

### Simultaneous substitution in high lithium ion conducting garnet-type oxides;



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A demand for lithium-ion batteries has continued to expand with the market growth in HV, PHV and other electric vehicles. However, those lithium-ion batteries suffer some limitations considering their safety for using a combustible organic liquid electrolyte. All-solid-state batteries have been focused as a safer alternative candidate with an incombustible solid electrolyte. Garnet-type oxides,  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$  (LLZ), found by Weppner's group have been one of the promising solid electrolytes because they have excellent chemical stability and wide potential window.<sup>[1]</sup> LLZ shows high lithium-ion conductivity for oxide-base electrolytes, but it is still required to improve the lithium-ion conductivity for practical application.

Some studies have tried to improve the lithium-ion conductivity of LLZ by substitution to regulate framework atoms. The structural control of framework atoms is expected to modify the lithium ion path way and vary the lithium-ion conductivity. We have successfully found that LLZ with Nb substitution at Zr site shows higher lithium-ion conductivity.<sup>[2]</sup> When either one of La or Zr site in LLZ is substituted by an element, the lithium content usually varies as well as the framework structure. Hence, it has not been clear which factor(s), structure or lithium content, would mainly control the lithium-ion conductivity in LLZ.

In order to regulate both the structure and lithium content, we have substituted not only Nb(+5) at Zr(+4) site but also Ca(+2) or Sr(+2) at La(+3) site simultaneously in  $\text{Li}_{7+x}\text{La}_{3-y}\text{A}_y\text{Zr}_{2-z}\text{Nb}_z\text{O}_{12}$  (A,Nb-LLZ, A=Ca, Sr). Interestingly, an optimal lattice parameter which can be considered as a factor of framework structure was obtained under constant lithium content seven for the substituted LLZ series.<sup>[3]</sup> Here, we found that samples with Ca exhibited the higher lithium-ion conductivity than that with Sr. The results imply that samples with Ca and Sr had a different characteristics in grain-boundary resistance ( $R_{gb}$ ). The  $R_{gb}$  will be the main problem when applying garnet-type oxides to industrial use. Thus, we focus on the  $R_{gb}$  of substituted LLZ samples and discuss the difference between Ca and Sr in this study.

Bulk ceramic samples with optimized chemical compositions of garnet-type oxide, A,Nb-LLZ, were synthesized by conventional solid-state reaction.<sup>[1]</sup> The crystal structure of the samples was identified by powder XRD analysis. The lithium ion conductivity and chemical stability of the samples were measured in open air by the AC impedance method using Au-electrodes. The elemental distribution at the grain boundary of the samples was analyzed by electron probe micro analyzer (EPMA).

It was found that A,Nb-LLZ has both high lithium ion conductivity at 25 °C and chemical stability in air. The potential window was wide enough that no reaction between the sample and electrodes was observed after CV measurement. Figure 1, lithium-ion conductivity of A,Nb-LLZ, exhibits that lithium-ion conductivity shows the highest value regardless of the substitution element. However, the samples with Sr substitution had

high ratio of  $R_{gb}$  to total resistivity with increasing substitution amount (Fig. 2). In contrast, a low ratio of  $R_{gb}$  was observed for Ca,Nb-LLZ over the full range in this experiment. All samples exhibit a single cubic garnet phase from XRD analysis. The results from EPMA illustrated their clear difference in elemental distribution around the grain boundary that may induce the difference in  $R_{gb}$ .

We have synthesized A,Nb-LLZ (A=Ca, Sr) with high lithium-ion conductivity by partial substitution of Ca or Sr for La site and Nb for Zr site. The samples with Ca exhibited the lower ratio of  $R_{gb}$ , while those with Sr had the higher ratio of  $R_{gb}$  at the elevated level of substitution amount. This difference was considered to be caused by the elemental distribution at the grain boundary based on EPMA results. We will report the effect and difference of the substitution of Ca and Sr in LLZ.

### References

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- [3] Y. Kihira *et al.*, *ECS Electrochem. Lett.*, **2**, **7**, (2013) A56-A59.

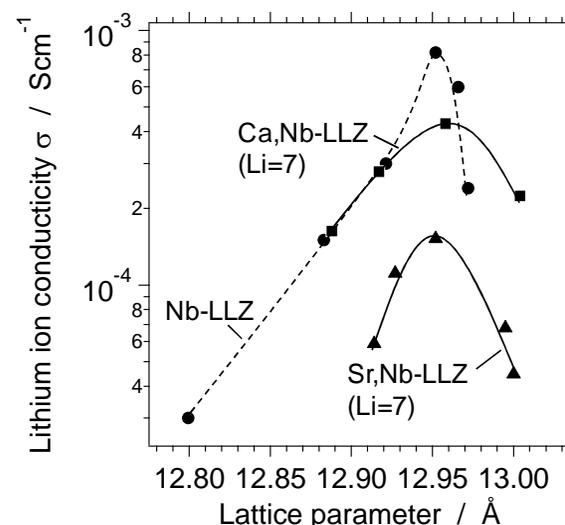


Fig. 1 Lithium-ion conductivity of  $\text{Li}_{7+x}\text{La}_{3-y}\text{A}_y\text{Zr}_{2-z}\text{Nb}_z\text{O}_{12}$

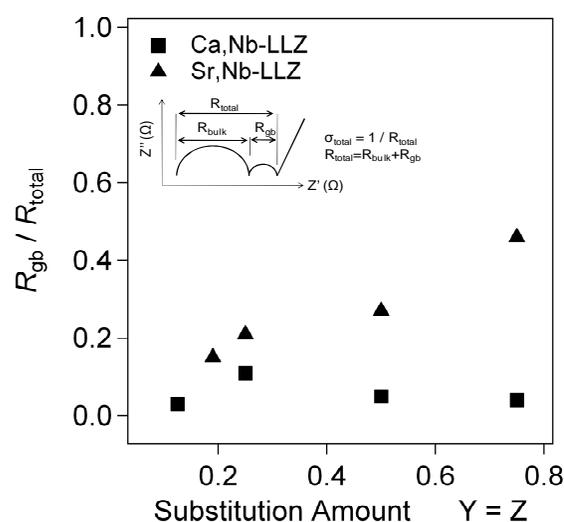


Fig. 2 Ratio of grain-boundary resistivity to total resistivity of  $\text{Li}_{7+x}\text{La}_{3-y}\text{A}_y\text{Zr}_{2-z}\text{Nb}_z\text{O}_{12}$