoms are desirable since they tend to give rise to low frequency phonons which help slow down heat transfer through a material leading to low thermal conductivity. The fact that Bi_2Te_3 is the best material known to date suggests that it combines many of the necessary features for high figure of merit. If there is something special about bismuth in giving rise to simultaneously high electrical conductivity and thermoelectric power, it could be manifested in other compounds of bismuth as well. This suggests a research direction where we could explore other, more complex, chalcogenides of bismuth in the hope that some (or all) of the key properties would be superior to those of Bi_2Te_3. Further, structurally and compositionally more complex bismuth chalcogenides would, most likely, have a low lattice

thermal conductivity. This is because a structure with a large unit cell is expected for complex materials, which would decrease the acoustic phonon mode velocities that are responsible for the transfer of heat in materials. The relatively weak Bi-Te bonding and the large atomic masses contribute as well to the low phonon velocities. Therefore, we decided to perform exploratory synthesis in this region of the periodic table and, as our results show, promising new materials can be found.

While there are several approaches to minimizing κ_{ph} the most intriguing is the one associated with the concept of "phonon glass electron crystal" which was introduced by Slack as the limiting characteristic for a superior thermoelectric.[18] Because $\kappa = \kappa_{el} + \kappa_{ph}$, one way to increase ZT is to minimize κ_{ph}. A material which is a "phonon glass electron crystal" features cages (or tunnels) in its crystal structure inside which reside atoms small enough to "rattle". This situation produces a phonon damping effect which results in dramatic reduction of the solids lattice thermal conductivity. If the atomic orbitals of the "rattle" ions do not participate in the electronic structure near the Fermi level, the mobility of carriers throughout the rest of the structure may not be substantially affected, potentially giving rise to high electrical conductivity as well as thermopower. The presence of alkali metals in the structures of ternary and quaternary bismuth chalcogenides induce the stabilization of Bi-chalcogen frameworks with cages or tunnels which accommodate the charge-balancing alkali atoms.

Ternary and Quaternary Bismuth Chalcogenides

We have obtained many interesting new bismuth containing phases by reacting the metal with alkali metal chalcogenide salts in polychalcogenide melts. One such phase is the orthorhombic $BaBiTe_3$, which was prepared at 600 °C from a K_2Te_5 or Cs_2Te_x flux in which a mixture of Bi and Ba were dissolved.[19] The structure of this material is two-dimensional with $[BiTe_3]^{2-}$ layers alternating with Ba cations (Figure 1). Many interesting features exist in the structure, one of which is the presence of Te-Te bonds between Te atoms arranged in ribbons. The flat Te ribbons contain zig-zag Te chains and they are alternating between Bi-Te blocks, which look like they have been excised out of a rock-salt structure.
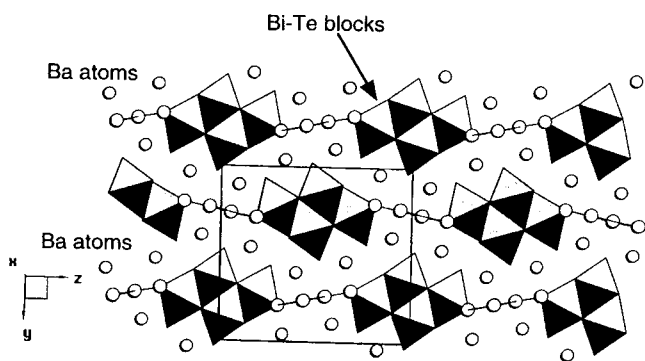
$BaBiTe_3$ is a semiconductor with a narrow band-gap of

~0.35 eV and promising electrical properties.[20] When first synthesized (from potassium polytelluride flux), the material is p-doped with an electrical conductivity in the range 10-100 S/cm and a thermoelectric power in the range of 200-400 $\mu V/K$ at room temperature. The thermal conductivity, which is crucial in assessing the compound's potential, is only 65-70% that of the rhombohedral Bi_2Te_3. The thermal conductivity is suppressed because of the low symmetry and the much larger unit cell compared to that of Bi_2Te_3. The compound also contains additional soft phonon modes from the Ba-Te interactions which are absent in Bi_2Te_3. This result suggests that generally ternary or quaternary compounds may possess lower thermal conductivity than the corresponding binary compounds. In order to fully assess the potential of this material for cooling devices, controlled n and p doping to moderately high levels must be achieved. Samples of $BaBiTe_3$ can be doped n-type and possess very high room temperature thermopower in the range of -200 to -400 $\mu V/K$. N-type material forms from Te-rich cesium polytelluride flux. In Cs_2Te_x flux Te substitution of Bi atoms could account for the n-type nature of the material. Given the similar size of K^+ and Ba^{2+}, one may speculate that in K_2Te_x flux some substitution of Ba^{2+} by K^+ atoms renders the compound p-type by creating holes in the valence band. A problem which we have to solve is the fact that the crystals, produced by this method, seem to be inhomogeneously doped so that the thermopower varies significantly from crystal to crystal even in specimens obtained from the same reaction batch. On several occasions we have observed both p-doped and n-doped crystals present in the same batch. This could be due to large temperature and composition gradients in the flux. We need to refine the preparation procedure so that these complications will be overcome.

Band structure calculations were performed at the density functional theory level for $BaBiTe_3$. The calculations suggest the material to be an indirect narrow-gap semiconductor and the electronic structure near the Fermi level is rather complex. In fact there is also a direct energy gap lying slightly higher in energy at the Z point. Several "peaks" and "valleys" are observed, see Figure 2, and these may contribute substantially to the complexity in the electronic structure giving rise to high thermopower values according to the Mott formula, see eq (1).
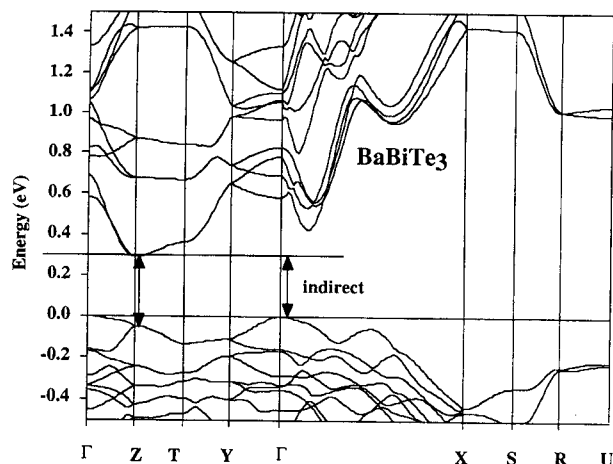

Figure 1. The low-dimensional structure of $BaBiTe_3$.

