MLF Experimental Report	提出日 Date of Report 10/5/21
課題番号 Project No. 2008A0008 実験課題名 Title of experiment Investigation of subtle structural changes in impurity doped C12A7 実験責任者名 Name of principal investigator KIYANAGI, ryoji 所属 Affiliation IMRAM Tohoku university	装置責任者 Name of responsible person KAMIYAMA, takashi 装置名 Name of Instrument/(BL No.) SHRPD/BL08 実施日 Date of Experiment 09/02/23-09/02/25

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.

Sample A : $Ca_{11.4}Sr_{0.6}Al_{14}O_{33}$

Sample B : $Ca_{12}Al_{13.75}Ga_{0.25}O_{33}$

Sample C : $Ca_{12}Al_{13.25}Ga_{0.75}O_{33}$

All samples are in powder form.

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.

The samples were sealed in vanadium cans in ambient atmosphere, and the cans were attached onto a room temperature sample changer. The intensity data were collected using the back scattering bank in order to take the advantage of the high resolution that BL08 can provide. All measurements were conducted at room temperature. Each measurement runs for about 8 hours including the unplanned beam-off period. Some reflection profiles from each sample are shown in Fig. 1. As is seen in the figure, the peak positions of sample A, B and C were found to slightly differ from each other suggesting the success of the replacement of ions in the bulk of the samples. Note that the peak of sample A is much broader and has a little tail toward longer

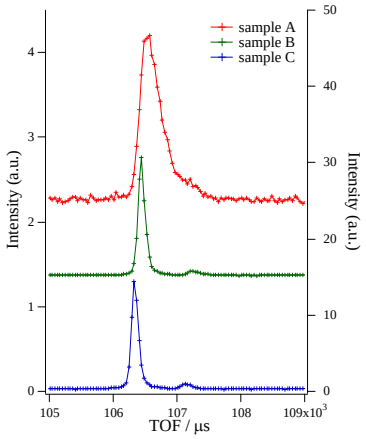

Fig. 1 Profile of (5 2 1) reflection of each sample.

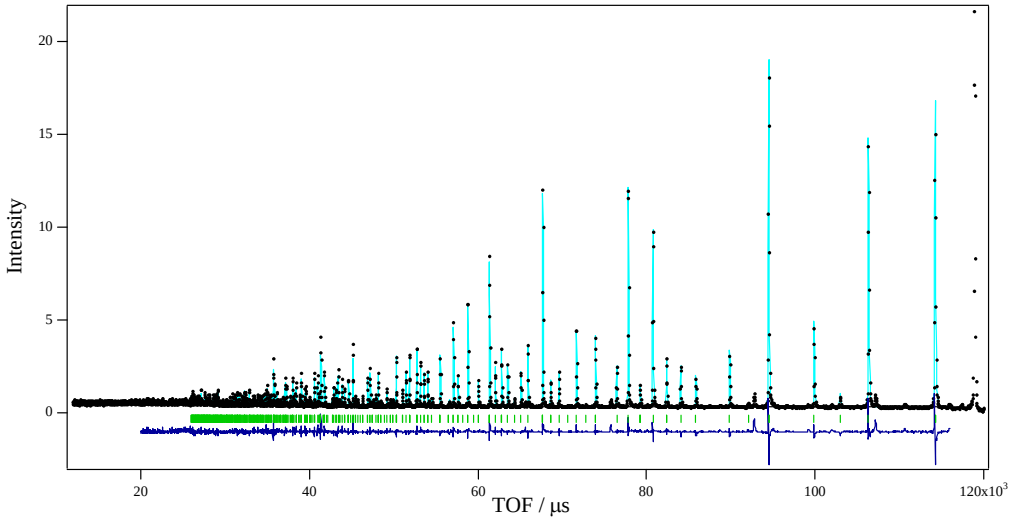

Fig. 2 Result of the Rietveld fitting on sample C.

The collected data from sample B and C were analyzed by the Rietveld method (The data from sample A could not be analyzed by the Rietveld method because of the peak broadening as mentioned above). Shown in Fig. 2 is an example of the Rietveld fitting on sample C. The R-factor of this refinement was RF = 7.0 %.

The obtained lattice parameters were a = 11.9778 Å and 11.9659 Å for sample B and C, respectively. The difference in these values is reasonable taking the ionic radii of Al^{3+} and Ga^{3+} into account.

One of the conspicuous result obtained from both samples are very high occupancies of so-called "free oxygen ion". This material forms a cage structure and captures various negative ions such as O^{2-}, O^{-}, O_2^{-}, OH^{-}. In the case where O^{2-} is captured, the ideal value of the occupancy is about 0.04. However, the obtained values from the present analyses are about 0.12, implying the existence of other forms of oxygen ions inside the cage. In other words, the replacement of Al^{3+} with Ga^{3+} may enhance the storage of the radicals other than O^{2-}. Note that the possibility of the existence of OH^{-} ion should be eliminated since the observed powder pattern shows no trace of the incoherent scattering from hydrogen atoms.

As for the internal structure, the effect of the replacement of Al^{3+} with Ga^{3+} is most pronouncedly seen in Al-O bond length. First of all, it was confirmed that there are three types of bonds among Al-O bonds. One is with long bond length, one is short and another is medium. Each bond exhibits deviation in length between sample B and C. As shown in Fig. 3 the bond of Al(1)-O(1) shows largest elongation from sample C to

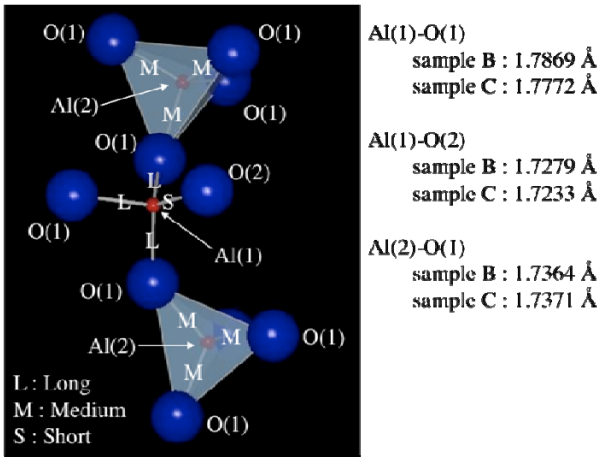

Fig. 3 Schematic drawing of Al-O tetrahedrons and Al-O bond lengths.