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Viewpoint Paper

Efficacy of lone-pair electrons to engender ultralow thermal conductivity ☆

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ARTICLE INFO

ABSTRACT

I$_B$–V$_A$–VI$_A$ compounds with intrinsically low lattice thermal conductivity have attracted considerable attention because of their potential for thermoelectric application. The anharmonicity in the lattice vibrations produced by the lone-pair electrons of nominally trivalent group V$_A$ elements may significantly reduce their thermal conductivity to a very low value (<1 W m^{-1} K^{-1}). We designed two types of material systems, AgLa$_x$Sb$_{1-x}$Te$_2$ (x = 0, 0.01, 0.03, and 0.05) and Cu$_{12}$Sb$_4$S$_{16-x}$ (x = 0, 1, 2, and 3) composites, to investigate the effect of electronic bonding at the Sb site on thermal conductivity. In both cases the experimental results support our hypothesis that the anharmonicity introduced by lone pair electrons significantly reduces thermal conductivity.

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1. Introduction

Large amounts of energy from fossil fuels are released into the environment as waste heat by power plants, industries, and vehicles. Efficient technologies to recover even a small fraction of the waste heat would make a significant contribution to reducing fossil fuel consumption and limiting greenhouse gas emission. One of the recognized technologies is thermoelectric (TE) energy conversion, which is capable of recovering energy from vehicle exhaust and industrial waste heat whenever a temperature gradient is available [1–5]. The efficiency of a TE material is determined by a figure of merit that is defined as $ZT = \alpha^2 \sigma T / (\kappa_{carr} + \kappa_{latt})$, where κ_{carr} and κ_{latt} are the carrier and lattice thermal conductivities, T the absolute temperature, and α, σ the Seebeck coefficient and electrical conductivity, respectively.

Since α, σ, and κ_{carr} depend on interrelated material properties, such as electronic band structure, Fermi level, and atomic arrangement [1,6], the most effective way to improve TE efficiency is to reduce lattice thermal conductivity κ_{latt} [2,7]. Recently, one of the strategies to reduce lattice thermal conductivity is based on the incorporation of nano-scale 'guest domains' in a 'host matrix' which enables tuning of thermal and electrical properties simultaneously

[8–10]. Benefiting from the mean free path difference of charge carriers and heat-carrying phonons, a high-density of nano-grain boundaries lowers the thermal conductivity by introducing additional strong phonon scattering without serious degradation of electrical conductivity [11,12]. Another strategy is to design a complex crystal structure with distinct atomic groups/layers to decouple the interrelated thermal and electrical attributes [13,14] which accords with the 'phonon glass-electron crystal' (PGEC) concept coined by Slack in the mid 1990s [15]. For instance, the Na/Ca–Co–O and Bi–O–Cu–Te/Se systems consist of one crystal structure layer with excellent electronic transport properties and a second type of layer, which serves as a phonon scatterer [16,17]. Skutterudites and Zintl clathrates with guest rattler atoms, which vibrate anharmonically with a large displacement in electron-crystal cages, provide another approach to designing materials with low thermal conductivity while still maintaining good electronic properties [18,19].

Compounds with intrinsically low lattice conductivity are potential candidates for high performance TE materials [14]. In 2008, ultralow thermal conductivities were reported in rock-salt structure I$_B$–V$_A$–(VI$_A$)$_2$ compounds with abnormally high Gruneisen parameters and soft frequency phonon modes, such as AgSbTe$_2$ and AgBiSe$_2$ [20–22]. Due to strong anharmonicity of the bonding arrangement in these compounds the lattice thermal conductivity is limited to a minimum possible value (<0.6 W m^{-1} K^{-1}), where the phonon mean free path equals the interatomic distance, by intrinsic Umklapp and normal phonon–

phonon scattering processes alone [20]. This seminal work has motivated further research on the effect of bonding on lattice thermal conductivity in other ternary compounds with similar bonding as $AgSbTe_2$ compound [5,23–25].

