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Structure and Thermoelectric Properties of New Layered Compounds in the Quaternary System Cs-Pb-Bi-Te

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ABSTRACT

By introducing of various equivalents of PbTe into the layered framework of $CsBi_4Te_6$, the four new compounds $CsPbBi_3Te_6$ (**1**), $CsPb_2Bi_3Te_7$ (**2**), $CsPb_3Bi_3Te_8$ (**3**) and $CsPb_4Bi_3Te_9$ (**4**), were discovered. The compounds adopt layered structures built up of anionic slabs of progressively increasing thickness. The $[Pb_mBi_3Te_{5+m}]^-$ (m = 1, 2, 3, 4) slabs in the four structures can be viewed as fragments excised from the PbTe-type structures with 4-, 5-, 6- and 7-monolayers, respectively. As prepared, these materials are off-stoichiometric and n-type conductors. We present preliminary results of the crystal structures and thermoelectric properties of these materials and classify them as members of the new homologous series $CsPb_mBi_3Te_{5+m}$ (m = 1 to 4).

INTRODUCTION

The incorporation of alkaline or alkaline earth cations into the Bi_2Q_3 (Q= Se, Te) lattice led to many new phases such as α-, β-$K_2Bi_8Se_{13}$ [1,2], $K_{2.5}Bi_{8.5}Se_{14}$ [2], $BaBiTe_3$ [3], $CsBi_4Te_6$ [4], $A_2Bi_8Se_{13}$ (A = Rb, Cs) [5], $CsBi_{3.67}Se_6$ [5] and $BaBi_2Se_4$ [5]. We continued to improve the thermoelectric properties of these materials by composition doping, as in the case of β-$K_2Bi_8Se_{13}$ and $CsBi_4Te_6$. In an effort to explore the ultimate performance of $CsBi_4Te_6$ (a low temperature thermoelectric material), we introduced PbTe into its layered framework. Consequently, the four new compounds of $CsPbBi_3Te_6$ (**1**), $CsPb_2Bi_3Te_7$ (**2**), $CsPb_3Bi_3Te_8$ (**3**) and $CsPb_4Bi_3Te_9$ (**4**) were discovered by the reactions of $CsBi_4Te_6$ with increasing content of PbTe. The Pb/Bi/Te system was extensively studied for thermoelectric applications in past work [6-10]. The Pb and Bi atoms are well known to disorder on the same crystallographic positions due to their similar size and coordination preferences. In general, this results in low thermal conductivity by increasing phonon scattering. The four new compounds adopt novel layered structures built up of anionic slabs with progressively increasing thickness. These anionic slabs can be viewed as fragments excised from {PbTe}-type structure with the thickness of 4-, 5-, 6- and 7-{PbTe} monolayers. This family offers a brand-new homologous series $CsPb_mBi_3Te_{5+m}$ (m = 1 to 4) available for structural and thermoelectric investigations.

Table 1. Summary of Crystallographic Data for the $CsPb_mBi_3Te_{5+m}$ Compounds

Compounds	**1**	**2**	**3**	**4**
Formula	$CsPbBi_3Te_6$	$CsPb_2Bi_3Te_7$	$CsPb_3Bi_3Te_8$	$CsPb_4Bi_3Te_9$
Crystal Habit	needle	needle	needle	needle
a, Å	6.3326(6)	4.3456(6)	6.3736(8)	4.4524(6)
b, Å	28.667(3)	32.476(5)	37.731(5)	42.132(6)
c, Å	4.3637(4)	12.508(2)	4.4416(6)	12.742(2)
V, $Å^3$	792.1(2)	1765.2(7)	1068.1(4)	2390.3(9)
Z	4	8	4	8
Space Group	*Cmcm*	*Cmcm*	*Cmcm*	*Cmcm*
Temperature (K)	293	293	293	293
$R_1{}^a$	0.0391	0.0410	0.0597	0.0489
$wR_2{}^b$	0.1095	0.1179	0.1695	0.1250

$^aR_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $^bwR_2 = [\sum[w(F_o^2 - F_c^2)^2/\sum[w(F_o^2)^2]]^{1/2}$

