



Temperature dependent band gap in PbX (X = S, Se, Te)

Zachary M. Gibbs,¹ Hyoungchul Kim,^{2,3} Heng Wang,⁴ Robert L. White,⁵ Fivos Drymiotis,⁴ Massoud Kaviani,² and G. Jeffrey Snyder^{4,a)}

¹Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125, USA

²Department of Mechanical Engineering, University of Michigan, Ann Arbor, Michigan 48109, USA

³High-Temperature Energy Materials Research Center, Korea Institute of Science and Technology, Seoul 136-791, South Korea

⁴Department of Materials Science, California Institute of Technology, Pasadena, California 91125, USA

⁵Department of Chemistry and Biochemistry, University of Oklahoma, Norman, Oklahoma 73019, USA

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PbTe is an important thermoelectric material for power generation applications due its high conversion efficiency and reliability. Its extraordinary thermoelectric performance is attributed to band convergence of the light L and heavy Σ bands. However, the temperature at which these bands converge is disputed. In this letter, we provide direct experimental evidence combined with *ab initio* calculations that confirm an increasing optical gap up to 673 K and predict a band convergence temperature of 700 K, much higher than previous measurements showing saturation and band convergence at 450 K. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4858195>]

Thermoelectric materials convert waste heat to useful electrical energy. The thermoelectric conversion efficiency is described by the figure of merit, $zT = \frac{S^2\sigma}{\kappa}T$, where S is the Seebeck coefficient, σ is the electrical conductivity, and κ is the thermal conductivity. A large Seebeck coefficient is found in low carrier concentration (n) insulators, while high electrical conductivity ($\sigma = 1/\rho$) is found in high carrier concentration metals. As a consequence, most good thermoelectric materials are heavily doped semiconductors with carrier concentrations between 10^{19} and 10^{21} carriers/cm³. Current state-of-the-art thermoelectric materials that are used in waste heat recovery have zT values near 1.0, which corresponds to less than 10% energy conversion efficiency when device losses are taken into account. An average zT in the range from 1.5 to 2 would enable substantial waste-heat harvesting and up to a 10% fuel reduction in the case of automotive applications.¹

Recent reports on PbTe and its alloys have suggested an extraordinarily high peak zT of between 1.5 and 2.2 depending on the specific dopant and alloy.^{2–6} The reports have led to a renewed interest in the lead chalcogenides and have generated a debate concerning the mechanism for their high thermoelectric performance. The mechanism is believed to be the enhanced degeneracy arising from band convergence, which yields higher thermopower without greatly reducing carrier mobility.⁷ P-type PbTe has a complex valence band structure that involves a light band at the L point (direct gap) and a region of electronic states centered along the Σ line. This region along the Σ line has been described and modeled as a separate, heavy band, even though recent work suggests it may be associated with the band at L.^{8–10} However, two-band analysis, e.g., when both bands are considered separately, is consistent with most experimental observations and is useful for rational thermoelectric material design.^{3,7,11,12} Based on historical evidence^{13–15} and calculations,^{9,10,16,17}

the band extremum at Σ is believed to lie about 0.1–0.15 eV below that of the band at L at room temperature (see Figure 1(d)). Still, the exact band energies and their temperature dependence continue to be disputed.^{7–10} Knowledge of the specific band offset and its temperature dependence in these materials is crucial since band convergence is thought to be responsible for the improved thermoelectric properties. Hence, this work is motivated by the hope that a more accurate understanding of the electronic band structure can provide a clearer route forward to band structure engineering in the lead chalcogenides for further improvement of zT .

Electrical and magnetic measurements have been performed previously to characterize the energy band structure—including estimates of the valence band offsets and their temperature dependence.^{8,13–15,18–23} Nevertheless, interpretation of the results depends upon transport models. Optical absorption edge spectroscopy in semiconductors is a more direct route to obtain information about electronic states near the band edge and specifically information concerning the value of the band gap E_g . Optical data on single crystalline bulk samples and films of lead chalcogenides have been obtained using a variety of measurement techniques,^{24–30} but the analysis of these results, including the reported observation of band convergence, have recently been questioned.^{8,10} Here, we perform measurements using diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) on polycrystalline samples and use *ab initio* molecular dynamics (AIMD) to study the temperature dependent gap and to examine the band structure at high temperatures. DRIFTS has been shown to be a reliable technique capable of quantifying small shifts in the electronic band structure, especially the band gap with high resolution (± 0.004 eV).³¹ Our optical and calculation results indicate a higher convergence temperature, which is supported by an optical gap that continues to increase up to 670 K. This is contrary to historical literature observations and confirm claims made in a recent report by Jaworski *et al.*⁸ More importantly, we are presenting direct experimental evidence that clearly show that the band gap continues

