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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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