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Temperature dependence of the band gap of perovskite semiconductor compound CsSnI₃

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The temperature dependence of the bandgap of perovskite semiconductor compound CsSnI₃ is determined by measuring excitonic emission at low photoexcitation in a temperature range from 9 to 300 K. The bandgap increases linearly as the lattice temperature increases with a linear coefficient of 0.35 meV K^{-1}. This behavior is distinctly different than that in most of tetrahedral semiconductors. First-principles simulation is employed to predict the bandgap change with the rigid change of lattice parameters under a quasi-harmonic approximation. It is justified that the thermal contribution dominates to the bandgap variation with temperature, while the direct contribution of electron-phonon interaction is conjectured to be negligible likely due to the unusual large electron effective mass for this material. © *2011 American Institute of Physics.*
[doi:10.1063/1.3638699]

I. INTRODUCTION

CsSnI₃ belongs to the class of perovskite semiconductors with the chemical formula of ABX₃. It consists of a network of corner-sharing BX₆ octahedra, where the B atom is a metal cation, X is a monovalent anion, and A cation is incorporated to balance the total charge. The synthesis and characterization of CsSnI₃ have been described in our recent report.[1] It has been confirmed that CsSnI₃ compound in its black phase is a direct band-gap semiconductor with an energy gap of ~1.3 eV. Additional steady state and time-resolved photoluminescence (PL) studies have shown this compound may have application potentials for high efficiency solar cells, solar luminescent concentrators, new laser materials, and other near-IR optoelectronic devices. The nature of PL is determined to be excitonic, and the exciton binding energy is deduced to be 18 meV.[2] The large exciton binding energy is due to the two-dimensional exciton motion in the layers of strong coupled SnI₄ tetragons.

One of the interesting properties of CsSnI₃ is the strong and linear increase of the band (or energy) gap (E$_g$) with increasing temperature, which is opposite to what have been observed for most of common semiconductors. The electronic bandgap is an important fundamental parameter of a semiconductor in terms of its electric and optical properties. The first experimental work on E$_g$ dated back to the dawn of the semiconductor era. The successes of semiconductor based transistors, lasers, light-emitting diodes, and recently solar cells, have stimulated extensive works on the bandgap variation with temperature, E$_g$ (T), both theoretically and experimentally over many decades. These studies have successfully explained the normal behavior of the temperature dependence of bandgap: measured E$_g$ (T) curves show a monotonic decrease with temperature non-linearly at low T and linearly at high T. However, there are some exceptions, which exhibit anomalous temperature behaviors. An early example is PbTe.[3] A blue energy gap shift was reported for this material in the temperature range from 100 to 300 K. In addition, the measured band gaps of CuBr and CuCl increase monotonically from near zero to room temperature.[4] More recently, a similar anomalous behavior has been observed for PbS.[5] The reason for this anomalous bandgap behavior is not quite clear yet and needs to be further investigated. Exploring new materials with an anomalous temperature dependence of bandgap remains interesting and helpful for fully understanding this fundamental problem.

In this paper, we report on the measured bandgap as a function of temperature in a potentially important semiconductor compound CsSnI₃ by PL method. The bandgap is determined through a PL line shape analysis. It shows a linearly positive relationship with temperature from 20 to 300 K. We explain our experimental data from three aspects. We first revisit the theoretical background for the temperature dependence of a semiconductor bandgap. We then study the direct contribution of electron-phonon (e-p) interaction. Finally, we determine the thermal contribution to the bandgap variation for CsSnI₃ by means of the first-principles calculations.

II. EXPERIMENT

PL experiments in this work were carried out by a Nano-Log apparatus from Horiba. It consists of a 450 W Xe lamp as an excitation source, a double grating excitation spectrometer, a sample compartment with collection optics, an

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emission spectrometer equipped with a Hamamatsu P2658R photomultiplier tube. Analog signal is then fed to a single photon accounting electronics module for data acquisition. A $CsSnI_3$ thin film sample (silicon substrate in this case) was mounted on the cupper finger of a closed-cycle optical cryostat, which is capable of having temperature variation from 9 to 350 K. Excitation wavelength was 500 nm with a passband of 5 nm. Excitation power density was about 20 mW/cm^2. Spectra were corrected by using a standard light source purchased from Ocean Optics Inc.