Figure 2. Electronic structure of $BaBiTe_3$ near the Fermi level.

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KBi$_{6.33}$S$_{10}$

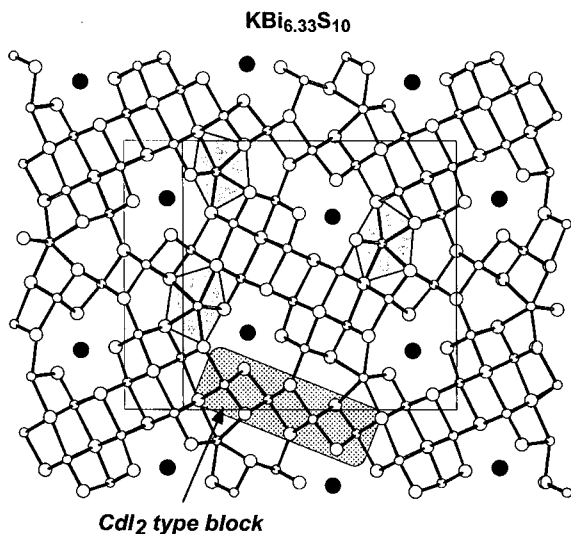**Figure 3.** Structure of KBi$_{6.33}$S$_{10}$. The shaded areas represent the high coordination sites which are occupied by both Bi and K atoms. The CdI$_2$ type block is also shown. Small open circles are Bi atoms and large dark grey circles are K atoms.

Two other interesting phases worth mentioning are the sulfides KBi$_{6.33}$S$_{10}$ and K$_2$Bi$_8$S$_{13}$.[21] They belong to the general family of compounds (A$_2$Q)$_n$(Bi$_2$Q$_3$)$_m$ (A=alkali metal; Q=S, Se) with n=1 and m=6.33, 4, respectively. Structurally, both compounds can be thought of as an intimate composite of two different structure types interconnected to form a three-dimensional network. They have orthorhombic and mono-clinic structures respectively made up of Bi$_2$Te$_3$-type (NaCl-type) blocks and CdI$_2$-type fragments that connect to form tunnels filled with eight-coordinate K$^+$ cations, see Figure 3. This may be beneficial to the electronic properties of the compounds which may bear similarities to those of Bi$_2$Te$_3$. The [Bi$_{6.33}$S$_{10}$]$^-$ framework is made of edge-sharing BiS$_6$ octahedra, as shown in Figure 3. The structure of KBi$_{6.33}$S$_{10}$ is closely related to that of the mineral cosalite Pb$_2$Bi$_2$S$_5$.[22] The relationship becomes more apparent if the formula is doubled and written as Pb$_2$Pb$_2$Bi$_4$S$_{10}$ and then compared to
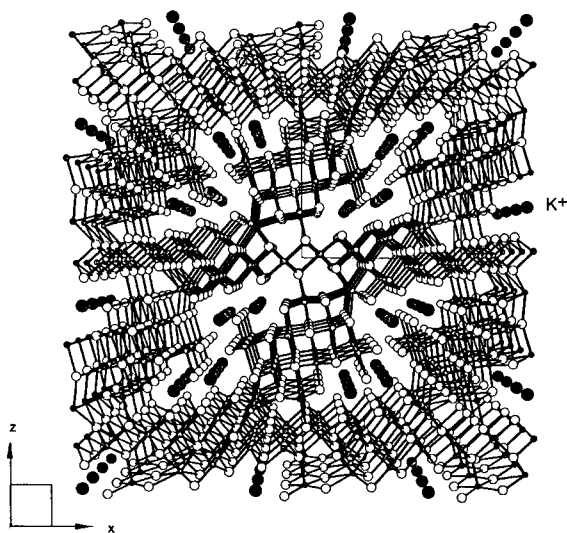

Figure 4. Perspective view of the structure of K$_2$Bi$_8$S$_{13}$. Large grey circles represent K ions, open circles represent sulfur atoms.

the rearranged formula of (☐K$_1$Bi$_{0.33}$)Bi$_2$Bi$_4$S$_{10}$ (☐=vacancy). The structure of KBi$_{6.33}$S$_{10}$ is a defect cosalite type in which the high coordination positions in the lattice are occupied by a mixture of K and Bi atoms. Perhaps this defect character of the structure gives rise to the observed very low thermal conductivity (see below).

The structure of K$_2$Bi$_8$S$_{13}$ is similar but the Bi$_2$Te$_3$-type (NaCl-type) blocks and CdI$_2$-type fragments are arranged differently, see Figure 4. In both compounds and in those described below, the alkali atoms interact with the metal chalcogenide framework via weak ionic bonds. The sizes of the tunnels in which they reside are often larger than the ionic size of the alkali metals and this gives rise to either vibrational motion or slight positional disorder.

These ternary bismuth sulfides have promising electrical properties with maximum conductivity and thermopower of 200 S/cm and ~90 μV/K, respectively. The conductivity of both compounds is in the range of 100-200 S/cm. These are unoptimized values, and we believe they can be greatly improved by further processing and systematic doping studies. Using the measured values of the electrical conductivity in conjunction with the Wiedemann-Franz law, we estimate the maximum possible value of the electronic thermal conductivity contribution to be below 1% of the total thermal conductivity. Thus, essentially all heat in these compounds is carried by lattice phonons. The pleasant surprise here comes from the rather low thermal conductivity they possess, especially KBi$_{6.33}$S$_{10}$. Taking as a bench mark the room temperature value of the total thermal conductivity of Bi$_2$Te$_3$ (κ=1.7 W/m·K)[1], we note that the total thermal conductivity of KBi$_{6.33}$S$_{10}$[23] is actually lower. This is an important finding because KBi$_{6.33}$S$_{10}$, being a sulfide, is expected to possess higher thermal conductivity compared to the heavier tellurides. If controlled doping can enhance the electrical conductivity and at the same time preserve or even increase the thermopower, in the case of KBi$_{6.33}$S$_{10}$ we indeed might have a promising thermoelectric material. To achieve this, we need additional information regarding the transport properties including carrier concentrations and mobilities. Preliminary results with polycrystalline samples indicate that KBi$_{6.33}$S$_{10}$ and K$_2$Bi$_8$S$_{13}$ have carrier concentrations of 3×10^{19} and 3×10^{20} respectively. Both KBi$_{6.33}$S$_{10}$ and K$_2$Bi$_8$S$_{13}$ melt with no decomposition at 710 °C and 713 °C, suggesting they will be amenable to thermoelectric element fabrication and processing similar to that currently used in Bi$_2$Te$_3$ technology. Doping experiments with SbI$_3$ indicate that the conductivity type of K$_2$Bi$_8$S$_{13}$ can be controlled to be n-type with room temperature thermopowers reaching - 100 μV/K. Further doping experiments are in progress.[24]

