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Resonant Oscillations in Multiple-Filled Skutterudites

L. GUO,[1] X. XU,[1,3] J.R. SALVADOR,[2] and G.P. MEISNER[2]

1.—School of Mechanical Engineering and Birck Nanotechnology Center, Purdue University, West Lafayette, IN 47907, USA. 2.—Chemical and Materials Systems Laboratory, GM Global R&D, Warren, MI 48090, USA. 3.—e-mail: xxu@purdue.edu

Partially filled skutterudites were investigated by ultrafast spectroscopy using a femtosecond laser system, which excites resonant oscillations due to the host–guest interactions. To investigate the effect of individual guest elements on phonon-mediated thermal transport, four skutterudite samples were studied: three samples partially filled with Ba, Yb, and La, respectively, and a fourth with a combination of these three elements. The spectrum of the oscillations in the transient thermoreflectance signal was analyzed by Fourier transformation. Comparison with the Raman spectra shows that different guest elements cause resonant oscillations with different frequencies, which can scatter phonons in different spectrum spans. This further demonstrates that multiple guest elements can scatter a wider spectrum of phonons than a single guest element at similar filling fractions, which results in lower lattice thermal conductivity (κ_L) in skutterudites. These findings are consistent with thermal conductivity measurements reported previously.

Key words: Multiple-filled skutterudite, ultrafast laser spectroscopy, resonant oscillation, phonon transport

INTRODUCTION

Skutterudites have been considered strong candidates for intermediate-temperature waste heat recovery applications, because they possess high *ZT* values and good mechanical strength. The binary skutterudite has intrinsic void cages in the crystal structure, which allows insertion of guest atoms. It has been shown that filling the void with guest atoms at an appropriate ratio can significantly reduce κ_L,[1–4] which together with the ability of the fillers to increase the carrier concentration further improves the thermoelectric performance of the skutterudites. Regarding the mechanism of the reduction in κ_L, investigation has been conducted both theoretically and experimentally and different possible explanations have been proposed. Bernstein et al.[5] performed molecular dynamics (MD) simulations and showed that the anharmonic interactions between host and guest atoms played an important role in decreasing κ_L. On the other hand, Baoling et al.[6] developed another potential and used MD simulations to show that the decrease in κ_L was more likely the result of the weaker interatomic interactions among host atoms and lattice distortions caused by guest atoms. The concept of localized rattlers, proposed by Slack[7] to describe the role of guest atoms in skutterudites, is supported by a number of studies, including Raman spectroscopy,[8] inelastic neutron scattering, heat capacity measurements,[9,10] and infrared reflectance spectroscopy.[11] Well-defined phase relations between guest and host dynamics were also found by neutron spectroscopy and *ab initio* calculations,[12] which disagrees with the explanation based on independent rattling of guest atoms. Ultrafast spectroscopy of skutterudites was first used by Wang et al., revealing that the resonant interactions of the host–guest system may also cause the reduction in κ_L.[13]

It has been found that filling skutterudites with multiple elements can suppress the lattice portion of thermal transport more effectively than a single element, which is usually explained by the notion that different elements can rattle at different frequencies and therefore scatter a broader range of

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phonons.[3,4] Since the concept of rattling is still open to question, this explanation needs further investigation. In this work, we utilized ultrafast spectroscopy to compare the resonant oscillations of single- and triple-filled skutterudites, and the results show that different elements can cause different resonant frequencies and that phonons with a broader frequency span can therefore be scattered by these oscillation modes.

EXPERIMENTAL PROCEDURES

Sample Preparation

High-purity Co and Sb shots were premelted by induction at 1400°C in boron nitride crucibles, followed by adding guest elements (Ba, Yb, La, or all three) and Sb to reach the desired composition and remelting at 1200°C for 5 min. These ingots were then annealed at 750°C for 2 weeks to obtain homogeneous samples of $M_xCo_4Sb_{12}$ (where M represents the guest element). The annealed samples were ground into powder for spark plasma sintering. The resulting samples were dense and nearly single phase with trace amounts of M_xO_y in samples containing this filler. Ba, Yb, and La were chosen as the fillers since they have been found to have substantially different vibrational frequencies and are therefore capable of scattering a broad range of phonons.[3,4] To elucidate the role of the individual elements, three single-filled samples containing each individual element were made, and a triple-filled sample with all of these elements was also prepared to see the effect of multiple-element filling. The compositions of these samples were determined by electron probe microanalysis to be $Ba_{0.26}Co_4Sb_{12.01}$, $Yb_{0.21}Co_4Sb_{11.92}$, $La_{0.14}Co_4Sb_{11.99}$, and $Yb_{0.05}La_{0.05}Ba_{0.08}Co_4Sb_{11.92}$.