Normalized PL spectra from 9 to 300 K are displayed in Fig. 1. The full width at half maximum (FWHM) of each spectrum is shown in the inset of this figure. Two important features are readily identified: (1) PL peak shifts to shorter wavelength and (2) PL spectrum broadens as the sample temperature increases from 9 to 300 K. We now turn to discuss how to deduce accurate band gaps from PL spectra at various sample temperatures. There are two contributions to the PL linewidth broadening. One is the temperature dependent asymmetric thermal broadening on the high energy tail of a spectrum arising from more energetic excitons. A constant two-dimensional density of states and a Boltzmann thermal distribution with an exciton temperature (T_x) were used for this part of line shape. The other one is due to the symmetric broadening resulting from both the inhomogeneous broadening because of the nature polycrystalline compound and the homogeneous broadening originated from the exciton scatterings with phonons and impurities. Main reasons for inhomogeneous broadening may include composition fluctuations and granular boundaries. We assume this symmetric broadening to be a Gaussian with a variance of σ. Combining the above two contributions, a PL spectrum at a given sample temperature can be fitted by the following convolution expression:

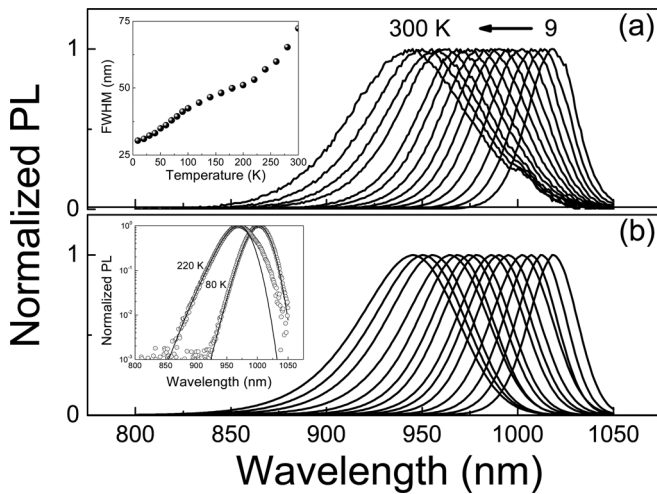$$PL(E) = G(E, \sigma) * \exp\left(-\left(E - E_g + E_{bx}\right)/(K_B T_x)\right). \quad (1)$$

FIG. 1. (a) Normalized photoluminescence spectra measured at various temperatures from 9 to 300 K. The inset shows the temperature dependence of the FWHM for the measured PL spectra. (b) Calculated PL spectra using Eq. (1), which were matched to each measured PL spectrum to obtain band gaps at different temperatures. The inset displays the two examples of spectrum fitting at 80 and 200 K. Discrete symbols represent the measured PL, while solid curves are calculated PL spectra.
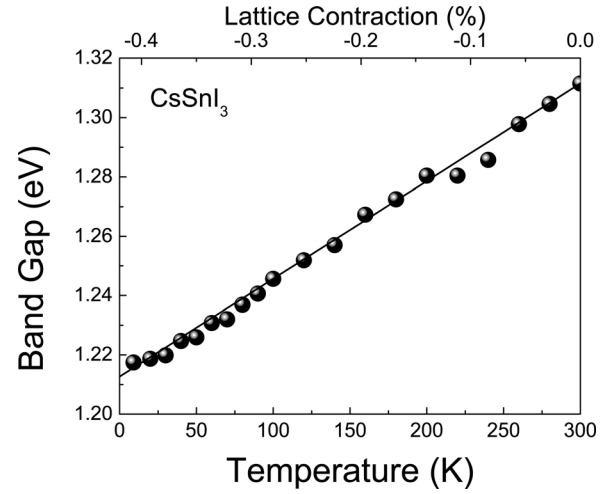
FIG. 2. Band gaps of $CsSnI_3$ at various temperatures deduced from photoluminescence spectra (solid spheres with bottom axis) and the bandgap variation with lattice contraction obtained from first-principles calculations (solid line with top axis). The top axis is the relative lattice contraction, $\Delta a/a_0$, where a_0 is the lattice constant at room temperature.