β-K$_2$Bi$_8$Se$_{13}$ is isostructural with the corresponding sulfide K$_2$Bi$_8$S$_{13}$. A previous version for this composition was found in α-K$_2$Bi$_8$Se$_{13}$ but the two structure types are completely different.[25] While both are three-dimensional, α-K$_2$Bi$_8$Se$_{13}$ has a more open structure than β-K$_2$Bi$_8$Se$_{13}$. Overall, the structure of β-K$_2$Bi$_8$Se$_{13}$ is slightly more dense than that of the α-form, because in the latter 25% of the Bi atoms are found in a trigonal pyramidal geometry, while in the former all Bi atoms are in an octahedral or higher coordination geometry, see Figure 5. The origin of the structural and property differences (see below) between these two forms
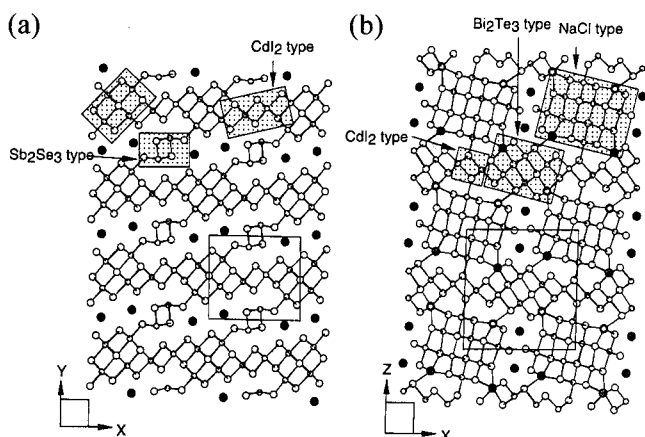
Figure 5. Comparison of the structure of α-$K_2Bi_8Se_{13}$ and β-$K_2Bi_8Se_{13}$.

lies partly in the ability of the $6s^2$ lone pair of Bi^{3+} to stereochemically express itself. As was found in the isostructural sulfide, in β-$K_2Bi_8Se_{13}$, the high coordination sites in the lattice (*i.e.* those with coordination number 7 or higher) are occupied by both K^+ and Bi^{3+} ions. The octahedral Bi sites have a smaller cavity size and do not accept K^+ ions.

$K_{2.5}Bi_{8.5}Se_{14}$ and $K_{2.5}Sb_{8.5}Se_{14}$ are isostructural to each other and also possess a complex three-dimensional anionic framework very similar to that of β-$K_2Bi_8Se_{13}$. Compositionally, $K_{2.5}Bi_{8.5}Se_{14}$ derives from β-$K_2Bi_8Se_{13}$ by addition of 0.5 equivalent of $KBiSe_2$. The main difference between the two structures is that in $K_{2.5}Bi_{8.5}Se_{14}$ only NaCl- and Bi_2Te_3-type blocks exist. $K_{2.5}Bi_{8.5}Se_{14}$ forms by addition of half "$BiSe_2$" atoms to CdI_2-type fragment in β-$K_2Bi_8Se_{13}$. In other words, the addition of "$BiSe_2$" in the CdI_2-type blocks of β-$K_2Bi_8Se_{13}$ generates Bi_2Te_3-type blocks which are five-bismuth atoms wide. This small structural modification preserves the same connectivity of the NaCl-type fragments as well as the size and shape of this K site as in β-$K_2Bi_8Se_{13}$. Although the width of the NaCl block in the structure of $K_{2.5}Bi_{8.5}Se_{14}$ is also that of three Bi polyhedra, the width of its Bi_2Te_3 block is five Bi polyhedra which is an important difference with β-$K_2Bi_8Se_{13}$, see Figure 6.
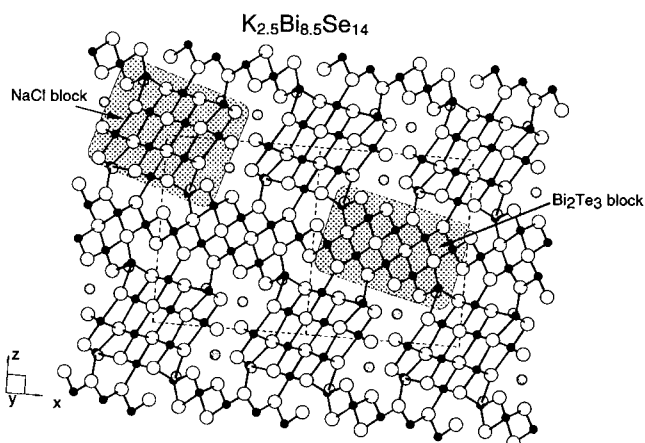

