（ ※本報告書は英語で記述してください。ただし、産業利用課題として採択されている方は日本語で記述していただいても結構です。 ）

CROSS TOKAI **Experimental Report** J-PARC	承認日 Date of Approval 承認者 Approver 提出日 Date of Report Oct. 31, 2016
課題番号 Project No. 2014B0115 実験課題名 Title of experiment Study of phonon anomaly in the thermoelectric material (Sr,La)(Ti,Mn)O_3 実験責任者名 Name of principal investigator Ryoichi Kajimoto 所属 Affiliation Japan Atomic Energy Agency	装置責任者 Name of Instrument scientist Ryoichi Kajimoto 装置名 Name of Instrument/（BL No.） 4SEASONS/BL01 実施日 Date of Experiment June 26–30, 2016

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.

$Sr_{0.95}La_{0.05}Ti_{0.98}Mn_{0.02}TiO_3$, single crystal

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.

Recently it was found that a few percent co-doping of electrons (substitution of Sr^{2+} by La^{3+}) and Mn ions in $SrTiO_3$ reduces the thermal conductivity substantially at room temperature (RT) [1]. In our previous inelastic neutron scattering studies on powder samples of $Sr_{1-x}La_xTi_{1-y}Mn_yO_3$ using 4SEASONS (2014A0083), we found that a low-energy part of the spectrum in a La and Mn co-doped sample is much enhanced compared with the other samples, which is probably related with the low thermal conductivity [1]. To elucidate phonons in the La and Mn co-doped $SrTiO_3$ in more detail, in the present experiment, we performed a single crystal inelastic neutron scattering study.

A 5 g single crystal of $Sr_{0.95}La_{0.05}Ti_{0.98}Mn_{0.02}O_3$ was prepared. The crystal structure is cubic with a = 3.9 Å. During the crystal alignment on the instrument, we found that a part of the sample consists of a different crystal grain. Then, we covered that part of the sample, whose size is roughly 2/3 of the whole sample, by a Cd mask. As a result, we were able to obtain a single-grain crystal whose mass is effectively about 3 g. Inelastic neutron scattering measurement was performed using incident neutron

energies E_i = 130, 50, and 26 meV. The measurement was performed at RT. The crystal was first aligned so that the [100] axis is parallel to $\boldsymbol{k}_i$. Then, it was horizontally rotated over $-67° < \psi < +75°$ with a 0.5° step, where ψ is a relative rotation angle to the initial position. The observed scattering spectra were compiled in the form of four-dimensional $S(\boldsymbol{Q}, E)$ by the software suite Utsusemi.

Figure 1 shows observed scattering spectra as cuts along (H, 1, 1), (2, K, K), and (H, 0.5, 0.5). Background intensity estimated from an empty run was subtracted. In the figure, dispersion relations of acoustic as well as optical phonons are clearly observed. By comparing the observed spectra with the phonon dispersions of $SrTiO_3$ reported by previous studies [2,3], we found that the present compound shows a clear softening of phonon at the R point [Fig. 1(a)]. It is well known that $SrTiO_3$ shows a structural transition from cubic to tetragonal structures at 105 K caused by softening of the zone boundary mode at the R point [2,3]. The present result shows that the La and Mn doping cause similar phonon softening even at RT. On the other hand, around the Γ points [Figs. 1(b) and 1(c)], we observed dispersions of acoustic modes, which coincide well with those of $SrTiO_3$ [2]. In addition, an optical mode is observed above the acoustic modes. This optical mode seems to correspond to the soft TO mode in $SrTiO_3$, but its energy is quite higher than that of the latter (~11 meV at the Γ point [2]). Furthermore, the spectrum of this optical mode seems to be broader than those of the acoustic modes. The behavior of the soft TO mode around the Γ point should be important for understanding the thermal conductivity, as recently reported in another thermoelectric material PbTe [4]. To unambiguously identify the anomaly in the TO mode, we are planning to measure phonons in $SrTiO_3$ similarly to compare them with the present result.

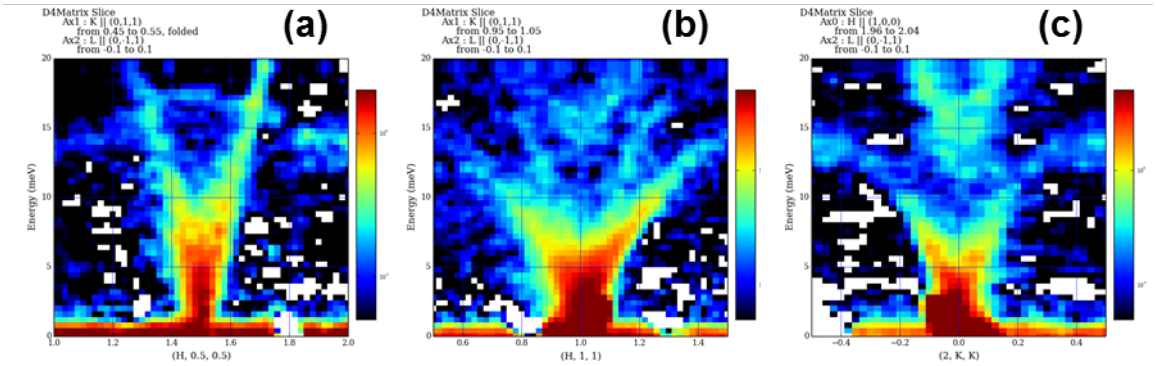

Figure 1. Phonon spectra of $Sr_{0.95}La_{0.05}Ti_{0.98}Mn_{0.02}O_3$ at RT along (a) (H, 0.5, 0.5), (b) (H, 1, 1), and (c) (2, K, K) observed with E_i = 26 meV. Note that in (b) and (c), the spectra are dominated by the contributions from transverse modes.

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[3] G. Shirane *et al.*, Rev. Mod. Phys. **46**, 437 (1974).
[4] O. Delaire *et al.*, Nat. Mater. **10**, 614 (2011); C. W. Li *et al.*, Phys. Rev. Lett. **112**, 175501 (2014).