

(Form: No.5)

Experiment Report for Prefectural Beamline

Proposal no. : 1604016P

Beamline no. : BL11/BL7

Report date : 02/08/2016

Study of Li^+ conduction pathway bottleneck size of M^{4+} doped $\text{Li}_7\text{La}_3\text{M}_x\text{Zr}_{2-x}\text{O}_{12}$ solid electrolytes using X-ray absorption fine structure

Yanhua Zhang¹, Lianmeng Zhang¹, Jiajun Gu², Di Zhang², Katsuhiko Saito³, and Qixin Guo³

¹*Wuhan University of Technology, China*

²*Shanghai Jiaotong University, China*

³*Saga University, Japan*

1. Summary (Note: Please include conclusions)

The effect of M^{4+} ionic radius on the Li^+ conduction pathway bottleneck size on $\text{Li}_7\text{La}_3\text{M}_x\text{Zr}_{2-x}\text{O}_{12}$ solid electrolytes were studied by X-ray absorption fine structure. In the substituted system $\text{Li}_7\text{La}_3\text{M}_x\text{Zr}_{2-x}\text{O}_{12}$ ($\text{M} = \text{Ti}^{4+}, \text{Te}^{4+}, \text{Hf}^{4+}, \text{Ge}^{4+}, \text{Sn}^{4+}, \text{Zr}^{4+}$), the length of M-O for M-doped $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ at Zr sites have been measured via EXAFS. The relationship between Li^+ conduction pathway size with various ionic radius and the Li^+ migration active energy can be established.

2. Purpose of experiment and background

The structure of LLZO is reported to consist of the garnet framework structure and Li atoms. The framework structure is composed of dodecahedral LaO8 and octahedral ZrO6 by polyhedron connection [1-4]. Li atoms fill in the interstices of the framework structure. The Li ionic conductivity can be improved by doping at Zr or La sites which adjusting the Li^+ conduction pathway bottleneck size [5-8]. So far, the optimized Li-ion conductivity of LLZO by super-valent cation substitutions such as Ta^{5+} at Zr sites reached to $1 \times 10^{-3} \text{ S cm}^{-1}$ which is available for practical application [9]. Cation substitutions by different ionic radius at Zr sites can modify the ZrO8 volume size which results in changing of the Li^+ conducting bottleneck size [10]. However, the relationship between the Li^+ conduction pathway bottleneck size and the Li^+ migration activation energy has not been studied yet.

The purpose of this proposal is to use x-ray absorption fine structure (XAFS) to study the effect of

different ionic radius (M element) doping at Zr sites on Li^+ conducting bottleneck size. By measuring the length of M-O bond via XAFS, one can obtain the corresponding lithium ion conducting bottleneck size. Thus we can build the relationships between lithium ion transport bottlenecks size and the Li^+ migration activation energy.

3. Experimental (Note: Description of sample, method of experiment and analysis, etc.)

The doped $\text{Li}_7\text{La}_3\text{M}_x\text{Zr}_{2-x}\text{O}_{12}$ (M= Ti^{4+} , Te^{4+} , Hf^{4+} , Ge^{4+} , Sn^{4+} , Zr^{4+}) samples were prepared by field assisted sintering technology. Field assisted sintering technology (FAST) is a combination of a uniaxial pressing process and a direct passing of electric DC current through the graphite tool to sinter the material, if the powder is not electrically conductive. The production of Joule heat within tool enables the densification of various materials with higher heating rates and shorter dwell times. Firstly, the powders were ball milled using zirconia balls in 2 - propanol for about 12 h and then the powders were dried in vacuum oven at $80\text{ }^\circ\text{C}$ for 6 h. Secondly, powders were loosely filled into the graphite die and then it was put into the FAST system. FAST consolidation was conducted with a plasma activated sintering system (ED - PASIII, Elenix Ltd., Japan). Before the sintering, there was an activation step running for 30 s with a pulse current of 30V/10A. Sintering process was performed at the temperature range of $900\text{ }^\circ\text{C}$ to $1200\text{ }^\circ\text{C}$ under a constant uniaxial pressure of 10 MPa with a holding time of 3min. The subsequent heating rate was set as $300\text{ }^\circ\text{C}/\text{min}$. Temperature measurement and control were conducted using pyrometer through the hole of the die. Ar was filled into the system as protect gas to balance the pressure in order to prevent the loss of lithium. After the dwell, sample was cooled down to room temperature naturally.