Figure 6. Structure of $K_{2.5}Bi_{8.5}Se_{14}$. The sites which display two different, nearly overlapping atoms are sites of mixed K/Bi occupancy. Open circles represent selenium atoms.
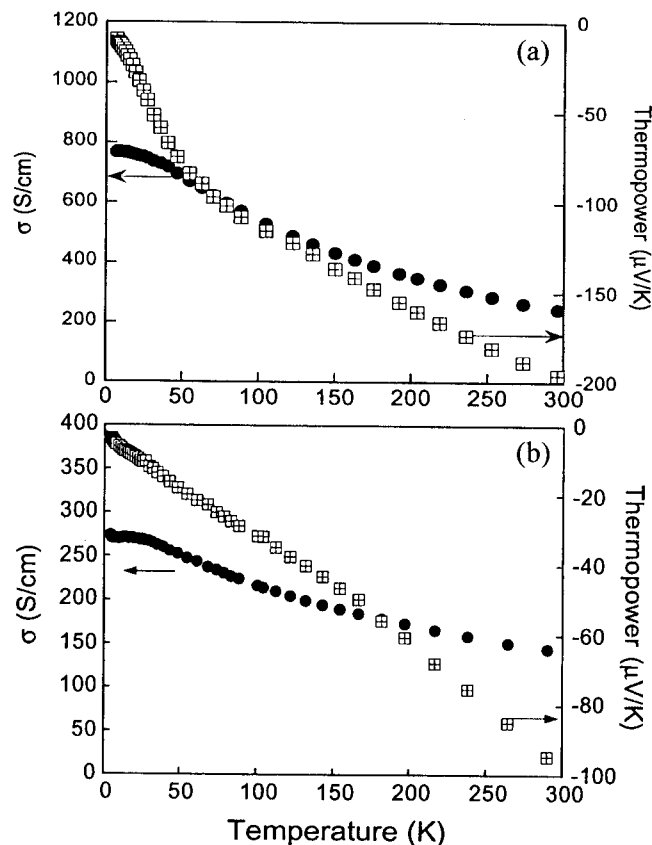

Figure 7. Electrical conductivity and thermoelectric power of (a) β-$K_2Bi_8Se_{13}$ and (b) $K_{2.5}Bi_{8.5}Se_{14}$.

A characteristic feature in the K-Bi-Q and K-Sb-Q materials is that whenever high coordination sites are found in the lattice (*i.e.* >6) a positional K/Bi or K/Sb disorder is encountered. This is attributed to the similar ionic sizes of K^+ and Bi^{3+} or Sb^{3+} in high coordination. In octahedral lattice sites, K^+/Bi^{3+} or K^+/Sb^{3+} disorder is less common. As a result, $K_{2.5}Bi_{8.5}Se_{14}$ and $K_{2.5}Sb_{8.5}Se_{14}$ show extensive mixed occupancy of K/Bi or K/Sb. This phenomenon is actually desirable in thermoelectrics because it contributes enormously to the very low thermal conductivity values found in these materials.

The electrical properties of β-$K_2Bi_8Se_{13}$ and $K_{2.5}Bi_{8.5}Se_{14}$ were measured from single crystal samples and polycrystalline ingots. The highest room temperature conductivity value obtained for single crystals of β-$K_2Bi_8Se_{13}$ was 250 S/cm with a weak negative temperature dependence consistent with a semi-metal or a narrow band-gap semiconducting material, see Figure 7. Between β-$K_2Bi_8Se_{13}$ and $K_2Bi_8S_{13}$ the selenide has a higher electrical conductivity as would be expected.

The charge carriers in these materials are electrons. The thermopower data for β-$K_2Bi_8Se_{13}$ and $K_{2.5}Bi_{8.5}Se_{14}$ show large negative Seebeck coefficients (-200 and -100 $\mu V/K$ at room temperature, respectively). The thermopower values in these materials become less negative as the temperature is decreased from 300 K to 4 K, reminiscent of a metallic behavior, but the very large Seebeck coefficients are more consistent with semiconductors.

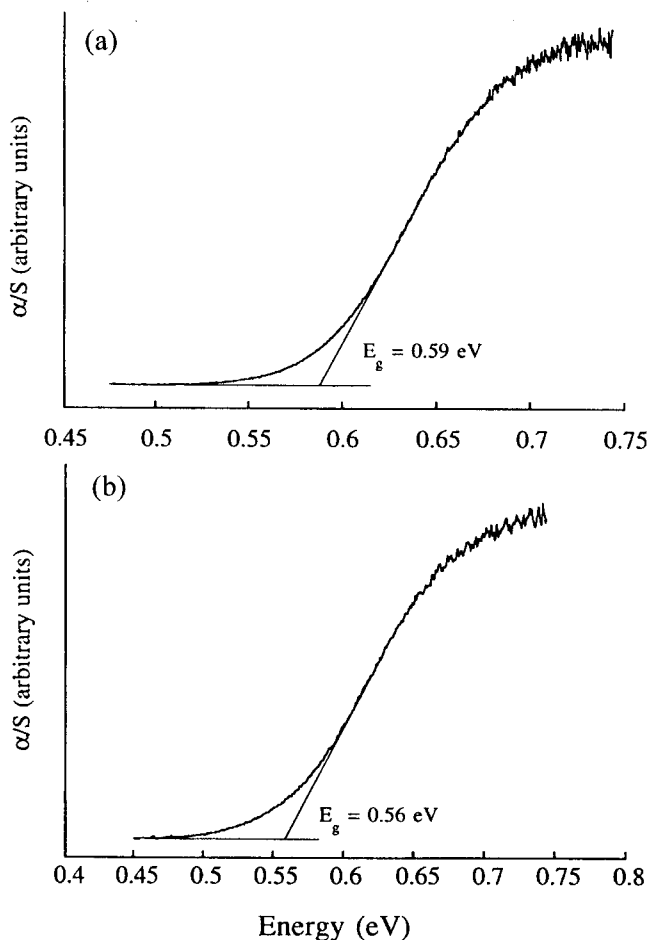Despite the metal-like temperature dependence of the

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Figure 8. Optical absorption spectra of (a) β-$K_2Bi_8Se_{13}$ and (b) $K_{2.5}Bi_{8.5}Se_{14}$.

