This manuscript is concerned with predicting phonon properties (frequencies, lifetimes, thermal conductivity) of PbTe and PbSe from ab-initio calculations. The results are compared to experimental measurements, which agree fairly well. While the thermal conductivities are nearly identical, the detialed phonon properties of PbTe and PbSe differ quite significantly. Results of the phonon properties spectrum indicates that bulk nanostructuring of length scales of 10s nm are required to significantly decrease the thermal conductivity for thermoelectric applications. Alloying is suggested as a more effective method to reduce the thermal conductivity. The paper is well written and makes a good contribution to the literature. Below are minor comments which may help the authors finalize their draft.

Comments

On the other hand, recent first principles calculations have shown that the distribution is much narrower for PbTe [20], and thus, further characterizations of the distributions and the associated detailed heat conduction of lead chalcogenides are important for better material design.

It would be nice to have a comment on the results of this study [20] (which is listed as submitted). For example, are the results for PbTe in terms of the cumulative conductivity (Fig. 7) much different in [20] than in the present study? Also, is DFPT used in [20], or is the approach in [18,19] used?

Previous work by some of the co-authors [20] on the lattice thermal conductivity of PbTe based on the IFCs from fitting the Taylor expansion of the interatomic potential [18-20, 41] has reached good agreement with the experiments. Applying the same method to PbSe, however, we are unable to capture the good frequency dependence of phonon lifetimes at the low frequency region because our cubic IFCs are not accurate enough. This is probably due to the large electronegativity of PbSe and the fact that only the nearest neighbor is included for cubic IFCs calculation.

If the issue with PbSe is that only nearest neighbors are included for cubic IFCs, then why not include more nearest neighbors? The algorithm in [41] is capable of significantly reducing the number of IFCs needed to be calculated by recognizing the symmetries of the crystal. Both PbTe and PbSe are simple cubic, so the number of independent IFCs should be of the same order as those reported for FCC in [41]. Could you make some comment why only first nearest neighbors are attempted?

Through the sensitivity study of the lattice thermal conductivity with SOI and without SOI, we find that for both PbSe and PbTe, SOI effect is important and the fully relativistic pseudopotentials are necessary.

How do the predicted thermal conductivities vary? Is the effect noticeable for particular modes/frequencies, or is the effect cumulative in the predicted conductivity?

The harmonic IFCs are obtained using the primitive cell calculation of 2 atoms. In the self-consistent calculation of electronic properties, a Monkhorst-Pack 10 × 10 × 10 mesh [46] is used to sample electronic states in the first Brillouin zone and an energy cutoff of 60 Ryd (~816 eV) is used for the plane-wave expansion.

This is a very large KGRID and Ecut. For example, the results for silicon in: Appl. Phys. Lett. 91, 231922 2007, use an 8x8x8 KGRID and Ecut=27 Ry. I would have thought a smaller Ecut could be used for PbTe/Se since it is a "softer" system. Could you comment on this?

We first perform the Γ point phonon calculation to generate the harmonic IFCs for two different atomic configurations namely involving displacement of an atom in the supercell along positive and negative Cartesian directions around the equilibrium position. All the required cubic IFCs are obtained by sequentially changing the atom displaced to be any of the atoms in the primitive cell.

Is this method equivalent to that in PHYSICAL REVIEW B 67, 144304 2003?

The phonon lifetime calculations are done for 30 × 30 × 30 q-mesh points within the first Brillouin zone. The convergence of the phonon lifetimes with respect to the number of q-points has been sufficiently satisfied.

This is quite a large KGRID for the phonons. For the next smallest KGRID you used, how large are the differences in predicted lifetimes and thermal conductivity?

Due to the softening of the optical phonons, the acoustic and optical phonons are strongly coupled, as observed in PbTe by Delaire et al. [37] in the experiment and by Shiga et al. in the calculation [20], and help lower the lattice thermal conductivity.

What is the meaning of "softening of the optical phonon"? Does this refer to the reduction in group velocities of the optical modes?

Fig. 7 Cumulative thermal conductivity with respect to phonon mean free path at 300 K for PbSe (red dashed line), PbTe (black solid line) and PbTe0.5Se0.5 (blue dotted line)

Previous studies [15-17] demonstrated the competence of the nanostructuring in suppressing the lattice thermal conductivity and thus improving zT .

Most of the recent experimental studies on the strong reduction of the lattice thermal conductivity in nanostructured PbTe [9, 10] emphasized the importance of dislocations, nanoscale precipitates and strain while pointing out that the mere presence of nanostructuring cannot sufficiently increase the phonon scattering.

It would be interesting to use the phonon lifetimes (MFPs) you have predicted in boundary scattering calculations, such as: *Applied Physics Letters* **100** (2012) 061911. In particular, it would be interesting to see what is predicted for PbTe/PbSe systems with grain boundaries, dislocation boundaries, etc., as in [9,10]. Also, your results indicate that not significant decrease in thermal conductivity should be expected until nanostructure geometries are smaller than 10 nm. It would be interesting to see what the boundary scattering method(s) predict for different nanostructures with the same characteristic length scales, such as thin film thickness, nanowire diameter, etc. Perhaps there is an optimal geometry.