実験報告書様式（一般利用課題・成果公開利用）

# MLF Experimental Report

| | |
|---|---|
| 課題番号 Project No.<br>2012B0063 | 提出日 Date of Report<br>April 06, 2013. |
| 実験課題名 Title of experiment<br>Diffusive behavior in Li-deficient olivine-type compounds | 装置責任者 Name of responsible person<br>Yasuhiro Miyake |
| 実験責任者名 Name of principal investigator<br>Jun Sugiyama | 装置名 Name of Instrument/（BL No.）<br>D1 |
| 所属 Affiliation<br>Toyota Central Research and Development Laboratories, Inc. | 実施日 Date of Experiment<br>January 21, 2013 – January 25, 2013 |

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.

Iron phosphate, $Li_0FePO_4$ and sodium iron phosphate $Na_{0.7}FePO_4$.

A powder sample was pressed in a disc with 27 mm diameter and 1 mm thickness, and then the disc was packed in an Au-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.

Following upon the $\mu^+$SR studies on the stoichiometric phospho-olivines, $LiFePO_4$ and related compounds (proposal #010A0041) [1,2], we have initiated a study to investigate the diffusive nature of the charged state compounds, $Li_xFePO_4$ with $x$<=1 in order for estimating a diffusion coefficient of $Li^+$ ($D_{Li}$) caused by a $Li^+$ jump between the regular occupied site and regular vacant site. In this beam-time, we have measured two phospho-olivines, $FePO_4$ and $Na_{0.7}FePO_4$. The former compound is very important for understanding the charge/discharge reaction of $LiFePO_4$, because such a reaction is represented by; $LiFePO_4 - x\mathrm{Li} \rightleftarrows (1-x)LiFePO_4 + xFePO_4$ [3]. On the contrary, $Na_xFePO_4$ is studied as a candidate for the cathode material of a Na-ion battery in near future [4,5].

Figure 1 shows the variation of the ZF-spectrum with temperature for (a) $FePO_4$ and (b) $Na_{0.7}FePO_4$. Since there are no mobile $Li^+$ ions in $FePO_4$, the implanted muons are most likely to sense a nuclear magnetic field due to $^{31}P$, which form a rigid $FePO_4$ skeleton. Therefore, ZF-spectrum does not vary with $T$, as expected. On the other hand, the ZF-spectrum for $Na_{0.7}FePO_4$ is found to change from a low-$T$ static behavior to a high-$T$ dynamic behavior. This is consistent with the fact that $Na^+$ ions are extracted from and intercalated into

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

the $Na_xFePO_4$ lattice, reversibly. The ZF-spectra for both samples were well fitted using a combination of an exponentially relaxing dynamic Kubo-Toyabe signal and a non-relaxing background signal from a titanium cell. Figure 2 shows the temperature dependences of the field distribution width (Δ) and field fluctuation rate (ν) for both samples. For FePO4, Δ is independent of *T* until 500 K, when we assume that ν=0 in the whole *T* range measured. Since the ZF-spectrum is not changed with T [see Fig. 1(a)], this assumption is reasonable.

For $Na_xFePO_4$, ν is found to gradually increase with *T*, while Δ is independent of *T* up to 450 K. The relationship between ν and 1/*T* suggests that Na+ ions start to diffuse above around 250 K [see Fig. 2(b)]. In order to estimate $D_{Na}$ in $Na_{0.7}FePO_4$, we need detailed information of the crystal structure, particularly the atomic position and occupancy of the Na site(s). However, since $D_{Na}$ is proportional to n, the estimated activation energy ($E_a$=113 meV) should correspond to $E_a$ for $D_{Na}$. Due to large magnetic moments of the Fe ion in $Na_xFePO_4$, it is most unlikely that Na-NMR provides reliable $D_{Na}$. In fact, there are, to our knowledge, no NMR work on $Na_xFePO_4$. We, therefore, wish to emphasize that $\mu^+$SR provides unique information on Na-diffusion in $Na_xFePO_4$.

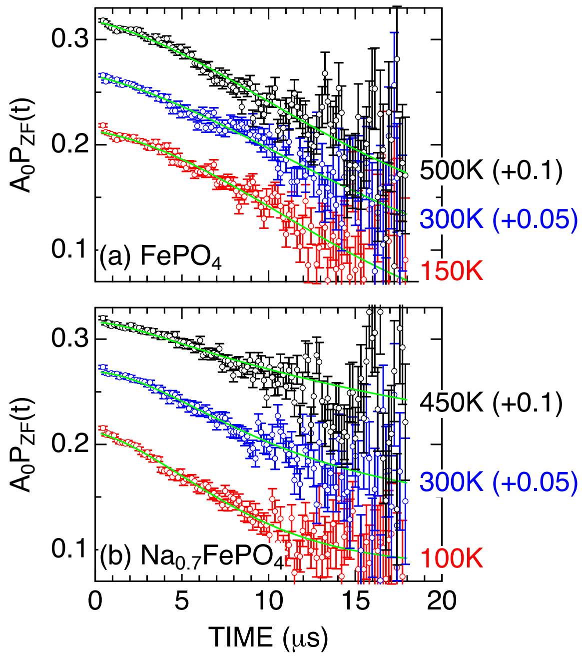


Fig. 1 (a) the ZF-spectrum obtained at 150, 300, and 500K for $FePO_4$ and (b) the ZF-spectrum obtained at 100, 300, and 450K $Na_{0.7}FePO_4$.

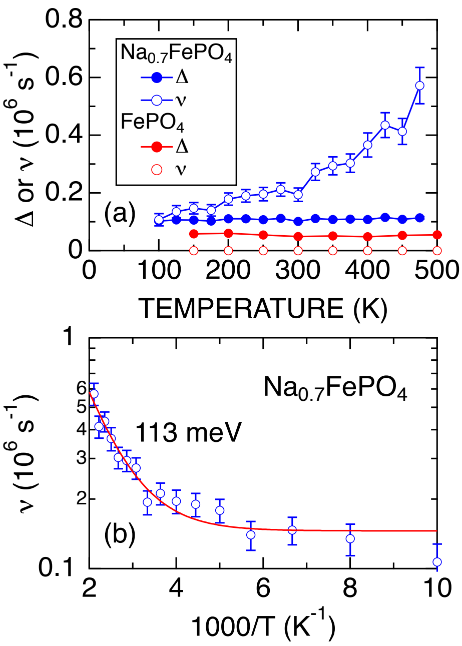


Fig. 2 (a) the temperature dependences of Δ and ν for $FePO_4$ and $Na_{0.7}FePO_4$ and (b) the relationship between ν and 1/*T* for $Na_{0.7}FePO_4$.

REFERENCES


[1] J. Sugiyama *et al.*, Phys. Rev. B **84**, 054430 (2011).

[2] J. Sugiyama *et al.*, Phys. Rev. B **85**, 054111 (2012).

[3] A. S. Andersson *et al.*, Solid State Ionics **130**, 41 (2000).

[4] P. Moreau *et al.*, Chem. Mater. **22**, 4126 (2010).

[5] K. Zaghib *et al.*, J. Power Sources **196**, 9612 (2011).