Figure 9. Optical absorption spectra of (a) β-$K_2Sb_8Se_{13}$ and (b) $K_{2.5}Sb_{8.5}Se_{14}$.

electrical conductivity and thermopower of β-$K_2Bi_8Se_{13}$ and $K_{2.5}Bi_{8.5}Se_{14}$, the valence precise character indicated by their structure and formulation suggest they should be semiconductors. Indeed, diffuse reflectance spectroscopy on β-K_2Bi_8-Se_{13} and $K_{2.5}Bi_{8.5}Se_{14}$ at room temperature revealed the presence of well defined electronic transitions associated with a band gap of 0.59 eV and 0.56 eV, respectively, Figure 8. By comparison, the less dense structure of α-K_2Bi_8-Se_{13}, which has a slightly more open framework, has a wider gap of 0.76 eV and consequently lower electrical conductivity. In the case of the Sb analogs, we found greater band gaps at 0.78 eV for $K_2Sb_8Se_{13}$ and 0.82 eV for $K_{2.5}Sb_{8.5}Se_{14}$, see Figure 9. This is expected since Sb orbitals have smaller radial extension than Bi orbitals and tend to give rise to narrower bands. Consequently, among isostructural chalcogenide compounds the Sb analogs have higher band gaps compared to their Bi analogs (*e.g.* 0.22 eV for Sb_2Te_3 *vs.* 0.13 eV for Bi_2Te_3). The wider band gaps of the Sb analogs, $K_2Sb_8Se_{13}$ and $K_{2.5}Sb_{8.5}Se_{14}$, lead to room temperature conductivities which are 500 times lower than those of the Bi compounds. These low electrical conductivities preclude the Sb analogs from serious consideration as potential thermoelectric materials. Nevertheless, they could be used to prepare solid solutions of the type $K_2Bi_{8-x}Sb_xSe_{13}$ and $K_{2.5}Bi_{8.5-x}$-Sb_xSe_{14}.

The negative thermopower of β-$K_2Bi_8Se_{13}$ and $K_{2.5}Bi_{8.5}Se_{14}$

indicates electrons as the carriers and is consistent with slight Se deficiency. The metal-like behavior of the charge transport properties are due to doping occurring during synthesis to the point where these materials can be classified as degenerate semiconductors. Such doping could be brought about via slight non-stoichiometry between K/Bi, slight Se deficiency or slight Se excess. Annealing of β-$K_2Bi_8Se_{13}$ under vacuum at a temperature of 50 deg below its melting point causes the electrical conductivity to rise substantially from ~250 S/cm to 670 S/cm at room temperature. The metal-like slope to the data as a function of temperature is enhanced. At the same time the thermopower decreases from -200 μV/K to -100 μV/K. The negative sign of the thermopower after annealing indicates that the carrier type has not changed. The decrease in magnitude, however, together with the substantial increase in electrical conductivity indicates the number of n-type carriers in the material has increased. This could happen through the creation of Se vacancies in the lattice which results in electron injection into the materials conduction band (each Se atom generates two electrons), however, other mechanisms could be responsible as well. Crystals of $K_{2.5}Bi_{8.5}Se_{14}$ can be obtained at 600 °C but they are highly doped. Their room temperature conductivity exceeds 1100 S/cm and has a strong metal-like temperature dependence. Unfortunately, the room temperature thermopower plummets to < -6 μV/K, a value typical of
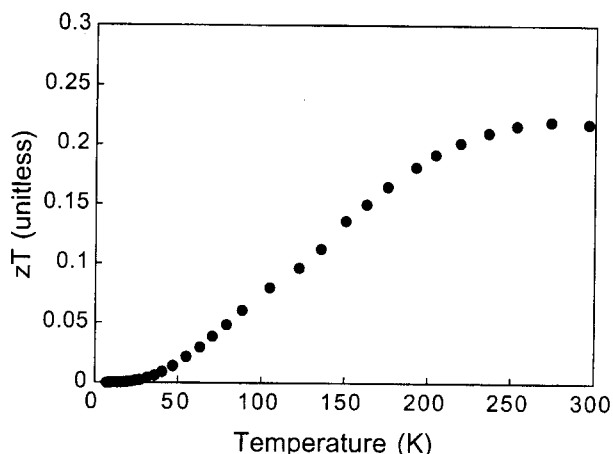
Figure 10. Thermal conductivity of a melt grown ingot of β-$K_2Bi_8Se_{13}$ as a function of temperature.

metallic materials.

The room temperature thermal conductivities of β-$K_2Bi_8Se_{13}$ and $K_{2.5}Bi_{8.5}Se_{14}$ are comparable (1.28 and 1.21 W/m·K, respectively) and similar to that of optimized Bi_2Te_3 alloy (κ_{ph}~1.3 W/m·K). A plot of the thermal conductivity of β-$K_2Bi_8Se_{13}$ as function of temperature is shown in Figure 10. These results demonstrate that it is possible to achieve lower thermal conductivity in ternary compounds with complex compositions and crystal structures compared to corresponding high symmetry binary compounds. Another reason for the very low thermal conductivities of these compounds may be the presence of alkali atoms in tunnels which are only electrostatically interacting with Se atoms on the tunnel walls. This means that these atoms are loosely bound and the fact that the thermal parameters of the K atoms are the largest in the unit cell of both compounds corroborates this. This is in agreement with Slack's suggestion of an "electron-crystal phonon-glass" being a key feature of a thermoelectric material. According to this idea, loosely bound atoms with large thermal parameters scatter phonons much more strongly than electrons so that they create a glass-like thermal conductivity without affecting the electronic mobility which is associated with the covalently bound part of the structure, that is the $[Bi_xSe_y]^{n-}$ framework. The thermal conductivity of β-$K_2Bi_8Se_{13}$ in the temperature range of 4-300 K is significantly lower than that of the isostructural compound $K_2Bi_8S_{13}$, which is consistent with the fact that the heavier Se atoms soften the lattice phonons thereby suppressing heat transport in the material. Using the measured values of the electrical resistivity in conjunction with the Wiedemann-Franz law, the maximum possible values of the κ_{el} contribution in both cases were estimated to be less than 10% of kT. Thus, essentially all heat in β-$K_2Bi_8Se_{13}$ and $K_{2.5}Bi_{8.5}Se_{14}$ is carried by lattice phonons.