Ultrafast Spectroscopy and Raman Spectra Measurements

An ultrafast laser system was used to excite and detect the resonant interactions between the guest atoms and the Co-Sb host lattice in the samples. The pump-and-probe technique was used in a two-color and collinear scheme to measure the transient thermoreflectance (TTR) signals of the skutterudite samples. The laser pulses were generated from a Spectra Physics Ti:sapphire amplified femtosecond system with central wavelength of 800 nm and repetition rate of 5 kHz. A barium borate (BBO) crystal was used to convert the wavelength of the pump beam to 400 nm. The higher photon energy ensures a higher kinetic energy of the photoexcited carriers, which can strengthen the carrier–phonon coupling. The probe had pulse duration (full-width at half-maximum, FWHM) of 70 fs as measured by autocorrelation, and the pump had pulse duration (FWHM) of 140 fs as measured by cross-correlation. The fluence of the pump was tuned to 193 J/m^2. The relative change of the reflectance of the sample surface within several ps was recorded. The Raman spectra measurements were taken with the excitation laser at wavelength of 633 nm. Considering the possible nonuniformity of the sample surface, the frequencies of the concerned modes were measured at seven points and the averages were used for analysis.

RESULTS AND DISCUSSION

The normalized TTR signal of the Ba-filled sample is shown in Fig. 1 together with a magnified-scale plot to show the oscillation of the signal. The signals of the other three samples showed similar trends and signatures, and for clarity are not shown. Compared with the results for the *p*-type

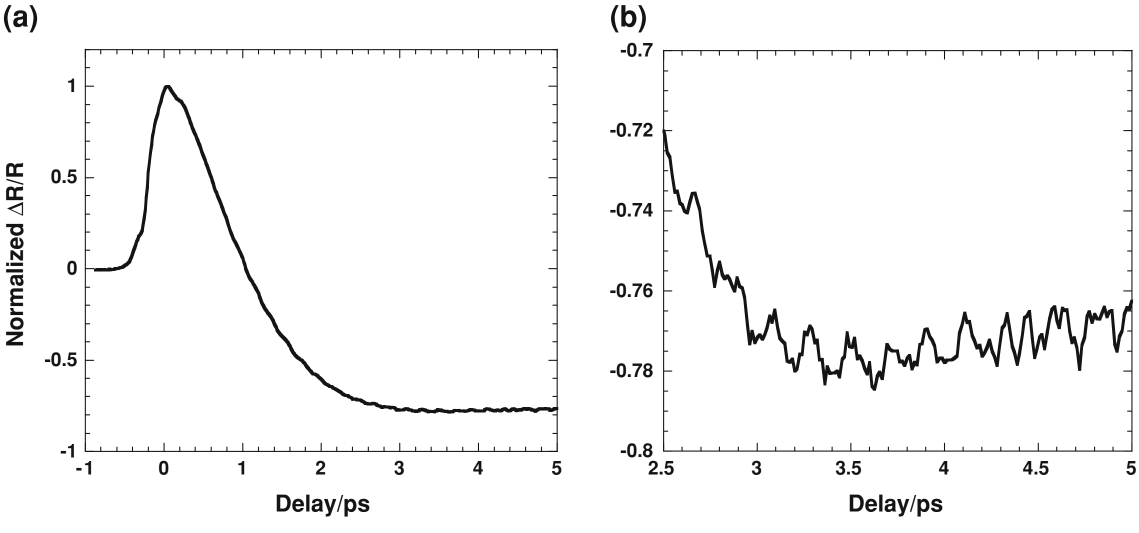

Fig. 1. (a) Normalized TTR signal of the Ba-filled sample. (b) Oscillations in the TTR signal shown on a magnified scale.

misch-metal-filled skutterudites,[13] there are two key differences. First, the background signals in this work cross zero, which indicates that the carriers are *n*-type in these samples. Second, the oscillations are much weaker in this work. This is due to the much lower filling ratios, which agrees with observations in previous work.[13] Also, the *n*-type samples in the present study may have smaller carrier effective mass, which can weaken the carrier–phonon coupling and thus the lattice oscillation strength.

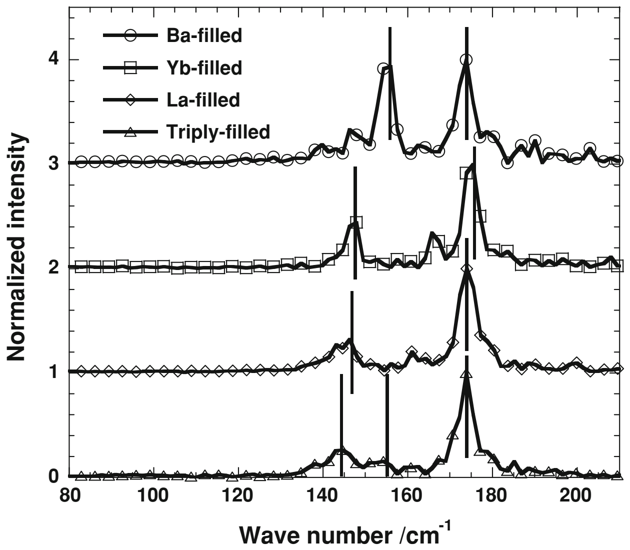

Fig. 2. Spectrum of the filtered TTR signals by Fourier transform.

