Synthesis, Structure and Ionic Conductivity of Sr-substituted 
Li$_{6.25}$Ga$_{0.25}$La$_3$Zr$_2$O$_{12}$ with garnet-type structure

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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$_3$Zr$_2$O$_{12}$ (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$_3$Zr$_2$O$_{12}$ (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$Sr$_x$Zr$_2$O$_{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$_2$CO$_3$, Ga$_2$O$_3$, 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$_2$O 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$Sr$_x$Zr$_2$O$_{12}$ synthesized at 1000 °C for 12 h in air.

References: