High temperature single crystal neutron diffraction analysis of the apatite-type oxide-ion conductors

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1. Introduction

Oxide-ion conductors attract many interests because of their potential use for oxygen separation membranes and cathodes of solid-oxide fuel cells (SOFCs). At the present time, oxide-ionic conducting ceramics are used at high temperature (800-1000°C) because the required oxide-ion conductivity is achieved at such high temperatures. Therefore, a development of high oxide-ion conductors at low or intermediate temperature (less than 800 °C) are strongly required. Apatite-type lanthanum silicates are good candidates for the electrolyte of intermediate temperature solid-state fuel cells (IT-SOFCs) because of their high oxide-ion conductivity at low temperature. Although understanding the mechanism of the oxide-ion conduction in the apatite-type lanthanum silicates is necessary for further development on the oxide-ion conductors, it has not been clearly understood. In order to resolve this issue, precise and accurate crystal structure information is necessary. Most of previously reported works were discussed using powder diffraction method and/or theoretical calculation, which are not sufficient to discuss the details. A single crystal neutron diffraction technique is most powerful method to reveal precise and accurate crystal structure including detail information on the oxygen atoms (atomic position, atomic displacement parameters, disorder, and occupancy factors) which is important to understand the mechanism of the oxide-ion conduction. From our previous experiment at Senju diffractometer of J-PARC, we have revealed the crystal structures of $La_{9.33}Si_6O_{26}$ and a La-rich material $La_{9.33+\delta}Si_{6-\delta}O_{26}$ at room temperature. In this proposal, we aim to conduct high-temperature single-crystal neutron diffraction experiments for $La_{9.33+\delta}Si_{6-\delta}O_{26}$.

2. Experiment

The single crystal of $La_{9.33+\delta}Si_{6-\delta}O_{26}$ with size of ca. 1 ×1 × 1 mm^3 is mounted on a Ta pin and used for the high-temperature measurement. The measurement was carried out at 1000 °C using a vacuum furnace. We planned to take the diffraction data at two different φ orientation. However, during the measurement of the second φ orientation set data, the measurement was stopped because of the beam dump. We have to take the data again in other beam time.

3. Results

Fig. 1 shows an example of the diffraction image of the single crystal of $La_{9.33+\delta}Si_{6-\delta}O_{26}$ at 1000 °C. The collected event data were converted into the time slicing data. The data reduction was carried out using the Stargazer package. The reflection data file was analyzed using the Jana2006. The room temperature structure was used as the initial model. Now we are doing least square refinements for the obtained data. Because there are several structure models, and many refinement conditions, we need time to make clear conclusion of this analysis. At the present, we confirmed that the crystal structure of $La_{9.33+\delta}Si_{6-\delta}O_{26}$ at 1000 °C belongs to the space group $P6_1/m$, which is same with that of the room temperature.

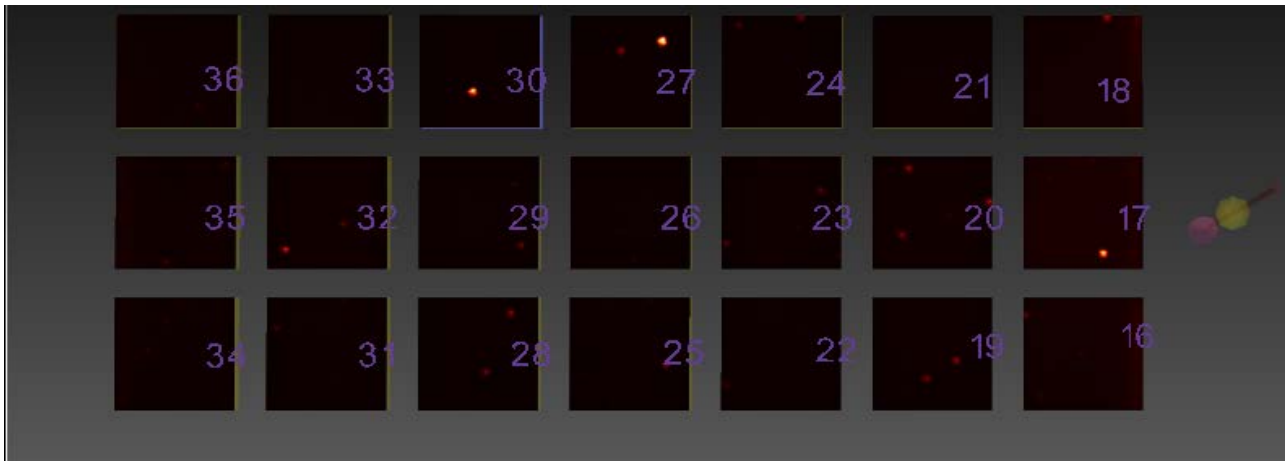

Fig. 1: An example of the diffraction image of the single crystal of the apatite-type lanthanum silicate.

4. Conclusion

The data analysis is now in progress and the result may obtain later. The data quality seems fine, but we need to take the data again because we met the beam dump during the measurements.