Based on the results presented above, the compound β-$K_2Bi_8Se_{13}$ and $K_{2.5}Bi_{8.5}Se_{14}$ are promising as a thermoelectric materials. The room temperature ZT value is ~0.22. By comparison optimized Bi_2Te_3 has a ZT of 0.87. Given that the compounds reported here have not been optimized, it may be more fair to compare the ZT of β-$K_2Bi_8Se_{13}$ with that of unoptimized (*i.e.* as prepared) Bi_2Te_3 which is typically in the neighborhood of 0.55. The better perfor-

mance of Bi_2Te_3 derives mainly from its higher electrical conductivity (σ_{RT}~850 S/cm) since the thermopower of the materials reported here is comparable, while their thermal conductivity is equal or lower. A sensible approach to improve the thermoelectric figure of merit of these ternary compounds could be sulfur alloying or solid solutions of $K_xBi_y(Se,S)_z$ and $K_x(Bi,Sb)_ySe_z$. This type of alloying is expected to lower the κ_{ph} further and increase the thermopower by increasing energy band-gap.

Interestingly, the structure of β-$K_2Bi_8Se_{13}$ is closely related to that of $Sr_4Bi_6Se_{13}$[26] by replacing two Sr^{2+} ions with two K^+ ions and the remaining two Sr^{2+} ions with two Bi^{3+} ions. These substitutions are isoelectronic on average and do not require compositional changes in the "Bi_6Se_{13}" part of the compound. Therefore an alternative way of representing this phase is $(K,Bi)_4Bi_6Se_{13}$. The K and high coordination sites of Bi in the structure of β-$K_2Bi_8Se_{13}$ are distinct from the rest of the metal sites which are essentially octahedral. The high coordination sites are susceptible to a substantial degree of chemical substitution, provided cations of similar size are used and electroneutrality is preserved. An interesting substitution here is the replacement of the four Sr^{2+} atoms in $Sr_4Bi_6Se_{13}$ with two Ba^{2+} ions and two Pb^{2+} ions, or the replacement of two Sr^{2+} ions with two Pb^{2+} ions. This results in the isostructural compounds $Ba_2Pb_2Bi_6Se_{13}$ and $Sr_2Pb_2Bi_6$-Se_{13} as well as the solid solution compounds $Ba_{2-x}Pb_{2+x}Bi_6S_{13}$ and $Sr_{2-x}Pb_{2+x}Bi_6Se_{13}$. Interestingly, the selenide analog Ba_{2-x}-
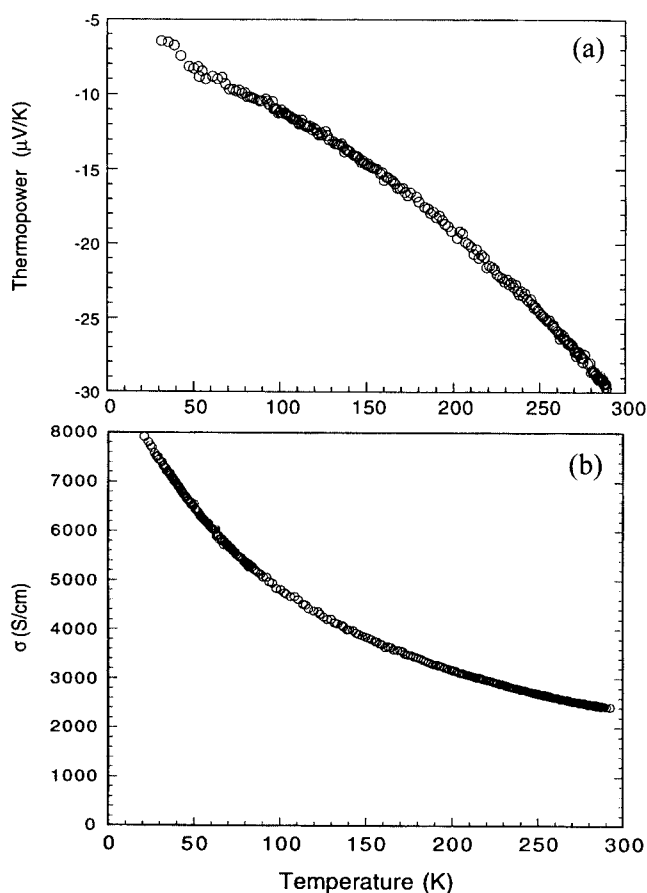

Figure 11. Thermoelectric power and electrical conductivity and as a function of temperature for a single crystal of $Ba_4Bi_6Se_{13}$.

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$Pb_{2+x}Bi_6Se_{13}$ has not been observed yet, instead a different structure type is adopted related to that of $A_{1+x}Pb_{4-2x}Sb_{7+x}Se_{15}$, see below.

The compounds $Ba_4Bi_6Se_{13}$ and $Eu_2Pb_2Bi_6Se_{13}$ are also isostructural to β-$K_2Bi_8Se_{13}$, again deriving from substitutions on the high coordination sites of the prototypical structure. Thus, in $Ba_4Bi_6Se_{13}$ the K^+ and Bi^{3+} cations are replaced with Ba^{2+} cations, while in $Eu_2Pb_2Bi_6Se_{13}$ they are replaced with Eu^{2+} and Pb^{2+} cations, see Figure 5. The remaining $[Bi_6\text{-}Se_{13}]^{4-}$ framework is shared by all these phases. Such modifications are useful in this research because they provide us with the ability to change they thermoelectric properties a great deal without changing the structure type. This should eventually help us learn more about structure-property relationships.