RESULTS AND DISCUSSION

Crystallographic data for compounds **1**, **2**, **3** and **4** are listed in Table 1. They all crystallize in the orthorhombic space group *Cmcm.* Crystals of the four compounds were initially obtained by the reactions of $CsBi_4Te_6$ and PbTe with molar ratios of 1/1 for **1**, 1/3 for **2**, 1/4 for **3** and 1/6 for **4**. The mixtures were heated at 600 ºC and slow cooling to 50 ºC. Pure phases can also be prepared by the reactions of Cs metal and pre-reacted Pb-Bi-Te mixtures of appropriate ratio.

The layered structures of the four compounds consist of infinite anionic $[Pb_mBi_3Te_{5+m}]^-$ slabs separated with Cs^+ cations, see Figure 1. The crystallographically distinct metal sites, M, in the $[M_{m+3}Te_{5+m}]^-$ slab are octahedrally coordinated with Te atoms. The average M-Te distance is 3.173(1) Å, which is very similar to the average Bi-Te distance of 3.18 Å in $CsBi_4Te_6$. Alternatively, the $[PbBi_3Te_6]^-$ slab can be viewed as a fragment excised from PbTe-type structure along the [110] direction with a thickness of four {PbTe} monolayers, see Figure 2a. It is interesting to compare and contrast the $CsPbBi_3Te_6$ and $CsBi_4Te_6$ structures since both of them posses a M_4Te_6" type of anionic slabs. $CsBi_4Te_6$ is made of parallel infinite $[Bi_4Te_6]^-$ rods arranged side-by-side and linked with Bi-Bi bonds [4]. As some of the Bi^{3+} ions are replaced by Pb^{2+} ions to give $CsPbBi_3Te_6$, Bi-Bi bonding is no longer possible, nor necessary, and the $[Bi_4Te_6]^-$ slabs reorganize by the cleavage of Bi-Bi bonds and formation of new Bi(Pb)-Te bonds between the PbTe-type rods generating the infinite slabs of $[PbBi_3Te_6]^-$ [11].

The structure of $CsPb_2Bi_3Te_7$ (**2**) has thicker $[Pb_2Bi_3Te_7]^-$ slabs, as displayed in Figure 1b. The $[Pb_2Bi_3Te_7]^-$ slab is also a fragment excised from PbTe-type structure with 5 {PbTe} monolayers, that is one monolayer thicker than the slab in **1**, Figure 2b. Remarkably, this architecture can sustain thicker anionic slabs to give $CsPb_3Bi_3Te_8$ (**3**) and $CsPb_4Bi_3Te_9$ (**4**) structures, Figures 1c and 1d. The anionic slabs in **3** and **4**