All measured PL spectra from 9 to 300 K were fitted by Eq. (1). The calculated spectra are shown in Fig. 1(b). To demonstrate the quality of fitting, two measured PL spectra at 80 and 220 K (discrete symbols) are plotted in an intensity-log scale in the inset along with the calculated spectra (solid-line curves). The spectrum fit over three orders of magnitude is highly satisfied for all spectra except a small deviation at low energy side for a few spectra with temperature greater than 200 K. However, this deviation will not affect the accuracy of the bandgap determination. Both fitting parameters σ and T_x are temperature dependent. We will discuss these two parameters elsewhere. The focus point, in this paper, is the deduced bandgap at different temperatures, which is summarized in Fig. 2 as solid spheres. This plot presents a salient feature: the bandgap follows a positive linear-dependence in the temperature range, we studied although it tends to be flat for temperature below 20 K. This feature is referred as the anomalous behavior of bandgap in literature,[4,5] and the reason still needs to be further investigated. In this paper, we will discuss this interesting behavior.

III. DISCUSSION

A. Theoretical background

The temperature dependence of bandgap is generally described by the following expression under a quasi-harmonic approximation:[6]

$$\frac{\partial E_g}{\partial T} = \frac{\partial E_g}{\partial V}\frac{\partial V}{\partial T} + \sum_{j,\vec{q}} \left(\frac{\partial E_g}{\partial n_{j,\vec{q}}}\right)\left(n_{j,\vec{q}} + \frac{1}{2}\right), \quad (2)$$

where $n_{j,\vec{q}}$ is the number of phonons at j branch with wave vector $\vec{q}$, and it follows the Bose distribution for bosons, $n_{j,q} = \frac{1}{\exp\left(\hbar\omega_{j,\vec{q}}/K_B T\right)-1}$, where $\omega_{j,\vec{q}}$ is the angular frequency of the phonon mode. It is important to note that the summation in Eq. (2) is overall possible phonon modes in the entire Brillouin zone, i.e., q from 0 to q_{max}. The first part in Eq. (2)

corresponds to the thermal expansion contribution, which arises from the anharmonicity of the inter-atomic potentials. The coefficient can be approximately considered to be temperature independent for a given semiconductor, and it can be either positive or negative. For instance, we have determined the sign of $\partial E_g/\partial V$ is positive for Si, while it is negative for GaAs.[7] The origin of bandgap in most semiconductors is the energy difference between bonding and anti-bonding of hybrid orbits. Thus, the value of $\partial E_g/\partial V$ depends on the specifics of the bonding parameters as well as the detailed orbits that form the band. In typical semiconductors, the thermal expansion contribution is considered to be a weak contribution to the temperature dependence of bandgap. However, in $CsSnI_3$, it is shown that this contribution dominates over the contribution of direct e-p interaction.

The second part in Eq. (2) is the direct contribution of e-p interaction, which consists of Fan[8] and Debye-Waller[3,9] terms. Fan term describes the virtual phonon emission and absorption processes as if e-p interaction is taken twice in 2nd-order perturbation theory. The Debye-Waller term represents the simultaneous interactions of an electron with two phonons in the branch j having the opposite wave vectors ($\vec{q}$ and $-\vec{q}$. This two-phonon interaction process is calculated using the 1st-order perturbation theory. Both processes are the 2nd-order approximation in the phonon amplitude, which will introduce an inverse dependence of atomic mass M and allows isotopic atom substitution studies. At relative high temperature $\left(K_B T \gg \hbar\omega_{j,\vec{q}}\right)$, $n_{j,q} = \frac{1}{\exp\left(\hbar\omega_{j,\vec{q}}/K_B T\right)-1} \sim \frac{K_B}{\hbar\omega_{j,\vec{q}}}T \gg 1$ hence a linear temperature dependence of bandgap is expected. At low temperature, however, the situation becomes more complicated. Cardona[10] investigated the Si bandgap below 5 K and showed that the bandgap followed the T^4 law. In principle, the coefficient $\frac{\partial E_g}{\partial n_{j,\vec{q}}}$ can be calculated with the full pseudo-potential description and phonon modes. In reality, however, it remains to be a challenging task to calculate the direct e-p contribution. As a result, many models have been developed to interpret experimental data, such as the Varshni empirical formula[11] $E_g(T) = E_g(0) - \alpha T^2/(T+\beta)$, where α and β are fitting parameters for a given semiconductor. Recently, the two-oscillator model[4,5,12,13] has been developed. Using this model, the bandgap variation with temperature can be expressed as

