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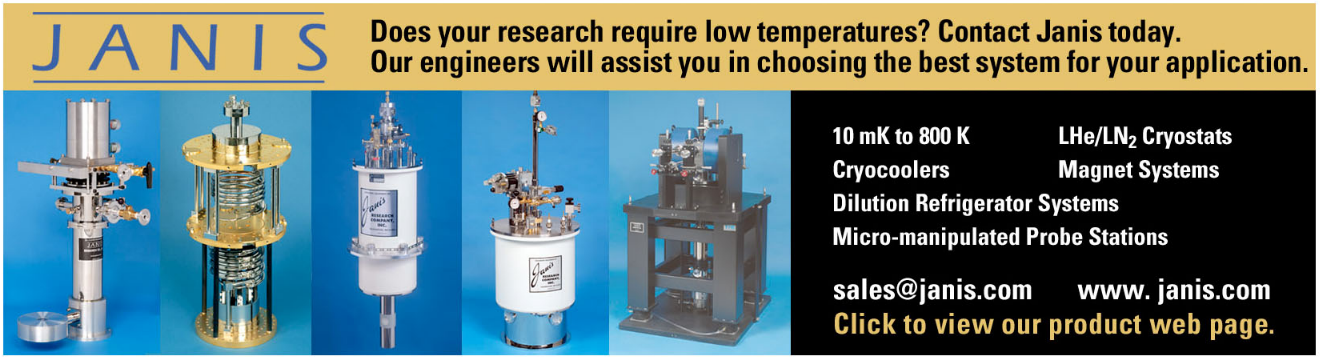

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Coupled vibrational modes in multiple-filled skutterudites and the effects on lattice thermal conductivity reduction

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The influence of guest atoms on thermal conduction in filled skutterudites was studied using ultrafast reflectance spectroscopy. Different filling species cause coupled vibrational modes between the guest atoms and the host lattice at different frequencies, which scatter phonons in different spectral spans. Using a Debye model for the measured lattice thermal conductivity together with the measured vibration frequencies and scattering rates, it is shown that scattering due to the coupled vibrational modes has a considerable contribution to the suppression of lattice thermal conduction. This demonstrates that filling with multiple species can efficiently reduce the lattice thermal conductivity in skutterudites. © *2013 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4796121]

Skutterudites have attracted much attention as a high temperature thermoelectric material due to their high figure of merit (ZT) in the temperature range from about 300 °C to 550 °C.[1–3] It has been discovered that filling the void in the skutterudite lattice structure with guest atoms can significantly reduce the lattice thermal conductivity κ_L and improve the thermoelectric figure of merit.[4–7] Many studies have been conducted to elucidate the mechanism of this phenomenon, and different viewpoints have been proposed. The concept of localized rattlers[8] for the role of guest atoms is supported by a number of studies including Raman spectroscopy,[9] inelastic neutron scattering, heat capacity measurements,[10,11] and infrared reflectance spectroscopy.[12] However, molecular dynamics (MD) simulations showed that anharmonic interactions between host and guest atoms were important for decreasing κ_L.[13] Another MD studies explained the lower κ_L as a result of lattice distortions and weaker interatomic interactions among host atoms due to filling atoms.[14] Using neutron spectroscopy and *ab initio* calculations, it was found that well-defined phase relations between guest and host dynamics existed,[15] which also contradicted the concept of independent rattlers. Therefore, there is still a controversy on the mechanisms of thermal conductivity reduction in filled skutterudites.

It has also been proposed to fill the skutterudite crystal structure with more that one species of guest atoms in order to scatter a broader range of phonons.[6,7] Recently, ultrafast spectroscopy was carried out successfully to study the interactions between the host lattice and the guest atoms in p-type misch-metal filled skutterudites[16] and n-type filled skutterudites.[17] In this work, we investigate the details of the interactions between the filled elements and the phonons in single and multiple filled skutterudites. These studies allow determination of the effect of filling skutterudites with multiple elements and the role of coupled vibrations in thermal conductivity reduction.

Three single-filled n-type samples with individual element and one triple-filled n-type sample with all the three elements were used. The compositions of these samples were determined to be $Ba_{0.26}Co_4Sb_{12.01}$, $Yb_{0.21}Co_4Sb_{11.92}$, $La_{0.14}Co_4Sb_{11.99}$, and $Yb_{0.05}La_{0.05}Ba_{0.08}Co_4Sb_{11.92}$ from electron probe microanalysis. Ultrafast spectroscopy for measuring the interactions between the host lattice and guest atoms is based on femtosecond time-resolved pump-probe technique to measure the transient reflectance of the samples irradiated by femtosecond laser pulses.[16] The femtosecond laser pulses were generated from a Spectra Physics Ti:sapphire amplified laser system with a central wavelength of 800 nm and a repetition rate of 5 kHz. A barium borate (BBO) crystal was used to convert the wavelength of the pump pulses to 400 nm. The probe and the pump had pulse durations (full width at half maximum (FWHM)) of 70 fs and 140 fs, respectively. Raman spectra of the samples were also measured to identify lattice-vibration modes.

The transient reflectance signals of the samples have similar features. Fig. 1 shows the signal of the La-filled sample, where the inset illustrates the oscillation in a magnified scale. The signal features are different from those of the p-type misch-metal-filled skutterudites for which part of the Co is substituted by Fe to stabilize the skutterudite phase.[16] First, the background signals of these n-type skutterudites have an initial drop instead of a rise, which indicates different carrier dynamics in these samples compared to p-type skutterudites. As predicted by density-functional band-structure calculations,[18] guest atom fillers tend to raise the Fermi level into the conduction band while substitution of Co by Fe moves the Fermi level down across an area of a low density of states towards the valence band. Second, the oscillations are much weaker, and there are several reasons for this. The first is the much lower filler concentrations used in these samples (∼10%–20%) compared with previously investigated misch-metal filled samples (55%–82%).[16] The second is the n-type samples in the present study have smaller effective carrier mass, which weakens the carrier-lattice coupling

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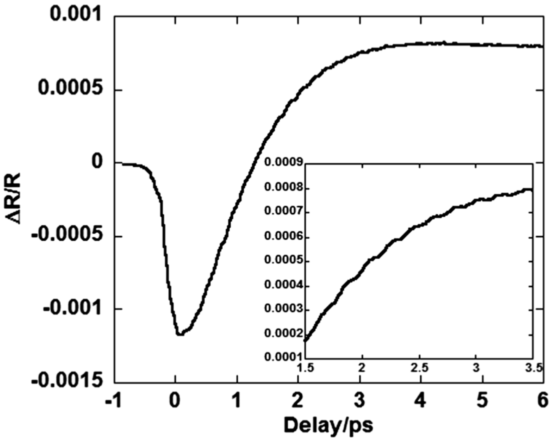

FIG. 1. Transient reflectance of the La-filled sample (magnified in the inset).

in terms of excitation of atomic vibration. The third is related to the different electronic band structures. Modulation of the optical signal by lattice vibration is generally most prominent when the probe is at the spectrum range where the slope of the absorption spectrum is large.[19] The difference in electronic band structures will change the absorption/reflection spectrum, which changes the sensitivity of the probed state to the lattice vibration.

In order to identify the detected oscillation modes, a second-order Butterworth bandpass filter was applied to remove the background carrier signal, and then a Fourier transform was performed to analyze the spectra of the oscillations, as shown in Fig. 2, with dominating peaks marked by the vertical dashed lines. The peaks at 174 cm^{-1} exist for all the samples which is one of the F_g modes[20,21] that involves motions of the Sb atoms but is not related to the filling atoms.[21] The peaks in the range between 146 and 155 cm^{-1} change with the filler species. For the triple-filled sample, there are two peaks in that range. The Raman spectra of all the samples are similar with regard to the positions of the Raman peaks, and the only detected mode near 147 cm^{-1} is the low-energy A_g mode, which is one of the breathing modes of the Sb_4 ring. The frequencies of the low-energy A_g modes from Raman spectroscopy are 145.8 cm^{-1}, 147.7 cm^{-1}, 147.5 cm^{-1}, and 147.7 cm^{-1} for the Ba-filled, Yb-filled, La-filled, and triple-filled samples, respectively.