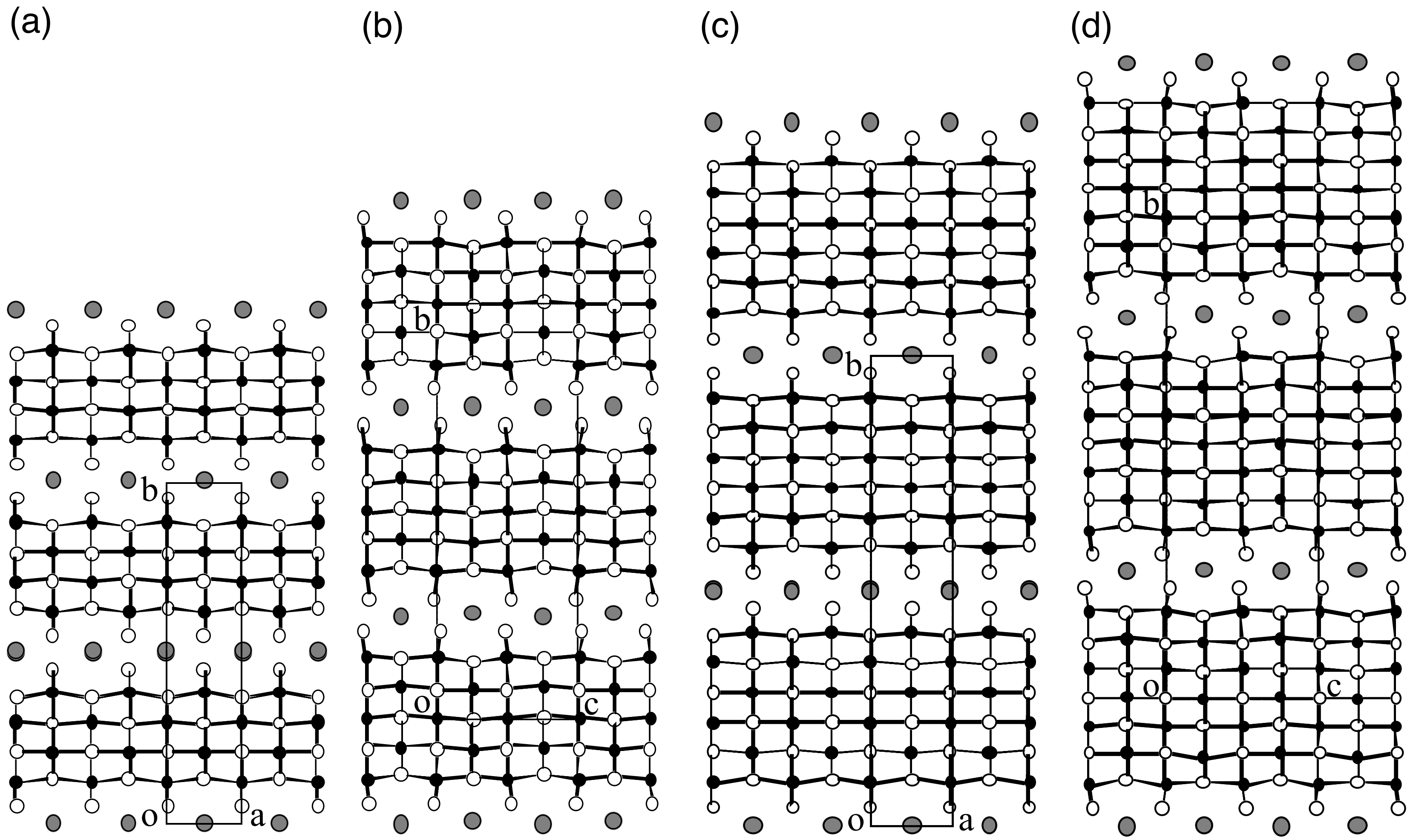

Fig 1. Projections of the structures of (a) $CsPbBi_3Te_6$, (b) $CsPb_2Bi_3Te_7$, (c) $CsPb_3Bi_3Te_8$ and (d) $CsPb_4Bi_3Te_9$. Large gray circles are Cs atoms, small dark circles are M (Pb/Bi) atoms and small open circles are Te atoms.

are also fragments of the PbTe-type structure with six and seven {PbTe} monolayers, Figures 2c and 2d. As a result, the longest *b* axes, perpendicular to the layers, are correspondingly increased and vary almost linearly with the number of monolayers. A brand-new homologous series $CsPb_mBi_3Te_{5+m}$ is then revealed by the four layered structures. As indicated by bond-valence calculations, both Bi^{3+} and Pb^{2+} ions occupy the M sites in the four structures [12]. This disordered behavior also occurs in the isostructural Sn analogs of **1** and **2**. In the latter cases with Sn the Sn/Bi disorder was resolved by single-crystal X-ray structural analysis [11].

There are some significant differences in the stacking and fine structural details of the slabs in the four compounds. First, as the slabs stack along the b axis the rows of terminal μ_2-Te atoms found on the surfaces of the slabs are arranged in staggered fashion in **1** and **3**, but they are eclipsed in **2** and **4**. Second, the μ_2-Te atom shifts away from its *m2m* site in **1** and **3** to a *m* site in **2** and **4**. The repeating units along the *c* axis in **2** and **4** are then doubled compared to the corresponding direction in **1** and **3**.