Preliminary charge transport data shows that $Ba_4Bi_6Se_{13}$ is obtained highly doped when first synthesized with a room temperature conductivity of 2500 S/cm, see Figure 11. The samples are n-type with corresponding Seebeck coefficient of -32 $\mu V/K$, see Figure 11. Not surprisingly, this degree of doping is not optimum for maximum ZT. The analogous $Eu_2Pb_2Bi_6Se_{13}$ is also not optimally doped with room temperature conductivity and Seebeck coefficient of 300 S/cm and -37 $\mu V/K$, see Figure 12. Both of these compounds show n-type charge transport, which is consistent with a number of possibilities including Se deficiency, Se occupation of Bi
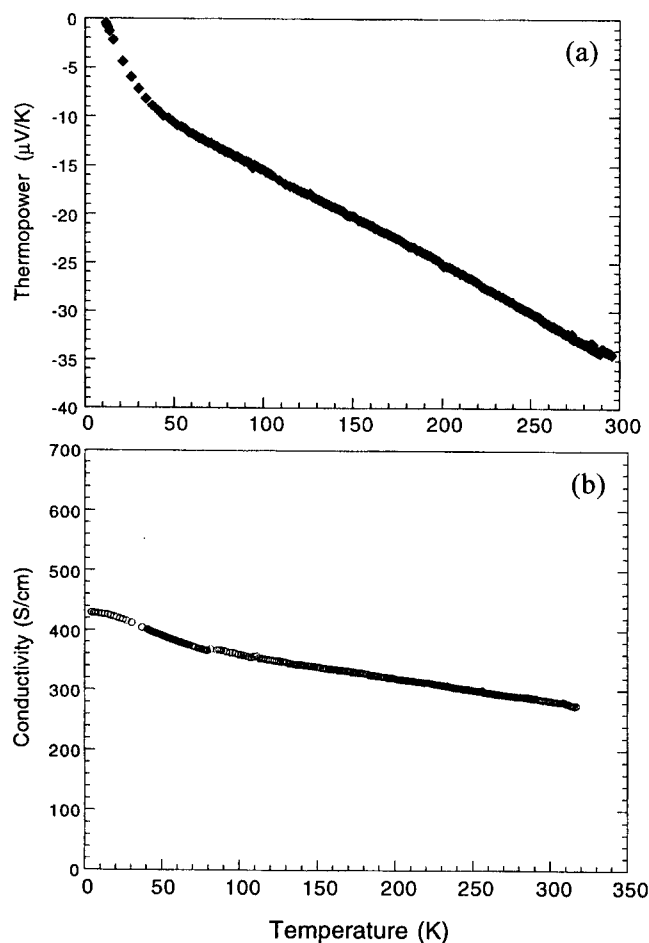

Figure 13. Structure of $A_{1+x}Pb_{4-2x}Sb_{7+x}Se_{15}$ (A=K, Rb; $0<x<2$).

sites or presence of accidental n-doping impurities. Systematic doping studies on these materials to find out whether the compounds can be doped p-type and to explore the prospects for optimization would be interesting.

The new compounds, $A_{1+x}Pb_{4-2x}Sb_{7+x}Se_{15}$ (A=K, Rb; $0<x<2$), which is closely related to $K_2Bi_8Se_{13}$ and $K_{2.5}Bi_{8.5}Se_{14}$, have recently been prepared. Figure 13 shows that these compounds also have a three-dimensional anionic framework composed of NaCl- and Bi_2Te_3-type units and K^+/Rb^+- filled channels running along the b-axis. The local environments of the alkali metal ions and sizes of the NaCl-type blocks for $K_2Sb_8Se_{13}$, $K_{2.5}Sb_{8.5}Se_{14}$, and $A_{1+x}Pb_{4-2x}Sb_{7+x}Se_{15}$ (A=K, Rb) are exactly the same. Only the width of the Bi_2Te_3-type unit in each compound is different. The relationship between these compounds can easily be seen if the composition of each compound is rewritten as the sum of the atoms in the anionic framework and the alkali metal in the channel. For example, in $K_2Sb_8Se_{13}$, one K^+ ion is stabilized in the channel and the other K^+ ion is disordered with Sb^{3+} ions in the anionic framework. Therefore, the formula can be described as K^+ $[KSb_8Se_{13}]^-$ or $K^+[M_9Se_{13}]^-$ (where M=K+Sb in the anionic framework). Similarly, $K_{2.5}Sb_{8.5}Se_{14}$ can be described as $K^+[M_{10}Se_{14}]^-$ and $A_{1+x}Pb_{4-2x}Sb_{7+x}Se_{15}$ (A=K, Rb) as $A^+[M_{11}Se_{15}]^-$ (M=K+Sb+Pb in the anionic framework). Therefore, $K_{2.5}Sb_{8.5}Se_{14}$ and $A_{1+x}Pb_{4-2x}Sb_{7+x}Se_{15}$(A=K, Rb) are the results of successively adding of "MSe" unit to $K_2Sb_8Se_{13}$.

$$K[KSb_8Se_{13}] \xrightarrow{+MSe} K[KSb_9Se_{14}] \xrightarrow{+MSe} K[K_xPb_{4-2x}Sb_{7+x}Se_{15}]$$

$$K[M_9Se_{13}] \xrightarrow{+MSe} K[M_{10}Se_{14}] \xrightarrow{+MSe} K[M_{11}Se_{15}]$$

This structure type is flexible enough to preserve the basic

Figure 12. Thermoelectric power and electrical conductivity and as a function of temperature for a single crystal of $Eu_2Pb_2Bi_6Se_{13}$.

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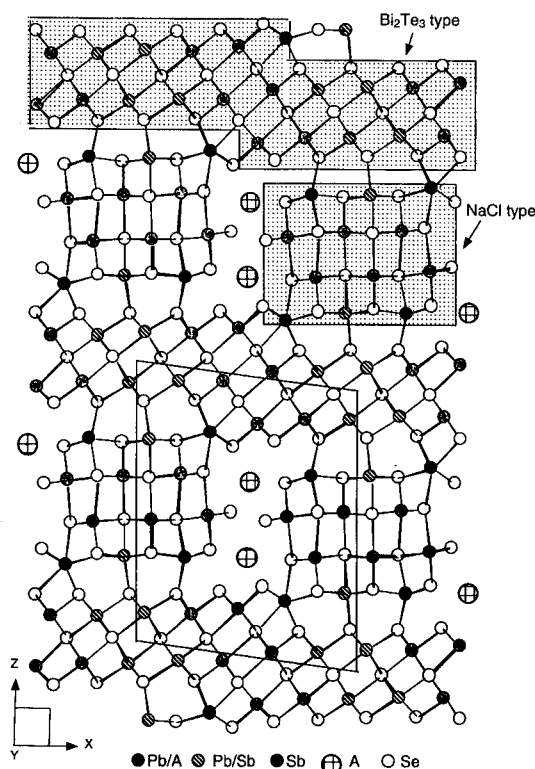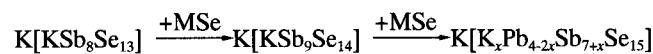*Bull. Korean Chem. Soc.* **1998**, Vol. 19, No. 12 1291
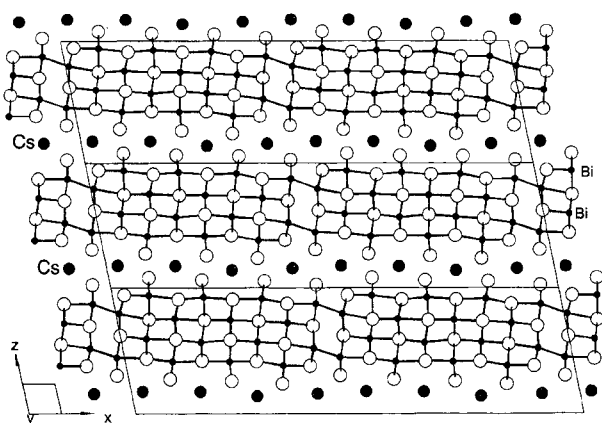