The compounds denoted as I_B–V_A–VI_A, containing group I_B (Cu, Ag), group V_A (P, As, Sb, Bi), and group VI_A (S, Se, Te) elements, can be visualized as ternary derivatives of the II_B–VI_A zincblende or wurtzite semiconductors, obtained by replacing type II_B atoms by type I_B and type V_A atoms [26]. Much attention has been paid to Cu–Sb–Se (CASe) [27–29] and Cu–Sb–S (CAS) [30] based compounds in the last few years. Recent work showed that Cu_3SbSe_3 possesses anomalously low and nearly temperature-independent lattice thermal conductivity [31], whereas Cu_3SbSe_4 does not exhibit a similar anomalous behavior [27,28]. In-depth studies suggest that s^2 lone pair orbital electrons are a key factor to achieve minimum lattice thermal conductivity in chalcogenide compounds that contain a nominally trivalent group V_A element [27]. Electrostatic repulsion between the lone-pair electrons and neighboring chalcogenide ions creates a strong anharmonicity in the phonon vibration spectroscopy [20]. The strength of the anharmonicity is determined by the coordination number of the group V_A atom and the morphology of the lone-pair orbital, for example, bond angles between V_A–VI_A bonds [27,32]. DFT calculations indicated that soft phonon modes and high Gruneisen parameters in Cu_3SbSe_3 arise from the electrostatic repulsion between the s^2 lone pair at Sb sites and the bonding charge of Sb–Se bonds [33]. The above discussion confirms that the lone s^2 pair at Sb sites plays a key role in obtaining ultralow thermal conductivity in the CASe system.

The four main crystalline phases of sulfur based CAS compounds are Cu_3SbS_4 (famatinite), $Cu_{12}Sb_4S_{13}$ (tetrahedrite) [34–37], Cu_3SbS_3 (skinnerite) [38], and $CuSbS_2$ (chalcostibite) [39,40]. Compared with materials such as $AgSbTe_2$, $AgBiSe_2$ and other selenides, the advantage of the CAS system is that copper replaces costly silver while sulfur is an alternative to toxic and less-abundant tellurium and selenium. All four phases are p-type semiconductors with band gap values between 0.5 and 2 eV, and low thermal conductivities (<2 W m^{-1} K^{-1}) [30]. Tetrahedrite crystallizes into a cubic structure, where half of the Cu atoms occupy four-coordinate distorted tetrahedral sites and the other half occupy three-coordinate triangular sites. Sb and S atoms form unique SbS_3 pyramids, and leave a void in the structure with a lone pair of electrons, just as in Cu_3SbSe_3 [27]. The Sb atoms occupy the tetrahedral site but are bonded to only three sulfur atoms, leading to the Sb 5s lone pair electrons "free" to orient along the missing vertex of the tetrahedron [41]. Sb atoms in skinnerite and chalcostibite are similarly coordinated to three S atoms in a trigonal pyramidal configuration [40,42]. However, Sb atoms in famatinite (Cu_3SbS_4) are coordinated by four sulfur atoms with ideal tetrahedral S–Sb–S bond angles, indicating that all of the Sb valence electrons form bonds with neighboring S atoms by sp^3 hybridization. No free Sb $5s^2$ lone pair electrons and void exist in famatinite. By adjusting the sulfur stoichiometry, the coordination number of Sb evolves from four to three, along with a lone pair of $5s^2$ electrons. Thus, CAS compounds are another model system to clarify the influences of lone-pair electron on thermal conductivity in addition to $AgSbTe_2$ and CASe. In this work, both $AgSbTe_2$ and CAS systems are chosen as the examples to clarify the roles of lone-pair electrons on thermal conductivity in I_B–V_A–VI_A compounds.