Pellets with 1~2mm in thickness and 10mm in diameter were measure by BL11 and BL7 Beam line. The corresponding absorption edge energy range: 2.0 KeV-22.0 KeV. The corresponding energy absorption edge of doping elements M are as following:

Ti K: 4966eV;

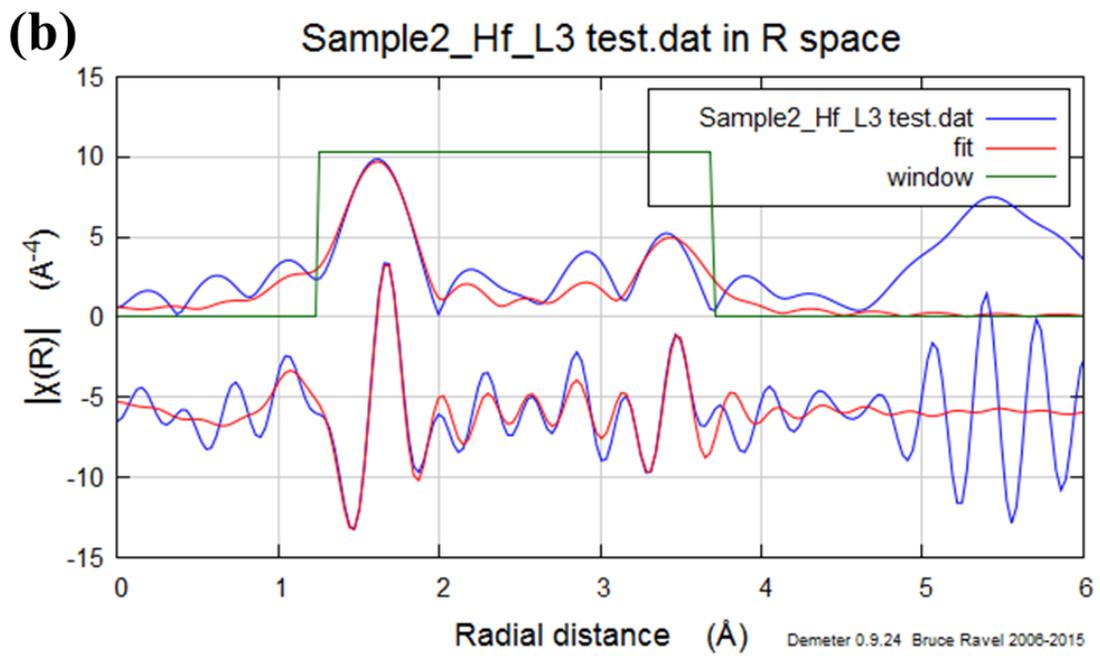
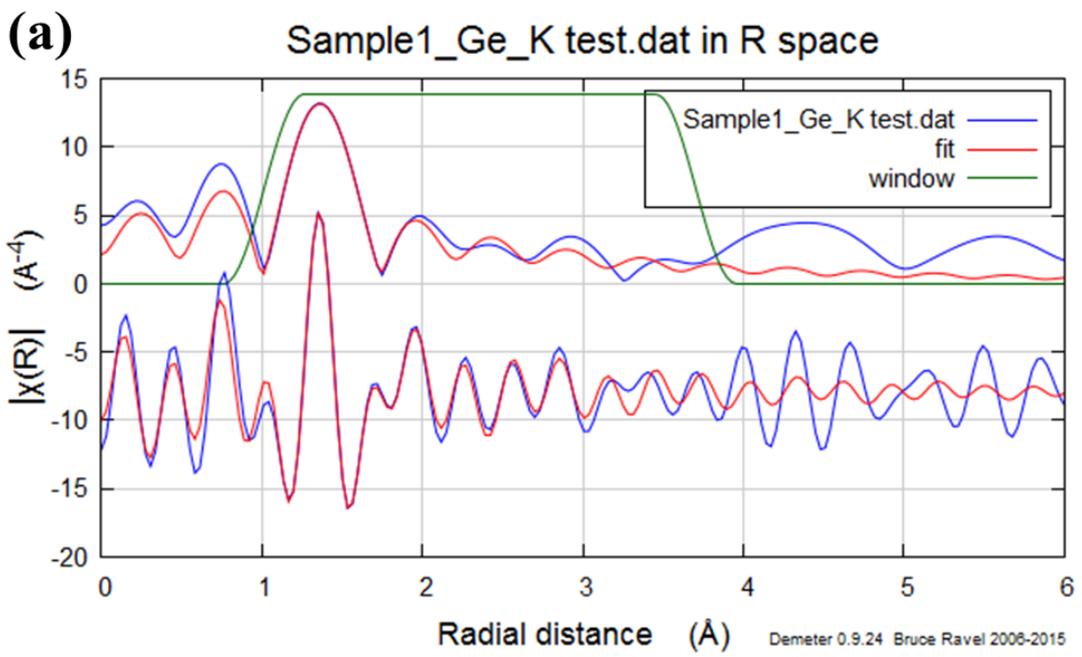
Te K:31814eV, L3:4341eV;

