Crystal Structure of La-Ge-O Ionic Conductor

Yoshitaka Matsushita, Naohito Tsujii, Kiyoshi Kobayashi, and Fujio Izumi
Quantum Beam Center, National Institute for Materials Science

The La-T (T = Si and Ge) oxyapatites having chemical composition written as $Ln_{9.33\pm x}T_6O_{26\pm 3x/2}$, attract attention for the most promising oxygen-ionic conductor of next generation, and it has been measured the various kind of properties until now.[1, 2] These compounds show better oxygen ionic conductivity in the intermediate-temperature range compared with other famous oxygen-ionic conductors (ZrO_2 and/or CeO_2-based materials). However, the excess oxygen sites have not been found out, yet. The germanate compounds have low-temperature ($P\bar{1}$) and high-temperature ($P6_3/m$) forms. The two crystal structure models of low-temperature form had been proposed.[3, 4] In this study, we measured the intensity data using neutron powder-diffraction technique to identify the crystal structure of low-temperature germanate.

The germanate apatite sample ($La_{9.8}Ge_6O_{26.7}$) was prepared by solid-state reaction. All processes are carried out under air. The mixture of La_2O_3 and GeO_2 were calcined at 1273 K for 50 hours. Starting La_2O_3 was pre-heated at 1273 K for a night. The ground sample was pressed into the pellets, and re-heated up to 1273 K for 24 hours.

The intensity measurement at room temperature ($5^\circ \leq 2\theta < 156^\circ$), was carried out using IMR-HERMES diffactmetor (T1-3), installed in the JRR-3M reactor. The wavelength of neutron was 1.8265(1) Å, which was vertically focused by a (331) Ge monochromator. The resulting diffraction data were analyzed by the Rietveld method with RIETAN-FP [5] and whole-pattern fitting approach based on the maximum-entropy method (MPF)[6].

The cation compositions were fixed as chemical analysis result ($La_{9.8}Ge_6O_{26.7}$) on the Rietveld refinement. The space group was selected to $P\bar{1}$, and both reported structural models were examined. In current refinement process, the Pramana's model gave better fit. However, the refinement is not fully satisfied. The current convergent indexes were Rwp = 3.96 %, Rp = 2.93 %, RR = 6.15 %, Re = 0.78 %, RI = 0.89 %, and RF = 0.41 %. The obtained cell parameters from the Rietveld analysis were a = 9.929(2) Å, b = 9.920(2) Å, c = 7.2914(6) Å, α = 90.46(1) °, β = 89.04(1) °, and γ = 120.36(1) °.

References

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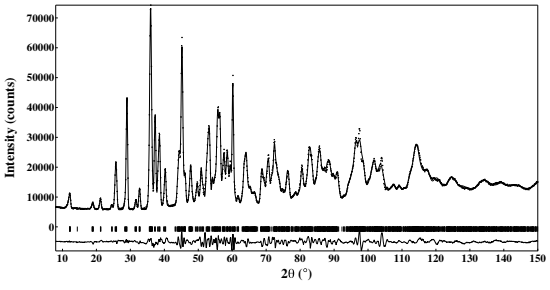

Fig. 1. Powder neutron diffraction profile of $La_{9.8}Ge_6O_{26.7}$.