$$\Delta E_g(T) = -\frac{S_1}{\Omega_1 M_1}\left(\frac{1}{e^{\Omega_1/K_B T}-1}+\frac{1}{2}\right) - \frac{S_2}{\Omega_2 M_2}\left(\frac{1}{e^{\Omega_2/K_B T}-1}+\frac{1}{2}\right), \quad (3)$$

where $\Omega_i(i=1,2)$ is the phonon energy, M_i is the atomic mass, and S_i is the relative weight for oscillator 1 and 2, respectively. Instead of summing overall possible phonon modes in entire Brillouin zone, the two-oscillator model only considers two dominant phonon modes with two constant energy levels. By fitting experimental data, combined with isotropic atom replacement studies, one can get the information about the constants of S_1 and S_2, which reflects the contribution of direct e-p interaction. In the previous studies of

the anomalous behavior of band gaps in CuCl and PbS systems, the values of S_1 and S_2 were determined to have different signs, and the term with negative sign dominated, thus resulting in a positive temperature dependence of bandgap. Although the two-oscillator model has been used to successfully explain the anomalous behavior of the bandgap variation with temperature, it also provides a feasible case that the constants of S_1 and S_2 might have a similar amplitude but opposite sign. If this case holds true in some semiconductors, then the contribution of direct e-p interaction to the bandgap change with temperature vanishes, leading to the dominant contribution by the thermal expansion as temperature increases. As an example, we describe in Sec. III B how it might be possible in case of $CsSnI_3$ that the Fan term may actually disappear after summing all the contributions in the entire q wave vector space.

B. Electron-phonon interaction

The Fan term is give by

$$\Delta E_g = -\sum_{\vec{q}} \frac{\left|\left\langle \vec{k}\left|H_{el-ph}\right|\vec{k}-\vec{q}\right\rangle\right|^2}{E\left(\vec{k}-\vec{q}\right)-E(k)+\hbar\omega_{\vec{q}}} - \sum_{\vec{q}} \frac{\left|\left\langle \vec{k}\left|H_{el-ph}\right|\vec{k}+\vec{q}\right\rangle\right|^2}{E\left(\vec{k}+\vec{q}\right)-E\left(\vec{k}\right)-\hbar\omega_{\vec{q}}}. \quad (4)$$

The first and second terms correspond to the emission and absorption of photon at wave vector q, respectively. We first examine acoustic phonons and limit our attention near the electronic bandedge, $k \approx 0$, Eq. (4) becomes

$$\Delta E_g = -A\sum_{\vec{q}} \frac{4m^*|q|}{q^2-Q^2} \cdot \frac{1}{e^{\hbar v_q/K_B T}-1}, \quad (5)$$

where A is a positive constant, m^* is the effective mass of carriers, and $Q = \left|\frac{2m^* v_q}{\hbar}\right|$ with $v_{\vec{q}}$ as the velocity of acoustic wave near the zone edge. If we consider a condition so that $K_B T \gg \hbar v_{\vec{q}}$, then,

$$\Delta E_g = -A\frac{K_B}{\hbar v_{\vec{q}}}\sum_{\vec{q}} \frac{4m^*}{q^2-Q^2}T. \quad (6)$$

