MLF Experimental Report	提出日 Date of Report 22, Aug. 2017
課題番号 Project No. 2017A0015 実験課題名 Title of experiment High-temperature phonon spectrum of thermoelectric bismuth chalcogenide $LaOBiS_{2-x}Se_x$ 実験責任者名 Name of principal investigator Yoshikazu Mizuguchi 所属 Affiliation Tokyo Metropolitan University	装置責任者 Name of responsible person Kenji Nakajima 装置名 Name of Instrument/(BL No.) AMATERAS/BL14 実施日 Date of Experiment June 22th – 28th, 2017

試料、実験方法、利用の結果得られた主なデータ、考察、結論等を、記述して下さい。(適宜、図表添付のこと)
Please report your samples, experimental method and results, discussion and conclusions. Please add figures and tables for better explanation.

1. 試料 Name of sample(s) and chemical formula, or compositions including physical form.

$LaOBiS_2$; powders
LaOBiSSe ; powders

2. 実験方法及び結果 (実験がうまくいかなかった場合、その理由を記述してください。)
Experimental method and results. If you failed to conduct experiment as planned, please describe reasons.

We examined phonons of $LaOBiS_2$ and LaOBiSSe at high temperature up to T = 890 K. We used powdered samples molded into a pellet by using a hydraulic press machine. Several pieces of sample were sealed in silica tubes and were attached to the bottom of a high temperature furnace. Weight of samples were about ~* g. Incident energies of neutron were 4.8, 7.4, 12.9, 27.4 and 94.3 meV.

Figure 1 shows the observed contour map of scattering intensity as a function of energy transfer (E) and momentum transfer (Q) of LaOBiSSe at T = 309 K. Signals from boson peak of SiO_2 was subtracted as a background. A flat band observed around E = 6 meV is attributed to optical phonons of LaOBiSSe. To visualize the energy spectrum of the phonons, the slice of contour maps in the Q range of 2.3 to 2.4 A^{-1} is demonstrated as intensity vs. energy plot in Fig. 2. Here, the SiO_2 boson peak was not subtracted but depicted by a green dashed line. The red solid line depicts the result of Gaussian fit with a SiO_2 boson peak and two optical phonons of LaOBiSSe. The

phonon observed around 6meV corresponds to the Bi rattling mode. The temperature dependence of the Bi rattling mode energy is depicted in Fig. 3. As shown, the energy decreases with heating from 10K to 400K. Above 400K, the softening stops and keep almost constant energy. This suggests that anharmonic behavior arises above 400K. Figure 4 shows Bose factor corrected intensities. The intensity of rattling mode (peak1) decreases with heating above 600K, demonstrating its anharmonic behavior. The results suggest that rattling without oversized cages also exhibit anharmonic vibrations contributing to the suppression of lattice thermal conductivity.

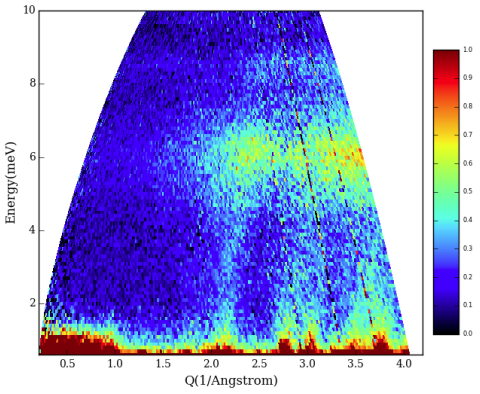

Fig. 1 Countour maps of the scattering intensity of LaOBiSSe at T = 309K with subtracting the boson peak of SiO_2.

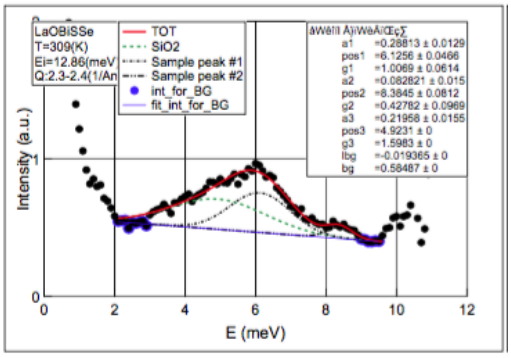

Fig. 2 Energy spectrum of phonons of LaOBiSSe in the Q range of 2.3 to 2.4A^{-1} at T = 309K.

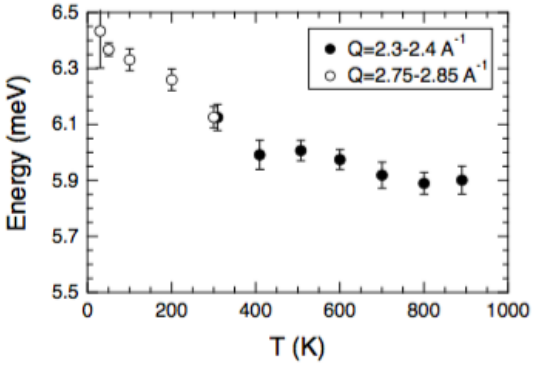

Fig. 3 Temperature dependence of phonon energy of the Bi rattling mode of LaOBiSSe.

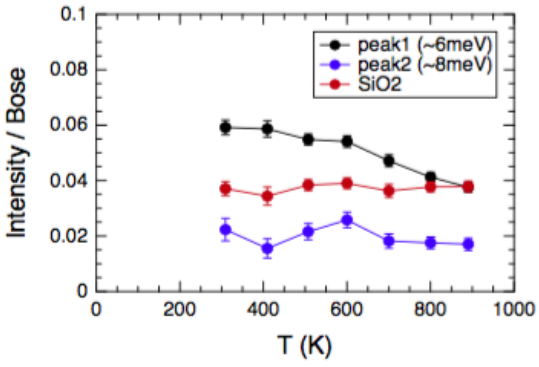

Fig. 4 Temperature dependence of Bose factor corrected intensity of phonons of LaOBiSSe and boson peak of SiO2.