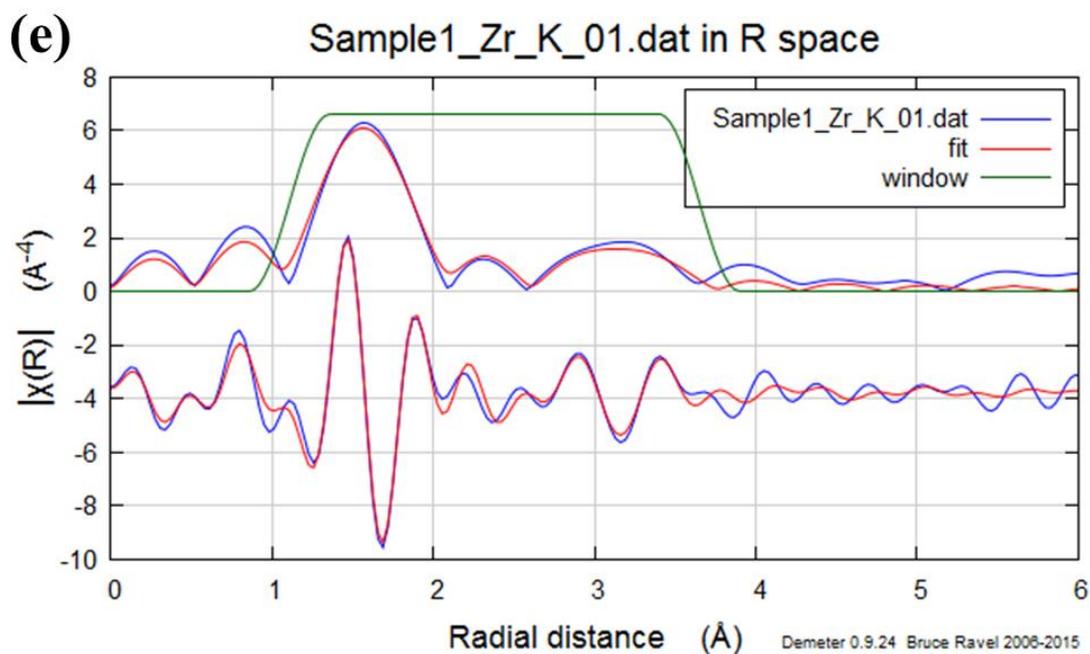
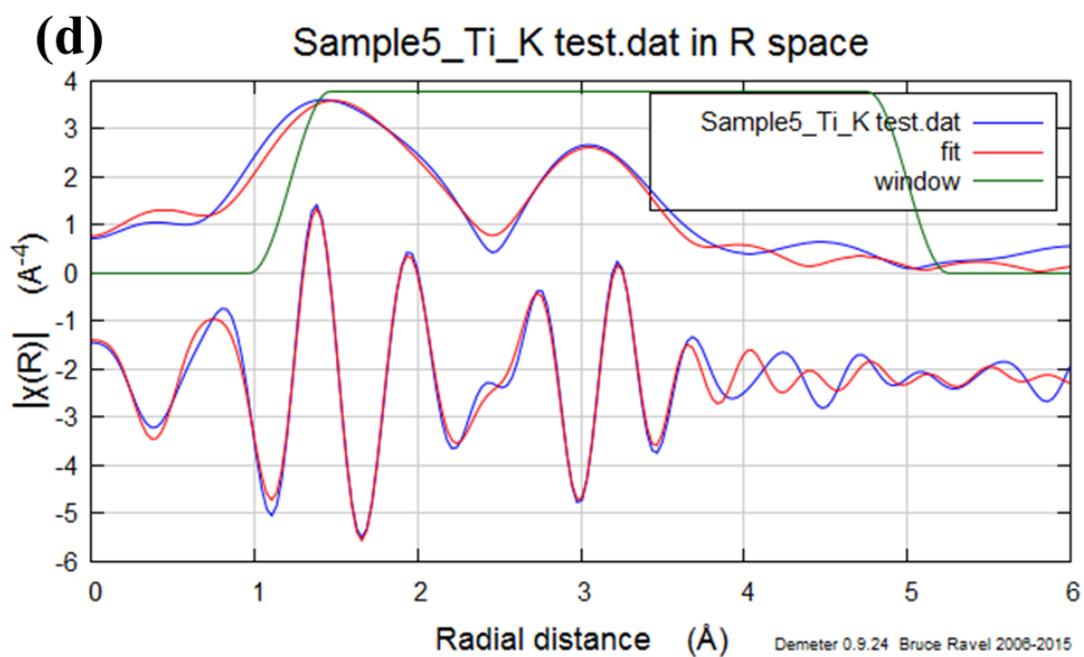
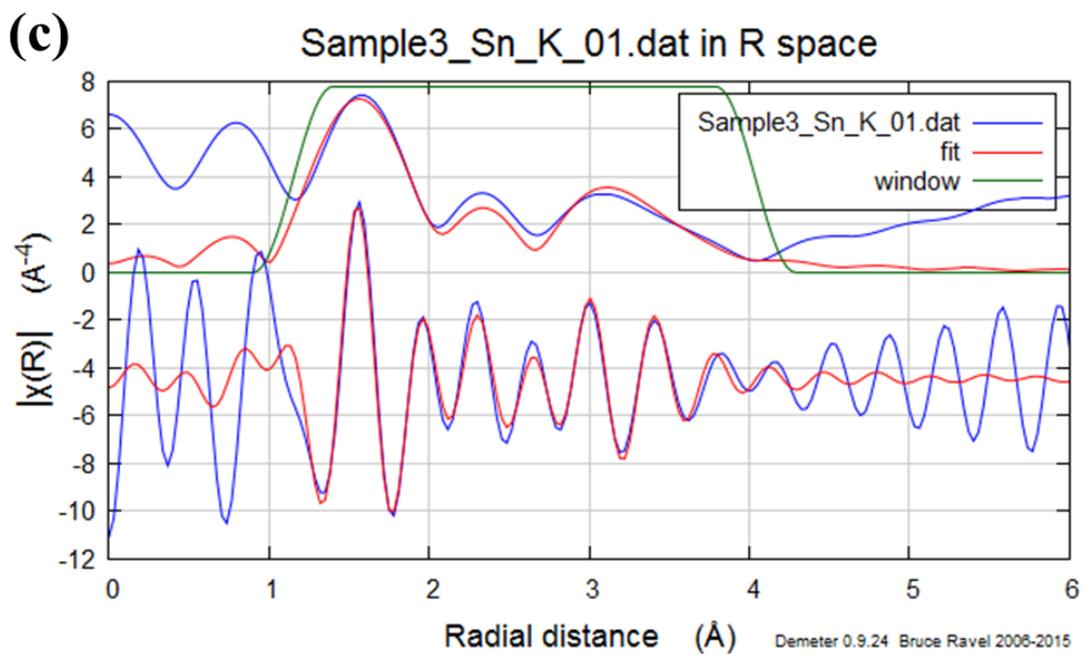
Hf K:65351eV, L3:9561eV;

