Vibrational properties and thermal transport in quaternary chalcogenides: The case of Te-based compositions

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Vibrational thermal properties of $CuZn_2InTe_4$, $AgZn_2InTe_4$, and $Cu_2CdSnTe_4$, derived from binary II-VI zinc-blendes, are reported based on first-principles calculations. While the chalcogenide atoms in these materials have the same lattice positions, the cation atom arrangements vary, resulting in different crystal symmetries and subsequent properties. The compositional differences have important effects on the vibrational thermal characteristics of the studied materials, which demonstrate that low-frequency optical phonons hybridize with acoustic phonons and lead to enhanced phonon-phonon scattering and low lattice thermal conductivities. The phonon density of states, mode Grüneisen parameters, and phonon scattering rates are also calculated, enabling deeper insight into the microscopic thermal conduction processes in these materials. Compositional variations drive differences among the three materials considered here; nonetheless, their structural similarities and generally low thermal conductivities (0.5–4 W/m K at room temperature) suggest that other similar II-VI zinc-blende derived materials will also exhibit similarly low values, as also corroborated by experimental data. This, combined with the versatility in designing a variety of motifs on the overall structure, makes quaternary chalcogenides interesting for thermal management and energy conversion applications that require low thermal conductivity.

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I. INTRODUCTION

Multinary chalcogenides are a diverse group of materials with tunable electronic behaviors via a variety of possible dopants. This versatility has driven significant interest for both fundamental studies and practical applications [1,2]. For instance, chalcogenide glasses are mostly transparent from the visible to infrared spectrum and can be used in all-optical switching with suitable doping [3,4]. Some chalcogenides are also used as active catalysts in various chemical reactions [5]. The constituents of these materials are earth-abundant environmentally friendly compositions, which brings further benefit in commercial applications [6].

Multinary chalcogenides can be obtained from binary II-VI structures by a cross-cation substitution method [7], which gives rise to ternary and quaternary systems with varying properties [8–10]. Among the families of materials possible, the quaternary chalcogenides with chemical formula units I_2-II-IV-VI_4 and I-II_2-III-VI_4 (I = Cu or Ag; II = Zn or Cd; III = In, Ga, Al, or Tl; VI = S, Se, or Te) are especially interesting. They have similar structures and chemical stoichiometry, and the possibility to rearrange cations in different atomic sites gives many opportunities for fine property tuning.

The I_2-II-IV-VI_4 family of systems has been intensively investigated in the past several years due to their potential applications in photovoltaics and solar cells [11,12]. By properly choosing the cation atoms and doping configurations, one can achieve a 1.0–1.5 eV semiconducting energy gap, which is desirable for such applications [6–8,13,14]. Despite the sizable gap, the I_2-II-IV-VI_4 systems have also been shown to be attractive for thermoelectric applications. They have inherently low thermal conductivities, and with appropriate doping their energy gaps can be reduced [15,16]. On the other hand, researchers only recently began investigating the I-II_2-III-VI_4 family of materials. Experimental and theoretical studies have shown that $CuZn_2InSe_4$, $CuZn_2InTe_4$, $CuCd_2InTe_4$, $CuMn_2InTe_4$, and $AgZn_2InTe_4$ also have low thermal conductivities and varying electronic properties [17–20]. Additionally, first-principles simulations have given a comprehensive examination of the structural and electronic stabilities in terms of several possible lattice structures for this class of materials [21].

First-principles simulations have also shown that the remarkably low thermal conductivities in Cu_2ZnSnS_4 and $Cu_2ZnSnSe_4$ are directly related to the lattice structure and different phonon-phonon scattering channels limiting the phonon conduction processes [22,23]. However, no such investigations have been reported for representatives of the I-II_2-III-VI_4 class of materials.

In this work, we focus on the vibrational and thermal transport properties of $CuZn_2InTe_4$, $AgZn_2InTe_4$, and $Cu_2CdSnTe_4$. More specifically, lattice dynamical behaviors (e.g., dispersions, densities of states, and mode Grüneisen parameters) are calculated from density functional theory (DFT). These are then incorporated with quantum perturbation theory and the phonon Boltzmann transport equation to