From the above equation, the positive contribution of ΔE_g arises from all the phonon modes with $|q| < Q$, while its negative contribution comes from the phonon modes with $|q| > Q$. If Q is smaller than $|q|_{max}$ by two to three orders of magnitude, most of phonon modes will satisfy $|q| > Q$ leading to a negative value of ΔE_g in Eq. (6). That is the case for most of tetrahedral semiconductors. For Si and GaAs, Q_e is about $10^7 m^{-1}$, which is two orders of magnitude smaller than there $|q|_{max} = 5.6 \times 10^9$ m^{-1}. For $CsSnI_3$, $Q_e = 1.6 \times 10^8$ m^{-1} and $Q_h = 3.3 \times 10^7$ m^{-1} are calculated using the electron effective mass of 0.734 m$_0$ and the hole effective mass of 0.151 m$_0$ near Γ point,[1] respectively. The maximum phonon wave vector is estimated to be 3.9×10^9 m^{-1} for $CsSnI_3$ using the lattice constants obtained by

experimental x-ray diffraction data[14] at room temperature. The large Q value because of the large electron effective mass in CsSnI$_3$ makes it possible that the value of ΔE_g in Eq. (6) becomes negligible.

For optical phonons, the situation is quite similar. For simplicity, we consider the longitudinal optical (LO) phonon mode and assume very flat dispersion for LO phonons, then, the Eq. (4) becomes

$$\Delta E_g = -B \sum_{\vec{q}} \frac{m^* q^2}{q^4 - P^2} \frac{1}{e^{\Omega/K_B T} - 1}, \qquad (7)$$

where $P = \sqrt{2m^*\Omega}/\hbar$. Use the same parameters as the case of acoustic phonons and the measured[15] LO phonon energy (Ω) of 32 meV. We obtained $P_e = 0.78 \times 10^9$ m^{-1} and $P_h = 0.35 \times 10^9$ m^{-1} for electrons and holes, respectively, which is comparable with $|q|_{max}$. Similar to the argument for the acoustic phonon case, the value of ΔE_g in Eq. (7) may also be insignificant.

To fully determine the value of Fan term with the large $Q(P)$ in CsSnI$_3$, we need to know all possible phonon modes, which is extremely difficult. However, if we only count for two major phonon modes, Eqs. (5) and (7) will apparently lead to the two-oscillator model. The sign of $\frac{1}{q^2 - Q^2}$ ($\frac{1}{q^4 - P^4}$ in case of LO phonon modes) determines the sign of S$_1$ and S$_2$ in Eq. (3). With the large $Q(P)$ such as in CsSnI$_3$, it is possible that one mode satisfy $|q| < Q(P)$, while for the other $|q| > Q(P)$ resulting in opposite sign for S$_1$ and S$_2$. When S$_1$ is close to S$_2$ in magnitude, it is then possible the contribution of direct e-p interaction to $\Delta E_g(T)$ vanishes. We conjecture this is the case for CsSnI$_3$ and work out the thermal expansion contribution to compare with the measured data.

C. Thermal expansion contribution

We treat this problem by freezing the lattice (i.e., always at T = 0 K, neglecting the effect of phonon), and then calculate the bandgap of CsSnI$_3$ as we rigidly reduce the lattice constant from a_0 to $a_0 - \Delta a$, where a_0 is the lattice constant at 300 K. We use a to represent three different lattice constants in an orthorhombic structure. Of course, the lattice can never be frozen in equilibrium even at 0 K because of the none-zero ground state energy. However, it is possible to investigate solely the bandgap change with increasing or decreasing volume. By assuming a linear relationship between lattice constant and temperature, the calculated bandgap E$_g$ ($\Delta a/a_0$), can be used to fit the experimental data E$_g$ (T). From this fitting, the value of linear thermal expansion coefficient α_L can be obtained. In this approach, we use our assumption that the direct e-p interaction contribution is negligible and thermal expansion effect is dominant for the temperature behavior of the bandgap in this material. The validation of this assumption will be checked by comparing the deduced value of linear thermal expansion coefficient with the experimentally measured one for CsSnI$_3$. However, the information of this coefficient for CsSnI$_3$ is not yet available. We will then compare the reduced parameter with the coefficient of other perovskite materials with a similar crystal structure, to verify our assumption.

