

Using Lone s^2 Pairs to Design Crystalline Compounds with Minimal Thermal Conductivity

V. Ozolins¹, M. Nielsen², J. Heremans²

¹Department of Materials Science and Engineering, University of California, Los Angeles, California 90095, USA

²Department of Physics, Ohio State University, Columbus, Ohio, USA

e-mail: vidvuds@ucla.edu

Good thermoelectric materials should possess a combination of seemingly incompatible properties, such as high electronic mobility and low lattice thermal conductivity. Therefore, search for crystalline materials with glass-like thermal conductivity has been an active field of research. Several cubic I-V-VI₂ semiconductors, the paradigm for which is AgSbTe₂, have been shown to exhibit minimal values of lattice thermal conductivity at ambient temperatures when the phonon mean free path equals the interatomic distance. These modes are due to the existence of highly polarizable lone s^2 electron pairs on the group V cations. Hybridization and repulsion between the lone pairs and the valence p electrons on group VI anions tends to favor locally distorted bonding configurations and may lead to unstable phonons. We present the results of first-principles density functional theory (DFT) calculations of phonon dispersion and electron-phonon interactions in cubic I-V-VI₂ semiconductors, where the group I elements are Cu, Ag, Au or alkali metals, the group V elements are P, As, or Bi, and the group VI elements are S, Se, or Te. Compounds that have only marginally stable phonons have extremely large Grüneisen parameters that result in a thermal conductivity limited by Umklapp processes to values at the amorphous limit above 200 K. Following the *ab initio* calculation, we synthesized AgSbTe₂, AgSbSe₂, AgBiTe₂, NaSbTe₂, NaSbSe₂, and NaBiTe₂ and report their thermal conductivity and specific heat: in all cases, the experiments confirm the theory.