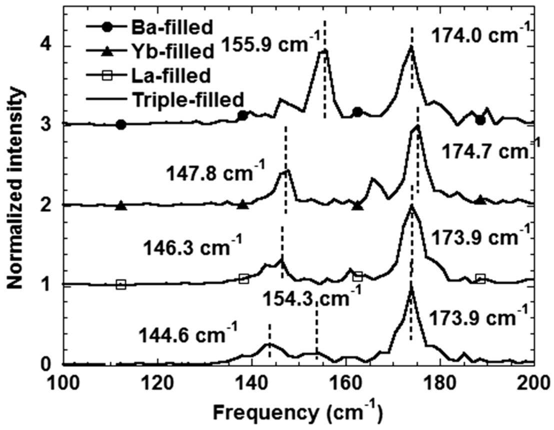

FIG. 2. Normalized transient reflectance spectra (the curves were vertically shifted for clarity).

Compared with Fig. 2, it is clear that the oscillations observed in the transient reflectance measurements are shifted from the low-energy A_g mode. These oscillations are caused by the filling atoms and the coupling between the filling atoms and the host lattice vibration. They are not phonon modes since a phonon mode would be observed in Raman spectroscopy. In the skutterudites with low filling ratio, moreover, there will be no translation symmetry or periodicity of a host-guest structure. Figure 2 also shows that Yb and La generate coupled vibrational modes with close frequencies but different from the mode frequencies produced by Ba. The oscillation spectrum for the triple-filled sample includes two frequencies with one close to the frequency caused by Yb or La and the other close to that caused by Ba. We thus see that filling the skutterudite crystal structure with different elements causes different frequencies for the host-guest system.

To evaluate the contribution of the coupled modes to the thermal conductivity reduction, we obtain the lattice thermal conductivity from the total thermal conductivity using Wiedemann-Franz relation (Lorenz number set equal to $2.0 \times 10^{-8}\ \mathrm{V^2/K^2}$) and take the model based on the Debye approximation to fit the measured results from 4 K to 300 K[22,23]

$$k_L = \frac{k_B}{2\pi^2 v}\left(\frac{k_B T}{\hbar}\right)^3 \int_0^{\frac{\theta_D}{T}} \frac{x^4 e^x dx}{\tau^{-1}(e^x - 1)^2}, \qquad (1)$$

where $x = \hbar\omega/k_B T$, $\hbar$ is the reduced Planck constant, ω is the phonon angular frequency, k_B is the Boltzmann constant, and T is the temperature. The sound velocity v and the Debye temperature θ_D are 2700 m/s and 287 K, respectively.[23] The phonon relaxation time τ is given by

$$\tau^{-1} = \frac{v}{L} + A\omega^4 + B\omega^2 T \exp\left(-\frac{\theta_D}{3T}\right) + \frac{1}{\tau_0}\exp\left[-\frac{(\omega - \omega_0)^2}{\omega_b{}^2}\right], \qquad (2)$$

where L represents the average grain size and ω_0 is the frequency of the coupled mode determined experimentally. The four terms in Eq. (2) represent scattering by grain boundary, point defects, phonon-phonon Umklapp processes, and the coupled mode, respectively. Unlike the rattling mode, which

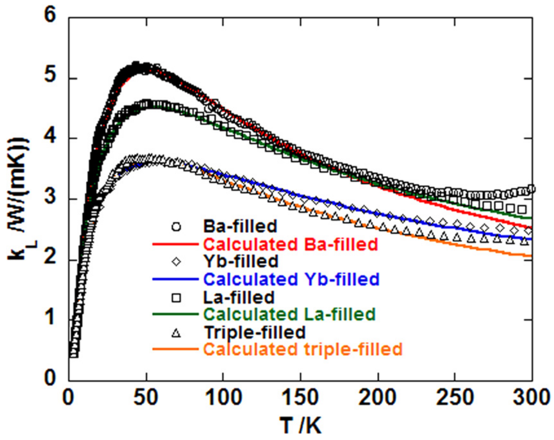

FIG. 3. Comparison between measured and fitted lattice thermal conductivity.

