MLF Experimental Report	提出日 Date of Report February 3, 2015.
課題番号 Project No. 2014A0290 実験課題名 Title of experiment μ^+SR study for oxygen-ion diffusion in solids 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 November 22, 2014 – November 23, 2014

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.

Lithium iron manganese phosphate $LiFe_{0.5}Mn_{0.5}PO_4$, $LiFe_{0.2}Mn_{0.8}PO_4$ and $LiFe_{0.1}Mn_{0.9}PO_4$.
A powder sample was packed into 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.

Originally, we planned to measure μSR spectra for oxygen-ion conducting materials at high temperatures until 1273 K using an oven heated with an infrared lump (proposal #2014A0290). However, due to the upgrade of the spectrometer of D1, the size of the sample space was significantly changed. As a result, such oven was unavailable in 2014. Therefore, we measured a diffusive nature of lithium iron manganese phosphates ($LiFe_{1-x}Mn_xPO_4$) up to 400 K using a liquid He flow-type cryo-oven (proposal #2014B0266).

According to our μSR study on $LiMnPO_4$ [1], the ZF-spectrum was found to show a rapidly relaxing behavior due to large magnetic moments of Mn^{2+} ions (S=5/2) even at 300 K. This means that it is difficult to know the diffusive behavior in LiMnPO4, because a Kubo-Toyabe-type relaxation caused by nuclear magnetism of Li was entirely hindered by the rapid relaxation. We have, thus, attempted to measure μSR spectra of a solid solution system between $LiFePO_4$ and $LiMnPO_4$ in order to extrapolate the diffusive nature of $LiMnPO_4$ from the result of $LiFe_{1-x}Mn_xPO_4$.

Powder samples of $LiFe_{0.5}Mn_{0.5}PO_4$, $LiFe_{0.2}Mn_{0.8}PO_4$ and $LiFe_{0.1}Mn_{0.9}PO_4$ were prepared by a conventional solid-state reaction technique. Then, each powder sample (about 1 g) was packed into a titanium cell sealed

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

with a gold O-ring. The window of the Ti cell was Kapton foil with 100 μm thickness.

Figure 1 shows ZF- and two LF-spectra (5 and 10 Oe) for $LiFe_{0.5}Mn_{0.5}PO_4$ obtained at 100 and 300 K. Although the spectra indicate a static nature at 100 K, the internal field becomes dynamic at 300 K. The spectra were well fitted by a combination of a dynamic Kubo-Toyabe signal due to Li-diffusion [1,2,3,4], an exponential relaxation signal due to Mn moments in an early time domain, and time-independent background signal from the muons stopped in the Ti cell.

Figure 2 shows the temperature dependences of the field distribution width (Δ) and field fluctuation rate (ν) for the three samples. For the x=0.5 sample, the increase in ν above 200 K is not so drastic, while ν for the x=0.8 sample clearly increases with increasing temperature until 325 K. A similar behavior is also observed for the x=0.9 sample, although we have the data only below 300 K due to a limited beam-time. This implies that Li-diffusion in $LiFePO_4$ is enhanced by the Mn-substitution for Fe. This is consistent with the prediction from first principles calculations [5]; namely, a diffusion coefficient (D_{Li}) for $LiMnPO_4$ is predicted as 10^{-7} cm^2/s, while D_{Li} for $LiFePO_4$ 10^{-8} cm^2/s.

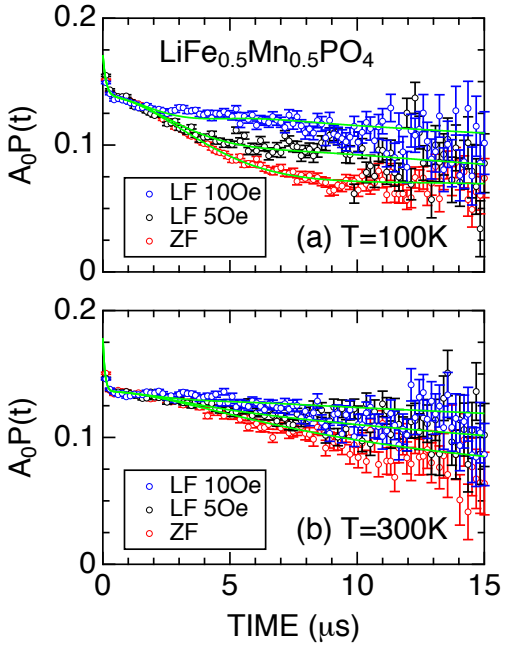

Fig. 1 ZF- and two LF-μSR spectra (5 and 10 Oe) for $LiFe_{0.5}Mn_{0.5}PO_4$ obtained at 100 and 300 K.

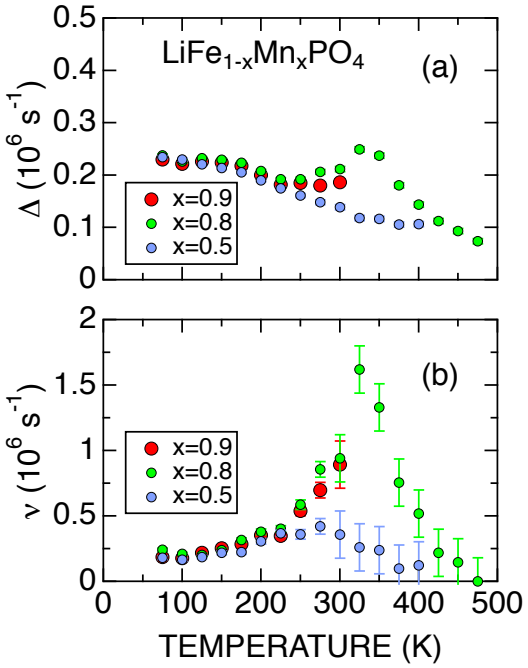

Fig. 2 *T* dependences of (a) the field distribution width (Δ) and (b) field fluctuation rate (ν) for $LiFe_{1-x}Mn_xPO_4$ with x=0.5, 0.8, and 0.9.

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