2. Gauging the efficacy of lone-pair electrons for ultra-low thermal conductivity

2.1. Lone-pair electron thermoelectric systems

To shed some light on the roles of lone-pair electrons on the ultralow thermal conductivity of I_B–V_A–VI_A compounds, we designed two types of material systems, $AgLa_xSb_{1-x}Te_2$ ($x = 0$, 0.01, 0.03, and 0.05) and $Cu_{12}Sb_4S_{16-x}$ ($x = 0$, 1, 2, and 3) composites, to investigate the effect of electronic bonding at the Sb site on thermal conductivity by modifying the electron charge distribution on the V_A site. First, trivalent rare earth La was chosen as a replacement element in $AgSbTe_2$ to partly remove the lone pair s^2 electrons from the Sb sites. Although there are reported results on the electrical properties of $AgLa_xSb_{1-x}Te_2$ and first-principles calculations of the properties of $La_{0.125}Ag_{0.875}SbTe_2$, the effect of La substitution on the Sb site on bonding and thermal conductivity have not been reported yet [43,44]. In $AgSbTe_2$ compound, the 5s lone-pair electrons of Sb atoms are non-bonding and form a shell of relatively large radius. But, in $AgLa_xSb_{1-x}Te_2$, all the outer shell electrons take part in the formation of hybridized sp^3 bonds around La sites due to the difference in the valence number between Sb and La atoms. In consequence, the nature of the bonding around La sites and the scenario based on lone-pair electrons may be changed totally. The influences of La substitution on electron charge distribution on Sb site and thermal properties were studied and correlated.

Then, a series of composites with an overall formula of $Cu_{12}Sb_4S_{16-x}$ ($x = 0$, 1, 2, and 3; $x = 0$ equals famatinite, and $x = 3$ tetrahedrite) were synthesized. The composition of famatinite Cu_3SbS_4 ($Cu_{12}Sb_4S_{16}$) and tetrahedrite $Cu_{12}Sb_4S_{13}$ can be defined using the same formula, $Cu_{12}Sb_4S_{16-x}$ with $x = 0$ and 3. By adjusting the S stoichiometry, the $Cu_{12}Sb_4S_{16-x}$ phases evolve from famatinite to tetrahedrite. The tetrahedrite with ultralow thermal conductivity and lone-pair electrons was added to famatinite 'matrix host' as a 'guest phase' ($x = 1$, 2). Famatinite exhibits a large positive Seebeck coefficient, along with the highest thermal conductivity of the four main crystalline phases of the sulfur based CAS compounds at room temperature [45]. The thermal conductivity of tetrahedrite is limited to a minimum possible value by the anharmonicity of the lattice vibrations, which is created by the complex unit cell which is four times as large as that of famatinite, the out-of-plane vibration of the Cu atoms on the trigonal planar sites, and the lone-pair electrons on the Sb sites [41]. Famatinite displays an indirect band gap of 1.2 eV and rather low electrical conductivity [30], while pristine tetrahedrite is metallic like with high electrical conductivity [35]. Thus, it is feasible to add metallic tetrahedrite as a second 'guest phase' to the famatinite 'matrix host' or make composites from tetrahedrite and famatinite. The thermal conductivities of the composites might also take advantage of the ultralow value of tetrahedrite and could be further reduced. That composite approach has been justified in several previous works [46,47].

2.2. Experimental details

Polycrystalline La-doped $AgLa_xSb_{1-x}Te_2$ ($x = 0$, 0.01, 0.03, and 0.05) compounds were prepared from high-purity elements La (99.9%, dendritic), Ag (99.995%, filament), Sb (99.9999%, shot) and Te (99.999%, shot) by a melt-quench-SPS method, which is described in previous papers [48,49]. The pure elements were weighed in an Ar filled glove box (MB10 Compact; MBRAUN, Germany) with oxygen and water concentration less than 1 ppm. The weighed materials were loaded into a quartz tube and sealed using an Ar plasma torch before removing from the glove box.

$Cu_{12}Sb_4S_{16-x}$ ($x = 0$, 1, 2, and 3) composites were synthesized by a mechanical alloying technique followed by SPS. Pure elements Cu (-150 mesh, 99.5%), Sb (-100 mesh, 99.5%) and S (reagent grade, purified by sublimation, -100 mesh) were loaded in a stainless steel jar filled with low pressure Ar. The mixed powders were then milled in a planetary mill at 450 rpm for 20 h. Finally the milled powders were sintered in a SPS furnace using a graphite die at 400 °C for 5 min.