^{a)}Author to whom correspondence should be addressed. Electronic mail: jsnyder@caltech.edu

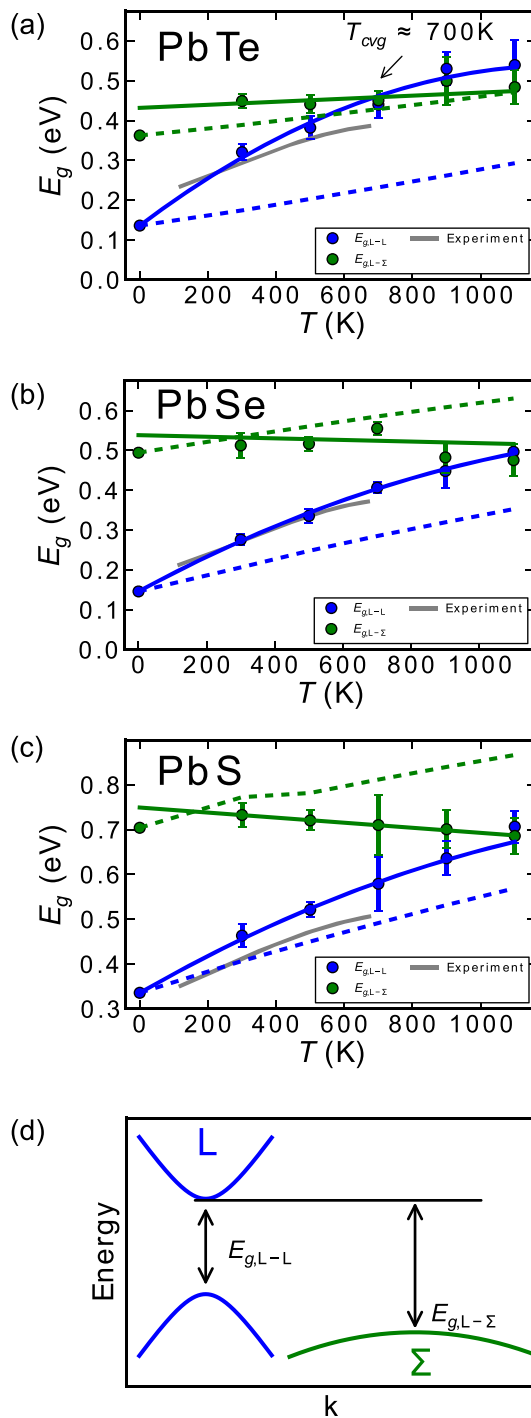


FIG. 1. (a) *Ab initio* MD/DFT calculation of the electron-phonon interaction and lattice expansion contributions to the temperature dependence of the band gap in PbTe plotted with experimental data (solid grey line). Solid lines (blue and green) are a guide to the eye, while dashed lines represent the calculated contribution due to lattice thermal expansion only. (b) and (c) show the same results for PbSe and PbS, respectively. (d) A near edge band structure diagram for the lead chalcogenides.

to vary with temperature above the previously reported saturation temperature of 450 K. Additionally, we have included lattice expansion in AIMD simulations in order to determine the relative contributions of thermal expansion and electron-phonon interaction to the shifting band gap as a function of temperature.

Absorption edge measurements were carried out using a Nicolet 6700 FTIR Spectrophotometer equipped with Praying

Mantis Diffuse Reflectance attachment (Harrick Scientific Instruments) as described in a previous work.³¹ A high/low temperature stage, also from Harrick, was used to vary the sample temperature from 120 to 673 K. Measurements were performed under an argon atmosphere after rough pumping and purging the sample chamber several times. The scans were referenced to KBr standard samples at the same temperatures. Optical gaps were extracted using the Tauc method,³² where $[(\alpha - \alpha_{min})\hbar\omega]^n$ was extrapolated to zero as a function of $\hbar\omega$; α is the absorption coefficient (whose proportionality was calculated using the Kubelka-Munk function), $\hbar\omega$ is the incoming photon energy, and n is equal to 2 for direct gaps and $1/2$ for indirect gaps. We justify the use of $n=2$ (direct gap) Tauc fits by noting that when $n=1/2$ (indirect) fits are performed, the extrapolated energy is about 0.03 to 0.05 eV below the direct band gap for $n=2$ fits at all measured temperatures, which is roughly consistent with the energy of phonons in this material. We thereby attribute the $n=1/2$ extrapolated fit values to phonon-assisted transitions from the L valence to L conduction bands—as suggested by Scanlon.²⁹ We do not observe a strong temperature dependence of the Urbach exponential edge and do not believe that it should greatly affect the value of the band gap obtained.