Ge K:11103eV;

Sn K:29200eV, L3:3929eV.

4. Results and Discussions





Figures (a)~(e) are the fitted XAFS results in Rq space of system $\text{Li}_7\text{La}_3\text{M}_x\text{Zr}_{2-x}\text{O}_{12}$ ($\text{M} = \text{Ge}^{4+}, \text{Hf}^{4+}, \text{Sn}^{4+}, \text{Ti}^{4+}, \text{Zr}^{4+}$). The lengths of M-O for M-doped $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ at Zr sites have been obtained via EXAFS fitting in R space. The fitting M-O length for $\text{Ge}^{4+}, \text{Hf}^{4+}, \text{Sn}^{4+}, \text{Ti}^{4+}, \text{Zr}^{4+}$ are 1.951 Å, 2.092 Å, 2.106 Å, 2.021 Å, 2.094Å, respectively, which is very close to the value calculated by First-principles calculations method, as shown in Table 1. The M-O length increases with the increase of cation radius which indicates that the substituted large radius cation can stretch the lattice skeleton. The increase of M-O length might expand the Li^+ conduction pathway bottleneck size which would reduce Li^+ migration active energy. These results will be related to our measured and calculated active energy thus the relationship between the Li^+ conduction pathway size and the Li^+ migration active energy will be established.

Table 1 The M-O length calculated and measured by First-principles calculations and XAFS, respectively.

Elements	Zr ⁴⁺	Ge ⁴⁺	Ti ⁴⁺	Sn ⁴⁺	Hf ⁴⁺	Te ⁴⁺
Ionic radius (Å)	0.72	0.53	0.605	0.69	0.71	0.97
Ion radius difference	0	-26%	-16%	-4.2%	-1.4%	+35%
Calculated average M-O length	2.110	1.940	2.012	2.104	2.096	2.221
XAFS measured M-O length	2.094	1.951	2.021	2.106	2.092	N/A

5. Future issues

The measured data have many noise signals and the data of Te-doped samples was not successfully obtained. We would like to measure one more time if it is possible.

6. References

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7. Publications, patents (Note: Typical deliverables related to this proposal.)

8. Keywords (Note: 2-3 words about samples and experimental methods.)

$\text{Li}_7\text{La}_3\text{M}_x\text{Zr}_{2-x}\text{O}_{12}$, Solid electrolyte, XAFS

9. About the publication of research results

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