The task of bandgap calculation for CsSnI$_3$ is accomplished by performing *ab initio* calculations in the framework of density functional theory. The Abinit code[16,17] was used. We also used a similar simulation package CASTEP[18] to do a cross check. The valence electron Kohn-Sham wave functions were expanded in plane wave basis up to a cutoff of 30 Hartees, and the core electrons were treated by the Perdew-Burke-Ernzerhof[19] pseudo-potential in Troullier-Martins scheme. A shifted k-point $4 \times 4 \times 4$ grid was used for sampling the Brillouin zone. The generalized gradient approximation was employed for the evaluation of the exchange-correlation energy.

The solid line in Fig. 2 shows the calculated E$_g$ versus $\Delta a/a_0$ (top axis). It can be seen that the bandgap decreases linearly as lattice constant contracts from its room temperature values.[1] It requires a linear lattice change of 0.42% from room temperature to 0 K to match the measured bandgap variation with temperature. The top axis $\Delta a/a_0$ and bottom axis can be overlapped by assuming a constant linear thermal coefficient α_L with a value of 0.42/100/300 = 1.40×10^{-5} K^{-1}. Thus, the solid line can be recognized as the calculated E$_g$ versus T due to thermal expansion or contraction. The calculated curve agrees with the experimental data very well except at low temperature less than 20 K. This agreement also supports our initial assumption that the thermal expansion is proportional to temperature. From the theoretical point of view, the thermal expansion is an effect of the anharmonicity of the inter-atomic potentials. It is shown to be closely related to the atomic vibration, i.e., phonon, and to be proportional to temperature at relatively high temperature.[6] The reason for the deviation below 20 K is that we have assumed expansion coefficient to be constant, which may not be accurate at low temperature. If we adjust the expansion coefficient to be temperature dependent at low temperature, it is possible to obtain a better fit with the experimental data. However, since we are more interested in a large temperature range of greater than 20 K, a lack of this adjustment will not influence our conclusion.

As we mentioned, the validity of this matching relies on the justification of the deduced value of linear thermal coefficient α_L, which is usually measured by x-ray diffraction method. The value of α_L for several perovskites with orthorhombic structure such as SrZrO$_3$,[20] ScAlO$_3$,[21] and MgSiO$_3$ (Ref. 22) has been experimentally measured to be 1.08×10^{-5} K^{-1}, 0.90×10^{-5} K^{-1}, and 1.57×10^{-5} K^{-1}, respectively. The value of α_L can be also obtained theoretically using various models such as molecular dynamics, lattice dynamics, and Debye model.[23] For example, the value for MgSiO$_3$ has been calculated[24] to be 2.09×10^{-5} K^{-1}. Our deduced value of α_L for CsSnI$_3$ is 1.40×10^{-5} K^{-1}, which is very reasonable comparing with the measured or calculated α_L values for other perovskites materials available in literature. Therefore, our assumption is justified that the contribution of direct e-p interaction is negligible and the variation of E$_g$ (T) is dominated by the thermal expansion contribution.

IV. CONCLUSION

We have determined the bandgap of newly synthesized semiconductor compound CsSnI$_3$ as function of temperature from 9 to 300 K by photoluminescence method. The bandgap

variation with temperature shows uncommon positive linear temperature dependence. It is conjectured that the contribution of direct electron-phonon interaction to the bandgap change is negligible likely due to the unusual large electron effective mass. We justified this conjecture by the calculated bandgap with various lattice constants using first-principles simulations, which changes linearly with temperature. By matching the experimentally measured bandgap variation with temperature to the calculated, we deduced a linear thermal expansion coefficient of 1.40×10^{-5} K^{-1} for CsSnI$_3$, which is consistent with several other materials having the same crystal structure as CsSnI$_3$.

ACKNOWLEDGMENTS

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