AIMD simulations were performed as described previously.³³ The temperature-dependent lattice dynamics were calculated using AIMD, considering the Fermi-Dirac smearing factor and the thermally expanded lattice parameter (a) and thermal expansion coefficient (TEC) from experimental results: (i) $a(T) = 6.422 + (0.9545 \times 10^{-4})T + (2.615 \times 10^{-8})T^2$ for PbTe; (ii) $a(T=300\text{ K}) = 6.124 \text{ \AA}$ and $\text{TEC} = 1.9 \times 10^{-5} \text{ 1/K}$ for PbSe; (iii) $a(T=300\text{ K}) = 5.936 \text{ \AA}$ and $\text{TEC} = 2.03 \times 10^{-5} \text{ 1/K}$ for PbS.^{34–37} Calculations were performed on large supercells (54 atoms), and the near edge band positions were averaged over three snapshots per temperature. In the calculations of band gap energy as a function of temperature, we only consider the maxima of the valence and conduction bands at the L and Σ points in the band structure. This is done to exclude some band splitting and shifting. We note that above-mentioned choices (data averaging of several snapshots and the different calculation schemes) result in some differences between our results and those reported previously.³¹

The positive temperature coefficient of the band gap in lead chalcogenides, unlike many common semiconductors, is favorable for thermoelectric materials. An increasing gap with temperature can act to suppress bipolar effects caused by intrinsic carrier activation, increasing the optimum zT . The temperature dependent gap in PbX is known to be due to both lattice expansion and electron-phonon interactions.^{33,38,39} The effect can be described by $\frac{dE_g}{dT} = \left(\frac{dE_g}{dT}\right)_V + \frac{3\alpha_L}{K} \left(\frac{dE_g}{dP}\right)_T$, where α_L is the linear thermal expansion coefficient ($\frac{1}{L} \left(\frac{dL}{dT}\right)_P$), K is the bulk modulus ($-\frac{1}{V} \left(\frac{dV}{dP}\right)_T$), $\left(\frac{dE_g}{dT}\right)_V$ describes the electron-phonon interactions, and $\left(\frac{dE_g}{dP}\right)_T$ describes the band gap dependence on pressure.^{38–40} By performing AIMD simulations coupled with density functional theory (DFT) band structure calculations on supercells, we calculated the effect of the thermal motion of the atoms in PbX on both the direct (L) and indirect (Σ) band gaps as shown in Figures 1(a)–1(c). For all of the chalcogenides, the direct (L-L) band gap increases from low

temperature with a slope (dE_g/dT) that decreases as temperature is increased. The indirect (L- Σ) gap varies at a slower rate with temperature—resulting in a convergence temperature (T_{cvg}) of about 700, 900, and 1000 K for PbTe, PbSe, and PbS, respectively. Figures 1(a)–1(c) indicate that both electron-phonon interaction and lattice expansion make significant contributions to dE_g/dT . The electron-phonon contribution does appear to become weaker as the temperature increases for all materials in comparison to contributions to dE_g/dT due to expansion. In the absence of electron-phonon interactions, the bands would not converge until a temperature greater than the melting point of PbX. Hence, the presence of electron-phonon interactions, exclusive to AIMD calculations, is required in order to predict the band convergence at the temperatures which are observed experimentally. Previous work on the lead chalcogenides by Prakash showed the pressure dependence of the gap,^{39,41} $(\frac{dE_g}{dP})_T$, and estimated that the electron-phonon interaction term accounted for roughly 50% of the band gap shift with temperature; the rest was due to thermal expansion of the lattice—which is consistent with this work's findings. Furthermore, our calculations show that the gap at Σ stays nearly constant and that band convergence is a direct result of electron-phonon interaction on the L bands.