Figure 14. Structure of $CsBi_4Te_6$. Large open circles are Te atoms.

framework through successive addition of "MSe" units by adjusting the width of the Bi_2Te_3-type blocks. $A_{1+x}Pb_{4-2x}Sb_{7+x}$-$Se_{15}(A=K, Rb)$ are expected to have substantially low thermal conductivity due to the presence of heavy Pb atoms which also enhance the degree of disorder in the structure. The Pb^{2+} ions are disordered with the alkali metal ions in 8-coordinate sites and disordered with Sb^{3+} ions in octahedral sites in the framework.

An interesting feature of $A_{1+x}Pb_{4-2x}Sb_{7+x}Se_{15}$ is that these materials can be synthesized with various Pb contents as long as the ratio of cations satisfies the formula, $A_{1+x}Pb_{4-2x}$-$Sb_{7+x}Se_{15}$ ($0<x<2$). The band gap values increase (0.35-0.75 eV) as the Pb content in the compound decreases. At room temperature, these compounds show very high thermopower (~900 $\mu V/K$) but low electrical conductivity (~10 mS/cm). Recently, a Bi-analog of these compounds, $K_{1.25}Pb_{3.5}Bi_{7.25}Se_{15}$, was prepared and is under investigation. In general, Bi analogs have narrower band gaps than their Sb counterparts and, therefore, we expect that this compound will have better thermoelectric properties.

Finally, the new phase $CsBi_4Te_6$ also seems very promising.[26,27] The compound is a layered anisotropic material which grows in a needle type morphology. It is composed of anionic $[Bi_4Te_6]$ layers alternating with layers of Cs ions, see Figure 14. The average oxidation state of Bi is less than three with some of the Bi atoms forming Bi-Bi bonds. The presence of such bonds is very unusual in bismuth chalcogenide chemistry and it is not clear at the moment whether they play a role in the enhanced thermoelectric properties of the material. The Bi coordination geometry is octahedral.

Crystals of $CsBi_4Te_6$ have room temperature electrical conductivities as high as 2440 S/cm which is much higher than that of optimized Bi_2Te_3 (~850 S/cm). The room temperature thermopower ranges from 90 to 120 $\mu V/K$, lower than the 220 $\mu V/K$ typically found for optimized Bi_2Te_3. Thermal conductivity measurements on pressed pellets show values in the range 0.9-1.8 W/m·K which is comparable to that of Bi_2Te_3. These values give rise to a relatively high room temperature ZT of 0.8 at a ZT_{max} of 0.95. To calculate the ZT we had to use thermal conductivity values obtained from a pressed pellet since we are unable to make such measurements on small single crystals. Therefore, the true ZT values may be off by 20-30%. These values are some of the highest ever reported (near room temperature) for a material

other than Bi_2Te_3, and we are optimistic that improvements in the sample preparation of $CsBi_4Te_6$ as well as appropriate doping will result in significant enhancements in these properties to approach or surpass those of Bi_2Te_3.

Concluding Remarks

As was discussed here, the search for new thermoelectric materials does use general "guidelines" that help focus our attention on broad classes of materials. The promising compounds have all the necessary features which are deemed desirable in an efficient thermoelectric materials such as very low thermal conductivities, high thermopowers and electrical conductivities and complex electronic structures. Nevertheless, we still cannot predict which specific materials will have significantly better thermoelectric properties. Generally, materials with electronic structures that are complex in a narrow range of energy near E_F are the focus of the searches underway. It is clear from the above discussion that a number of new and interesting materials have emerged through systematic exploratory synthesis. A few decades ago, when the last intensive effort was spent on this subject, such materials could not have been discovered at the same rate. This is mainly because of two reasons (a) the most important characterization step, the structural elucidation, was not routinely available then and (b) synthetic techniques which allow the rapid exploration and discovery of new materials had not been developed. It must be emphasized that because the nature of this research is highly exploratory and the available guidelines are only general, many new compounds discovered are interesting from the chemical and structural perspective but are not at all suitable for thermoelectric applications.[28,29] On the bright side, there is a lot of potential for spin-off discoveries of new materials which may impact other areas and technologies; on the down side, however, these unpromising new materials need additional time for characterization and evaluation.

The search is so far highly empirical: it is guided by our past knowledge, but it is not a predictable or easily definable path. We hope that a continued and growing interaction with theorists may provide better guidance in this process. The potential payoff is enormous in scientific, technological, economic and environmental terms; yet the "risk" is high: it may take many years of focused research to find such materials. And as is usually the case, it will likely take a considerable development and engineering effort before new devices will be affordable and generally available. However, without the ability to synthesize and characterize high quality materials of considerable complexity, our chances of success could be very slim indeed.

The compounds described here fall under the "phonon glass electron crystal" concept. Our work shows that high thermopowers and high conductivities are possible in ternary and quaternary alkali-bismuth-chalcogenide systems. It is also evident that low thermal conductivities in low symmetry, large unit cell compounds which contain loosely bound alkali atoms in tunnels, are relatively easy to achieve in these systems. The application of dopants to manipulate the electron density at the Fermi level and to control the conductivity type in these materials is necessary to maximize ZT. Knowledge of the electronic band structure of the

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compounds will be useful in gaining some insight in the nature of the bands near the Fermi level. We need improvements in our ability to compute the charge transport properties based on calculated electronic band structures of materials. It is encouraging that the great challenge of understanding and predicting highly efficient thermoelectric materials is finally capturing the attention of theorists.

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