TABLE I. Fitting parameters for the lattice thermal conductivity. The parameters ω_o and τ_o are experimentally determined values.

Sample composition	L/μm	$A/10^{-43}$ s^3	$B/10^{-18}$ s/K	$\omega_0/10^{12}$ rad/s	$\omega_b/10^{12}$ rad/s	τ_0/ps
$Ba_{0.26}Co_4Sb_{12.01}$	3.13	121.21	5.05	29.52	10.80	3.94
$Yb_{0.21}Co_4Sb_{11.92}$	4.34	298.99	2.45	27.63	8.85	2.93
$La_{0.14}Co_4Sb_{11.99}$	3.74	185.86	3.01	27.63	9.29	2.93
$Yb_{0.05}La_{0.05}Ba_{0.08}Co_4Sb_{11.92}$	4.22	230.30	4.13	27.00/28.89	9.36/8.85	2.53/1.92

is associated with random and independent motions of the filling atoms, the coupled mode involves phase-matched relative motions of the host lattice and the filling atoms and disturbs phonon transport by scattering. The relaxation time τ_0 (or the inverse of the scattering rate) was determined experimentally from the decay of the oscillation in the transient reflectance signal as a damping oscillator.[24,25] We further assume that the coupled mode also scatters phonons at frequency other than ω_0, with a spectral dependence of a Gaussian form and a bandwidth of ω_b. The variables L, A, B, and ω_b are fitted to the experimentally measured thermal conductivity. The fitting results for the lattice thermal conductivity are shown in Fig. 3, and the parameters used are listed in Table I. For the triple-filled sample, two resonance terms are used. Good fitting can be obtained except for deviations at higher temperature, which is attributed to the radiation loss that affects the measured thermal conductivity.[22]

We then evaluate and compare the contribution of each scattering term at the frequency ω_0 and 300 K, which is shown in Fig. 4. For the triple-filled sample, the low-frequency term is used. It is seen that the boundary scattering contributes the least at this temperature, and the other three terms have comparable magnitudes, indicating that the coupled vibrational mode has a considerable influence on the lattice thermal conductivity. For the triple-filled sample, the existence of two resonant terms increases the effect on the lattice thermal conductivity reduction.

In summary, ultrafast spectroscopy shows oscillations in single- and triple-filled skutterudites caused by filling the skutterudite host crystal structure with guest atoms. Comparison of the oscillations with the Raman spectrums indicated that the detected oscillations represent the coupled vibrational mode of the host-guest system, while filling with different elements produces different vibrational frequencies. Using a lattice thermal conductivity model together with measured vibrational frequencies and scattering rates, it is shown that the coupled vibrational mode has a considerable contribution to the reduction of the lattice thermal conductivity and that multiple-element filling can effectively suppress phonon-mediated thermal conduction in skutterudites.

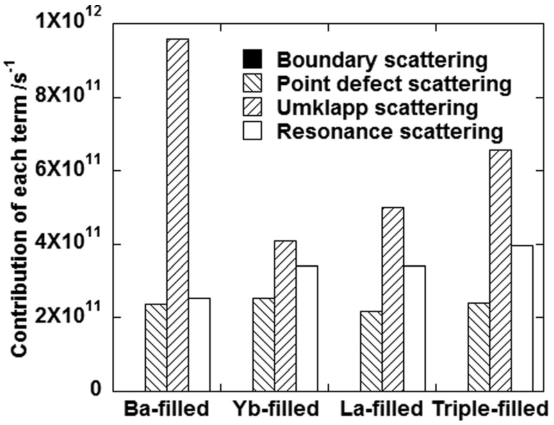

FIG. 4. Comparison of each scattering term at the resonance frequency and 300 K.

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