MLF Experimental Report	提出日 Date of Report 2015/2/16
課題番号 Project No. 2014A0175 実験課題名 Title of experiment Crystal structures at high temperature of layered gallate-based oxide-ion conductors with the Melilite structure 実験責任者名 Name of principal investigator Yasushi Idemoto 所属 Affiliation Tokyo University of Science	装置責任者 Name of responsible person Takashi Kamiyama 装置名 Name of Instrument/（BL No.） SuperHRPD/BL08 実施日 Date of Experiment 2014/6/12 - 2014/6/14 2014/12/3 - 2014/12/5

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.

$La_{1+x}Sr_{1-x}Ga_3O_{7+\delta}$, pellet

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.

Experimental method

$La_{1+x}Sr_{1-x}Ga_3O_{7+\delta}$ (x=0~0.62) were synthesized by a conventional solid-state reaction method using $La2O_3$, $SrCO_3$ and Ga_2O_3 as starting materials. Phase identifications of these samples were performed preliminarily by powder X-ray diffraction measurements, and the metal compositions were confirmed by inductively-coupled plasma (ICP) technique. Conductivities of their sintered pellets were measured at the temperature range of 300~900 ^oC by an AC two probe method. From dependencies of the conductivities on oxygen partial pressure, predominant oxide-ion conductions were confirmed in the case of $La_{1+x}Sr_{1-x}Ga_3O_{7+\delta}$ with $x > 0$.

In order to investigate crystal structures at elevated temperature, neutron diffraction patterns were recorded at 500 ^oC in addition to room temperature by SuperHRPD. In this experiment, a sintered pellet of each sample was loaded in a V can, and then the can was mounted in a furnace. The obtained data (BS bank) were analyzed on the basis of the Rietveld method and the maximum-entropy method by using the Z-Rietveld and Z-MEM.

2. 実験方法及び結果（つづき） Experimental method and results (continued)

Results

A Rietveld refinement pattern of $La_{1.5}Sr_{0.5}Ga_3O_{7.25}$ at 500 °C is presented in Fig. 1. In the analysis, we assumed a space group of the crystal structure as *P*-42$_1$*m* (the Melilite-type structure), and refined atomic positions and displacement parameters of all the elements. Site occupancies were fixed taking the metal composition and the nominal valences into account. It was demonstrated that the sample had a single phase of the Melilite structure even at high temperature as well as room temperature although the lattice parameters became larger due to thermal expansion.

Figure 2 shows a 2D image of nuclear-density distribution [(001) plane] of the sample at 500 °C. In this figure, the O4 represent interstitial oxide ions which can be considered as conduction species. It was found that the nuclear density of O4 was dispersed anisotropically within the (001) plane. This results indicates that the interstitial oxide ions can diffuse along with this plane, i. e. the Ga-O_4 tetrahedral network.

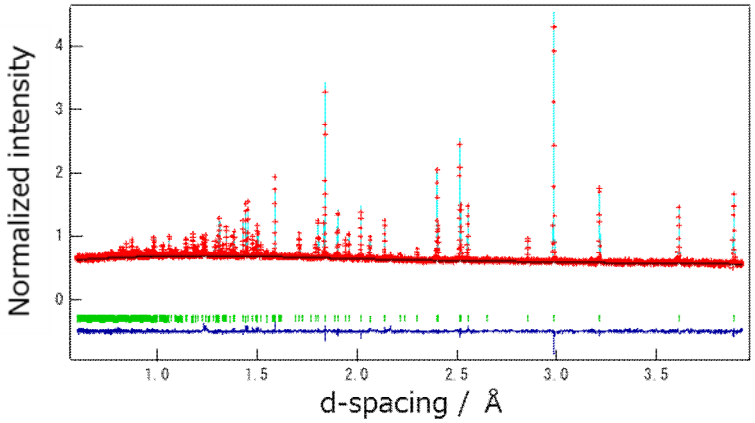

Fig. 1 Rietveld refinement pattern of $La_{1.5}Sr_{0.5}Ga_3O_{7.25}$ at 500 °C (S. G. *P*-42$_1$*m*). Plus marks show observed neutron diffraction intensities, and a solid line represents calculated intensities. Vertical marks indicate positions of the Bragg reflections. A curve at the bottom is a difference between the observed and calculated intensities. *R*-factors were R_{wp}=2.16 % and R_e=1.57 %.

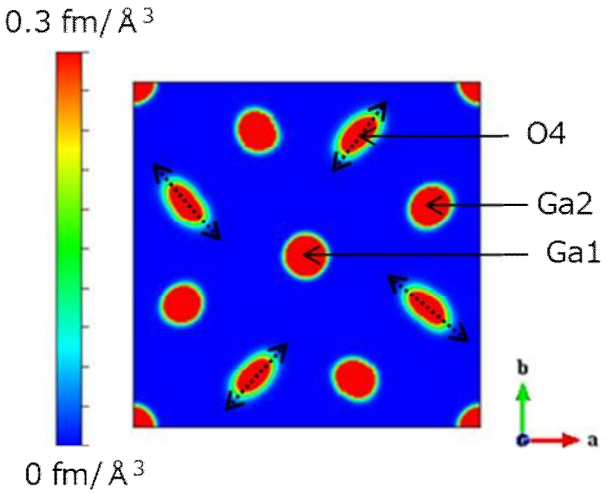

Fig. 2 Nuclear-density distribution [(001) plane] of $La_{1.5}Sr_{0.5}Ga_3O_{7.25}$ at 500 °C.