MLF Experimental Report	提出日 Date of Report July 24, 2012
課題番号 Project No. 2012A0044 実験課題名 Title of experiment Diffusive behavior of garnet-type compounds II 実験責任者名 Name of principal investigator Jun Sugiyama 所属 Affiliation Toyota Central Research and Development Laboratories, Inc.	装置責任者 Name of responsible person Yasuhiro Miyake 装置名 Name of Instrument/(BL No.) D1 実施日 Date of Experiment May 14, 2012 – May 20, 2012

試料、実験方法、利用の結果得られた主なデータ、考察、結論等を、記述して下さい。（適宜、図表添付のこと）
Please report your samples, experimental method and results, discussion and conclusions. Please add figures and tables for better explanation.

1. 試料 Name of sample(s) and chemical formula, or compositions including physical form.

Garnet-type compounds, $Li_xLa_3Zr_{x-5}Nb_{7-x}O_{12}$ with x=6.3, 6.5, and 6.85.
A 2g powder sample was pressed in a disc with 27 mm diameter and 1 mm thickness, and then the disc was packed in a gold O-ring sealed titanium cell.

2. 実験方法及び結果（実験がうまくいかなかった場合、その理由を記述してください。）
Experimental method and results. If you failed to conduct experiment as planned, please describe reasons.

In order to fabricate an all solid-state lithium-ion battery for improving safety and volumetric energy density, a solid electrolyte is unambiguously one of the key materials, because only the electrolyte is in a liquid state among the components for the present Li-ion batteries. Recently, a novel garnet-type compound, $Li_{6.75}La_3Zr_{1.75}Nb_{0.25}O_{12}$ [see Fig. 1], was found to exhibit the highest Li-ion conductivity ($\sigma_{Li}=10^{-3}$ S/cm at ambient temperature) [1,2] among several oxide electrolytes. Note that this σ_{Li} is lower only by one order of magnitude than σ_{Li} for the present liquid electrolyte, and is almost comparable to σ_{Li} for a gel electrolyte [3].
Here, the chemical formula of the garnet-type compound is represented by $Li_xLa_3Zr_{x-5}Nb_{7-x}O_{12}$, and σ_{Li} is known to depend on x; i.e. the $\sigma_{Li}(x)$ curve exhibits a maximum at x=6.75 [see Fig. 2(a)] [1,2], for reasons currently unknown. In order for clarifying the reason why x=6.75 is an optimal composition, we have attempted to investigate the diffusive nature of $Li_xLa_3Zr_{x-5}Nb_{7-x}O_{12}$ by μ^+SR.
According to ZF- and LF-μ^+SR measurements on the present (x=6.5 and 6.85) and previous (x=5, 6, 6.75, and 7) samples in the T range between 100 and 400 K, the field fluctuation rate (n) at 300 K is found to change with x. Assuming that n corresponds to the jump rate of the Li^+ ions between the

2. 実験方法及び結果（つづき） Experimental method and results (continued)

a diffusion coefficient of Li^+ ions (D_{Li}) as a function of x [see Fig. 2(b)].

Since all the six samples are a good insulator, D_{Li} and σ_{Li} is connected by a simple Nernst-Einstein formula;

$$D_{Li} = \sigma_{Li}RT/(F^2z^2),$$

where R is the gas constant, F is the Faraday's constant, and z is the number density of mobile Li^+ ions. In other words, we can estimate the change in z with x from the relationship between $(\sigma_{Li}/D_{Li})^{0.5}$ and x [see Fig. 2(b)]. This implies that not D_{Li} but z is the predominant parameter to determine σ_{Li} for $Li_xLa_3Zr_{x-5}Nb_{7-x}O_{12}$. The present result also suggests a novel μ^+SR power to determine the mobile carrier concentration in ionic-conducting materials, as in the Hall measurements for estimating an electron and/or hole concentration in solids.

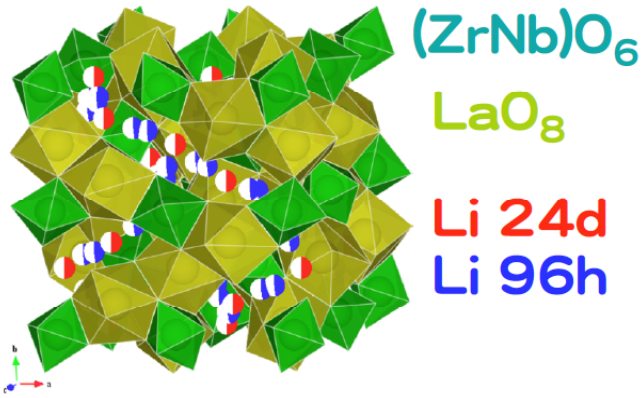

Fig.1: The crystal structure of $Li_{6.75}La_3Zr_{1.75}Nb_{0.25}O_{12}$ determined by neutron.

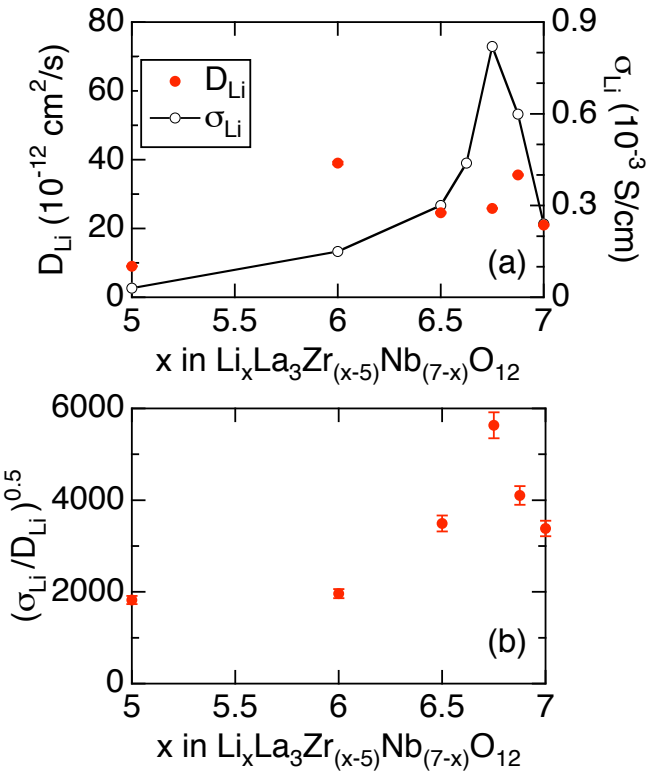

Fig. 2: The x dependences of (a) D_{Li} and σ_{Li} and (b) $(\sigma_{Li}/D_{Li})^{0.5}$ for $Li_xLa_3Zr_{x-5}Nb_{7-x}O_{12}$. In the 2012 experiment, two more data at x=6.5 and 6.85 are added. Although we also measured the x=6.3 sample, we were unable to evaluate its D_{Li} from the hopping rate due to the absence of a detailed structural data.

REFERENCES

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