Experimental results are also obtained in the form of temperature dependent optical absorption spectra. Figures 2(b) and 2(c) show the extrapolated gaps obtained from this work, as well as reported values from the literature. A linear fit of the changing direct gap up to 500 K returns a value for $dE_g/dT = 3.2 \pm 0.1$ (10^{-4} eV/K) and is almost the same for all PbX (X = S, Se, Te). Several works report a value for dE_g/dT in the range of 3.0 – 4.9×10^{-4} eV/K.^{24,26,30,38,39,42,43} According to the references, the rate of change is mostly linear from low temperature (<100 K) to room temperature and does not vary depending on the particular chalcogen—consistent with this work's results. However, the actual band gap value depends on how it is obtained from the absorption edge. In addition to the particular value of the band gap, its temperature dependence is important because of what it implies about the relative L and Σ extrema's contribution to the thermoelectric properties—which optical band gap measurements have played a role in determining.³⁰

Results presented by Gibson and Tauber both showed increasing band gaps that stopped changing above 400 K.^{26,30} Tauber interpreted this as a shifting primary valence band (which is now known as a direct gap at the L point) that is replaced by the secondary valence band (Σ) above 400 or 500 K in PbTe. Tauber's work has been cited as evidence of the convergence temperature, T_{cvg} , in PbTe. Band convergence, however, does not require a plateauing optical band gap. Direct transitions (L-L) have been shown to be 10–100 times as strong as indirect ones, which require both photon and phonon participation.⁴⁴ In fact, without sufficient separation between the indirect and direct gaps, it may be difficult to distinguish the smaller indirect absorption edge from the exponential Urbach tail—an exponential tail in density of states into the band gap resulting from impurities and disorder in the material. Consequently, we expect that the temperature dependent optical band gap should continue to increase even if the L and Σ bands had converged—suggesting that the

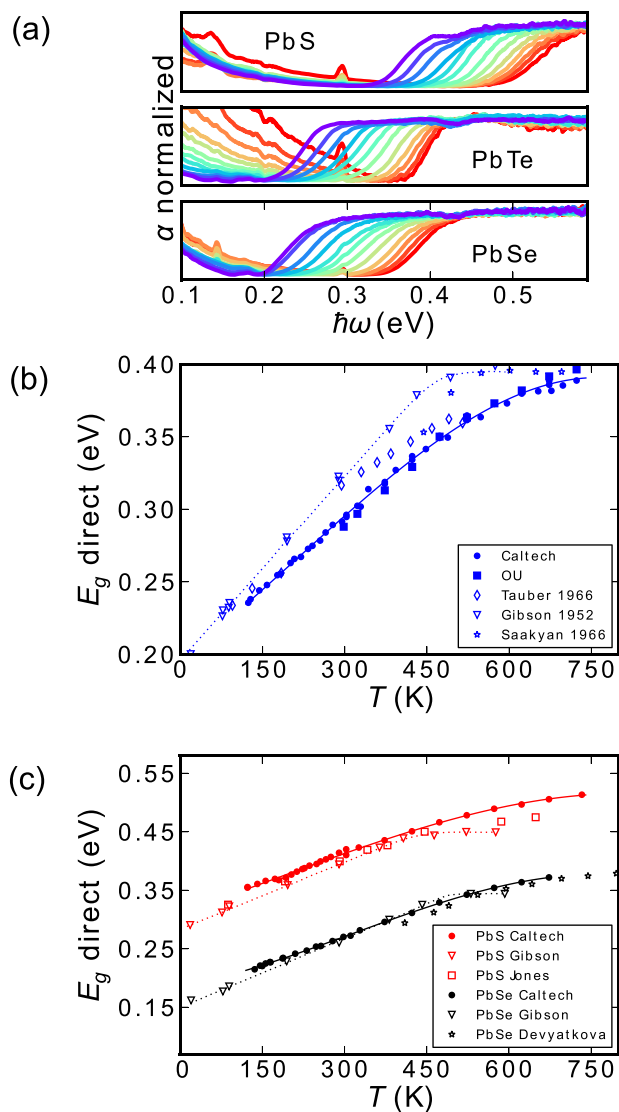


FIG. 2. Temperature dependent optical absorption in PbTe. (a) Normalized Kubelka-Munk function for various temperatures from 123 to 673 K separated by 50 K intervals. The peaks around 0.28 eV are due to vapor phase CO_2 vibrational modes. (b) Temperature dependent extrapolated direct band gap in PbTe from this work and several literature sources. (c) Temperature dependent direct gap for PbS and PbSe in this work and literature. Note that values from Tauber *et al.*³⁰ are extrapolated from the reported absorption data because the reported values were fit to an indirect gap.

