Title	ラマン散乱分光法による熱電材料中のマイクロ領域におけるフォノンの物性評価に関する研究
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Study on characterization of phonons in micro-regions on thermoelectric materials using Raman spectroscopy

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Thermoelectric has emerged as a promising power source for IoT (Internet of Things) sensors. However, challenges persist in reducing thermal conductivity and further enhancing the performance of thermoelectric materials. While significant advancements have been made in producing low thermal conductivity materials and measuring the macroscopic thermoelectric properties of them, the microscopic understanding of phonon properties and scattering processes responsible for low thermal conductivity remains limited. Recent researches suggest that optical phonons, previously considered irrelevant to thermal conduction in solids, can influence thermal conduction through optical phonon-acoustic phonon scattering processes. They may even contribute directly to heat transport in low-dimensional materials. Consequently, experimental evaluation of phonon properties at the microscopic scale in semiconductors has become critically important. This study aims to investigate the phonon temperature and phonon anharmonicity in micro-regions via Raman spectroscopy. By introducing a non-contact and non-destructive approach for evaluating phonons in thermoelectric materials, we expect to make a clear understanding for the origin of low thermal conductivity.

First, the optical phonon temperature, which is determined from the intensity ratio of anti-Stokes and Stokes peaks, were measured for van der Waals layered crystals, providing experimental insights into the energy relaxation processes from optical phonons to the lattice system. The result reveals that in the optical phonon temperature in MoX_2 (X = S, Se) single crystals becomes lower than the lattice temperature under the laser irradiation, suggesting that a local thermal non-equilibrium occurs, owing to the decay in the phonon distribution caused by the mismatch between the generation and decay rates of optical phonons. This mismatch may be originated from the high order phonon-phonon scattering process.

Building on these results, the phonon behavior and phonon anharmonicity of commercial thermoelectric materials Sb_2Te_3 and $Bi_2Te_{3-x}Se_x$ was investigated. By analyzing the full width at half maximum (FWHM) and Raman shifts of the Raman peaks, the phonon anharmonicity in Bi_2Te_{3-x}Sex (x = 0–3) has been fully evaluated quantitatively as a function of Se substitution. The results revealed that, despite crystal strain and variations in Se substitution, the third-order anharmonicity predominantly contribute to the phonon scattering processes in all samples. In contrast, higher-order nonlinear anharmonic terms (fourth-order and beyond) showed minimal contribution. This experiment emphasizes the importance of third-order anharmonicity when analyzing phonon-phonon scattering and thermal conductivity properties in this system.

Additionally, the Raman spectra of the new thermoelectric materials Ag_3SnP_7, which exhibits extremely low lattice thermal conductivity, were measured. The assignment of Raman peaks was confirmed using Quantum ESPRESSO, and the anharmonic effects of phonons were experimentally investigated. The result shows that the peaks below 100 cm^{-1} correspond to vibrational modes associated with Ag or Sn atoms. The low-frequency peaks are attributed to vibrational modes of the Ag 4f site, exhibiting strong higher-order anharmonic vibrations, which suggests a link to the anharmonic vibrations of Ag atoms. This observation is consistent with first-principles calculations explaining the origin of the material's low thermal conductivity.

KEYWORDS: thermoelectric materials, phonons, Raman spectroscopy, anharmonic lattice dynamics, micro-regions measurement