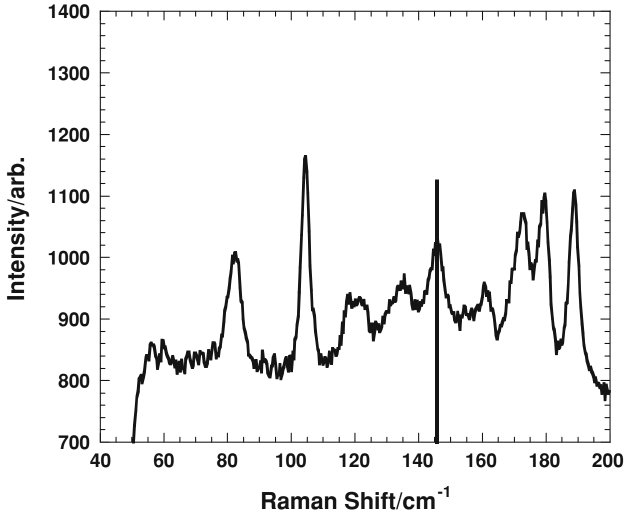

Fig. 3. Raman spectra of the $Ba_{0.26}Co_4Sb_{12.01}$ sample.

Fourier transformation was used to analyze the spectrum of the oscillations, and the result is shown in Fig. 2. A bandpass second-order Butterworth digital filter was applied to remove the carrier signal. The spectrum was normalized and shifted for clarity. For the single-filled samples, there are two dominating peaks for each, marked by vertical lines, one near 150 cm^{-1} (4.5 THz) and the other around 175 cm^{-1} (5.25 THz). For the triple-filled sample, there are two peaks near 150 cm^{-1}. The peaks around 175 cm^{-1} change little with the different filler species. In a previously published Raman spectra study on skutterudites, a phonon mode around this frequency was also found[14,15] and identified as an F_g mode.[15] The frequencies around 150 cm^{-1} are close to the resonant frequencies identified in Ref. 13 and are apparently affected by the nature of the filler species. For confirmation, Raman spectroscopy was also performed to identify these frequencies. The Raman spectra of all the samples are similar with regard to the positions of the Raman peaks, and the result for the Ba-filled sample is shown in Fig. 3 as an example. The only mode detected near 150 cm^{-1} is the low-energy A_g mode, marked by a vertical line in the plot. The frequencies from the TTR measurements together with the frequencies of the low-energy A_g modes from the Raman spectra measurements are listed in Table I, from which it is clear that the oscillations observed in the TTR measurement are sometimes spectrally close to, but are distinct from, the low-energy A_g mode.

From Fig. 2 and Table I, it is seen that the resonant frequencies caused by Yb and La filling are close in frequency and lower than that attributed to Ba filling. For the triple-filled sample, two resonant frequencies are detected, with one close to the resonant frequency caused by Yb or La filling and the other close to that caused by Ba filling. Also, if the magnitude of the peak around 175 cm^{-1} is taken as a reference, we can see that the resonant oscillations at the two frequencies for the triple-filled

Table I. Comparison of the frequencies from the TTR measurements and the frequencies of the low-energy A_g modes from the Raman spectra measurements

Sample	Frequencies from TTR Measurements (cm^{-1})	Low-Energy A_g Mode Frequencies from Raman Spectra Measurements (cm^{-1})
$Ba_{0.26}Co_4Sb_{12.01}$	155.9	145.8
$Yb_{0.21}Co_4Sb_{11.92}$	147.8	147.7
$La_{0.14}Co_4Sb_{11.99}$	146.3	147.5
$Yb_{0.05}La_{0.05}Ba_{0.08}Co_4Sb_{11.92}$	144.6/154.3	147.7

sample are both weaker than the corresponding single-frequency oscillation for the single-filled sample. This is because, for the triple-filled sample, the filling ratio of each element is lower and the absorbed energy is distributed into a larger number of oscillation modes. Therefore, we conclude that, by filling the skutterudite with different elements, different resonant frequencies can be created for the host–guest system, which can scatter a broader range of phonons, reducing κ_L.

CONCLUSIONS

TTR signals were obtained by ultrafast spectroscopy, showing weak but distinguishable oscillations in single- and triple-filled skutterudites. By analyzing the dependence of the oscillation spectrum on the filling material and comparison with the Raman spectra, we conclude that the oscillations detected in the TTR signals reflect the resonant interactions of the host–guest system caused by filling, and that filling with different elements can create different resonant frequencies. This work suggests that the resonant interactions are also a possible phonon scattering source in partially filled skutterudites, and that multiple-element filling can suppress phonon transport in skutterudites more effectively.

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