forementioned results cannot be used as direct evidence of L and Σ valence band convergence. Upon re-extrapolating the Tauber *et al.* absorption spectra (which was necessary since only indirect transitions were fit) using Tauc extrapolation, the resulting band gaps continuously increase—contrary to the conclusions of Gibson and Tauber. Our results, shown in Figures 2(b) and 2(c) (and others^{45–48}), show that the gap continues to increase for temperatures greater than 673 K, albeit at a lower rate above 500 K. Experimental and AIMD results in this work suggest that the band convergence temperature is much higher, closer to 700 K. The temperature dependence of electronic transport properties (resistivity, Hall effect, and Seebeck) can also be used to estimate the band gap. While early results from resistivity and Hall effect measurements^{28,49} showed large values of the thermal band gap (>1 eV), photoconductivity measurements by Moss showed a near unity quantum efficiency above 0.4 eV for PbS which was

concluded as evidence that the gap must be much smaller⁵⁰ and more consistent with the optical measurements of Gibson, Devyatkova, and Saakyan *et al.*^{22,51} (also shown in Figure 2(b)) measured both n and p-type samples in the bipolar regime to estimate the temperature dependent gap using an extrapolation technique for the single parabolic band model. They obtained a constant gap for temperatures greater than 550 K in PbTe and one that increased continuously until 800 K in PbSe. These estimates seem to be consistent with results from this work, although both calculation and optical measurement from this work suggest a bit higher convergence temperature than Saakyan.

A higher T_{cvg} implies that other conclusions about the temperature dependent band structure of PbTe may need to be reconsidered—in particular the L- Σ offset. Historically, valence band offsets in PbX samples have been determined by intra and inter-band free carrier absorption measurements with photon energies less than the fundamental gap;^{52–54} this is an experimental method for determining the L- Σ energy offset directly. Values of $2\text{--}4 \times 10^{-4}$ eV/K were reported for the temperature dependence of the offset between the two valence bands using these techniques. Free carrier absorption measurements, however, require analysis and interpretation that depend on relatively small features in the absorption spectra, which make them prone to error. Nonetheless, they have been used to estimate the band offset and its temperature dependence to explain electronic transport data in PbX. The direct method of estimating the L- Σ offset free carrier absorption, band gap measurements as shown in this work, and temperature dependent electronic transport properties are the main experimental methods used to estimate the valence band offset and T_{cvg} in PbX.

As an example of how electronic transport measurements have been used to estimate the band offset, it has been suggested that a peak in the Hall resistance with temperature implies band convergence and can be used as an estimate of T_{cvg} .^{7,11,13,14} Interestingly, these results show a peak around 450 K, consistent with the T_{cvg} estimate of Tauber *et al.* However, as pointed out by Jaworski *et al.*, this represents the temperature at which the conductivity of carriers in either band is equal and not when they are at the same energy.⁸ We tested this hypothesis using a two-band transport model consistent with Pei *et al.*⁷ with a different band convergence temperature (consistent with the 3×10^{-4} eV/K, convergence at 700 K and a slightly lower L-band effective mass of $0.26 m_0$). We modeled a Hall coefficient peak at around 450 K (approximately where the L and Σ band conductivities are equal) even though the band convergence does not occur until 700 K. This result suggests that a higher convergence temperature is not in conflict with the Hall coefficient peak observed around 450 K.

While this study shows that the band convergence temperature is higher than previously believed, it also confirms that such a convergence should indeed occur at high temperatures. The gradual approach to convergence at high temperatures ensures that the bands are effectively converged⁷ ($\Delta E \sim 3k_B T$) over a broad temperature range, consistent with experimental observations of high zT at high temperatures.

Optical absorption edge data show an increasing optical gap with temperature at a rate of $\sim 3.2 \times 10^{-4}$ eV/K for all

three lead chalcogenides up to 500 K (whereas the slope above that is smaller and steadily decreasing)). AIMD calculations deduce that about half of the contribution is due to lattice expansion, while the rest is due to electron-phonon interaction. Contrary to prior temperature dependent optical absorption literature, this work suggests that the optical gap continues to increase for temperatures up to 673 K. While previous work used the E_g plateau in PbTe as evidence of the convergence temperature, our results suggest that the plateau does not occur at such low temperatures. Both optical absorption and AIMD DFT calculations in this work suggest that the band convergence in PbTe occurs at about 700 K, a temperature higher than concluded previously.

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