Synthesis, Structure and Ionic Conductivity of Sr-substituted $Li_{6.25}Ga_{0.25}La_3Zr_2O_{12}$ with garnet-type structure

Daisuke Mori [a], Kaoru Sugimoto [a], Yasuaki Matsuda [b], Yasuo Takeda [a], Nobuyuki Imanishi [a]

[a] *Department of Chemistry for Materials, Mie University, 1577 Kurimamachiya-cho, Tsu 514-8507, Japan*

[b] *Department of Applied Chemistry, Osaka Institute of Technology, 5-16-1 Ohmiya, Asahi-ku, Osaka 535-8585, Japan*

E-mail: daisuke.mori@chem.mie-u.ac.jp

All solid-state lithium batteries attract much attentions as a next generation energy devices with superior properties. Garnet-type lithium ionic conductor $Li_{6.25}Al_{0.25}La_3Zr_2O_{12}$ (LLZ-Al) is known to be stable to Li metal and exhibit relatively high ionic conductivity. However, high temperature sintering is required to obtain the dense sintered body. Therefore, we focused on $Li_{6.25}Ga_{0.25}La_3Zr_2O_{12}$ (LLZ-Ga) in previous study and demonstrated that LLZ-Ga showed better sinterability and higher ionic conductivity of 9.6 x 10^{-3} Scm^{-1} than LLZ-Al [1]. In this study, Sr-substituted LLZ-Ga, $Li_{6.25+x}Ga_{0.25}La_{3-x}Sr_xZr_2O_{12}$ (LLZ-GaSr) was synthesized to improve sinterability and ionic conductivity of LLZ-Ga. The relationship between their composition, structure, sinterability and ionic conductivity is discussed,

LLZ-GaSr was synthesized at 1000 ˚C by a solid-state reaction. Li_2CO_3, Ga_2O_3, $La(OH)_3$, ZrO_2 and $Sr(NO_3)_2$ was used as starting materials. The samples were quenched from above 400 ˚C to avoid the reaction with H_2O and CO_2. Phase identification was carried out by XRD measurements. The sinterability and composition were confirmed using SEM-EDX. The ionic conductivity was evaluated by AC impedance measurements using Au sputtered electrodes.

The XRD patterns of LLZ-GaSr are shown in Fig. 1. The XRD measurements confirmed that cubic and tetragonal garnet phase was formed in x = 0-0.2 and 0.3-0.5 in LLZ-GaSr, respectively. An increase in Li content with increasing Sr content would lead to phase transition from cubic to tetragonal phase. The lattice parameter a increased linearly with increasing Sr content up to x = 0.1 and was constant further. It indicates that the solubility limit of LLZ-GaSr is around x = 0.1. The sintered density of the sample in $x \leq 0.2$ reached above 90% and the formation of dense pellets was confirmed by SEM observation. The sample in x = 0.1 exhibited lithium ionic conductivity of 1.3 x 10^{-3} Scm^{-1} at 25 ˚C. Sr substitution for LLZ-Ga was effective to enhance lithium ionic conductivity.

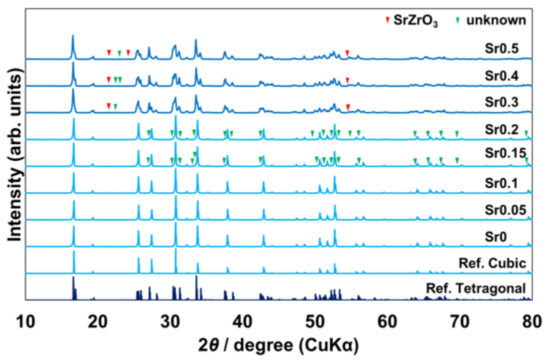

Fig. 1 XRD patterns for $Li_{6.25+x}Ga_{0.25}La_{3-x}Sr_xZr_2O_{12}$ synthesized at 1000 ºC for 12 h in air.

References:

[1] Y. Matsuda, A. Sakaida, K. Sugimoto, D. Mori, Y. Takeda, O. Yamamoto, N. Imanishi, *Solid State Ionics*, 311 (2017) 69.