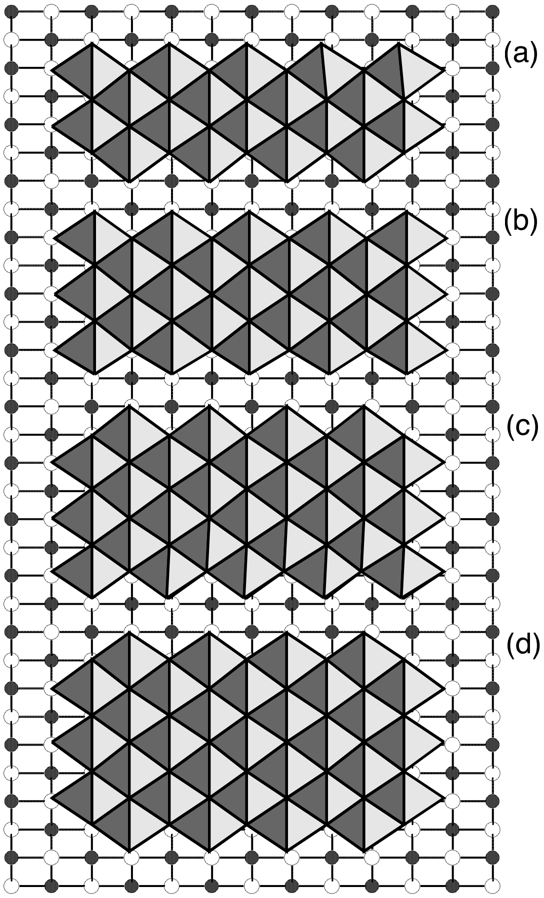

Fig 2. A view of the PbTe structure along the [110] direction. The anionic slabs in structures **1**, **2**, **3** and **4** are fragments excised from this lattice with (a) 4, (b) 5, (c) 6 and (d) 7 {PbTe} monolayers thick, respectively.

In the four structures, the Cs cations are surrounded by nine Te atoms and situated around the centers of tricapped trigonal bipyramids. Occupancy refinements showed that the Cs sites were not fully occupied in the four structures. Interestingly, the Cs atom sites are more fully occupied in the structures composed of thicker slabs and the occupancies are 85 % in **1**, 91 % in **2**, 93 % in **3** and 96 % in **4**. The final formulas of four compounds in this homologous series were then adjusted to be Bi-rich compositions for electroneutrality, which are $Cs_{0.85}Pb_{0.85}Bi_{3.15}Te_6$ of **1**, $Cs_{0.91}Pb_{1.91}Bi_{3.09}Te_7$ of **2**, $Cs_{0.93}Pb_{2.93}Bi_{3.07}Te_8$ of **3** and $Cs_{0.96}Pb_{3.96}Bi_{3.04}Te_9$ of **4**. The isostructural Sn analogues of **1** and **2** also gave similarly Cs-deficient stoichiometries, $Cs_{0.84}Sn_{0.84}Bi_{3.16}Te_6$ and $Cs_{0.88}Sn_{1.88}Bi_{3.12}Te_7$, which were determined by single-crystal X-ray diffraction analyses.

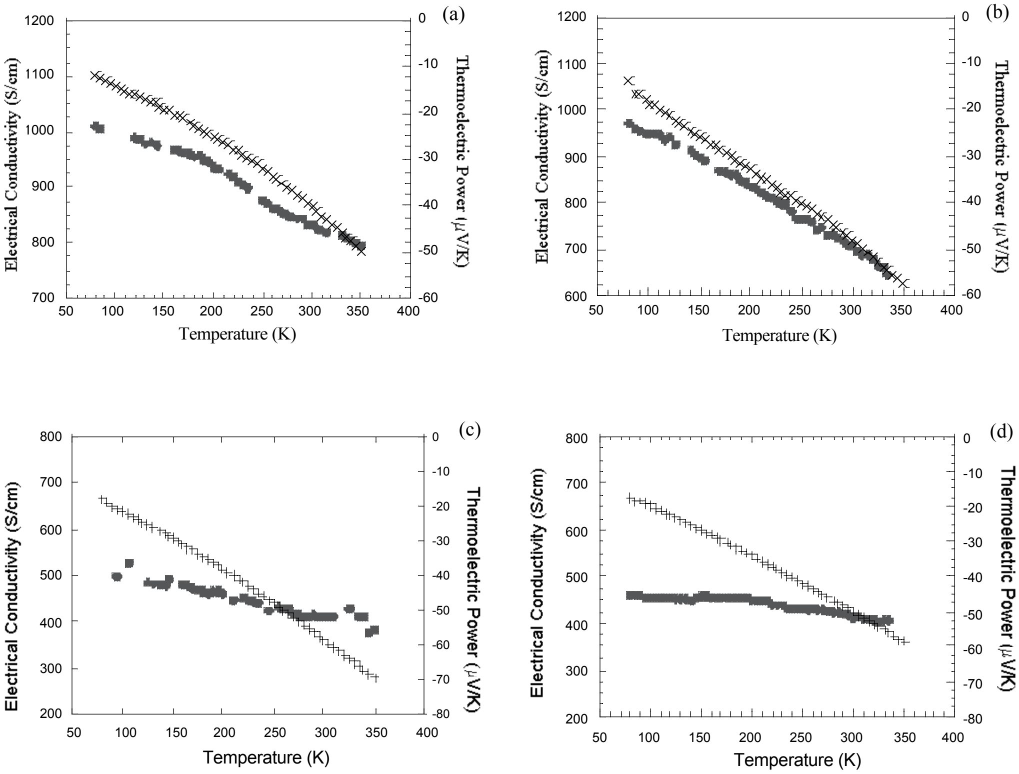

Fig 3. Variable temperature electrical conductivity and thermopower data for oriented polycrystalline ingot samples of (a) $CsPbBi_3Te_6$, (b) $CsPb_2Bi_3Te_7$, (c) $CsPb_3Bi_3Te_8$ and (d) $CsPb_4Bi_3Te_9$. The crosses are thermopower and circles are electrical conductivity.

Charge transport measurements on polycrystalline ingots of the $CsPb_mBi_3Te_{5+m}$ (m = 1, 2, 3 and 4) compounds show metallic behavior where the electrical conductivity increases as the temperature drops, Figure 3. The conductivity decrease from 1010 S/cm at 80 K to 800 S/cm at 350 K for **1**; from 970 S/cm at 80 K to 600 S/cm at 350 K for **2**; 500 S/cm at 80 K to 410 S/cm at 350 K for **3;** and from 460 S/cm at 80 K to 400 S/cm at 350 K for **4**. The values of thermopower are –50 μV/K for **1**, –57 μV/K for **2**, –70 μV/K for **3** and –50 μV/K for **4** at 350 K. The relatively low thermopower and metallic like temperature dependence of conductivity indicate that $CsPb_mBi_3Te_{5+m}$ materials are heavily doped. This is consistent with their Bi-rich non-stoichiometric nature suggested by the elemental analysis and crystallographic refinement. A Bi-rich stoichiometry will result in electron carrier excess in these materials giving rise to negative thermopower as Bi possesses an extra electron compared to Pb [11]. Remarkably, the thermal conductivities at room temperature were low for the four layered compounds. They are 1.8 W/m·K for $CsPbBi_3T_6$, 1.6 W/m·K for $CsPb_2Bi_3Te_7$ and 1.5 W/m·K for $CsPb_3Bi_3Te_8$ and $CsPb_4Bi_3Te_9$. The heavy atoms involved and long-period crystal structures play an important role in producing low thermal conductivities in the $CsPb_mBi_3Te_{5+m}$ family.

CONCLUSIONS

The four layered compounds, derived from $CsBi_4Te_6$ and PbTe, enrich the structural chemistry of multinary bismuth telluride systems and bring new groups of phases for thermoelectric studies. The compounds in this series are characterized with low thermal conductivity comparable to that of Bi_2Te_3 and $CsBi_4Te_6$. Based on this information, we will continue our efforts to improve their thermoelectric properties by compositional doping and by preparing additional analogs.

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