MLF Experimental Report	提出日 Date of Report
課題番号 Project No. 2010B0012 実験課題名 Title of experiment Relationship between oxide-ion conductivity and ordering of oxygen vacancy in the $Ln_2Zr_2O_7$ (*Ln* = La, Nd, Eu) system 実験責任者名 Name of principal investigator Takeshi Hagiwara 所属 Affiliation Kanagawa university	装置責任者 Name of responsible person 装置名 Name of Instrument/（BL No.） iMATERIA/(BL-20) 実施日 Date of Experiment Dec. 13th, 2010

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.

1) $La_2Zr_2O_7$, sub micro-meter powder.
2) $Nd_2Zr_2O_7$, sub micro-meter powder.
3) $Eu_2Zr_2O_7$, sub micro-meter powder.

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.

Powder samples of $Ln_2Zr_2O_7$ (*Ln* = La, Nd, Eu) were synthesized by a solid-state reaction method, using ZrO_2 (99.2%, Tosoh), La_2O_3 (99.99%, Wako), Nd_2O_3 (99.9%, Mitsuwa Chemicals), and Eu_2O_3 (99.9%, Mitsuwa Chemicals) as starting materials.

Weighed powders of starting materials were wet ball-milled for 20 h using a milling pot made of synthetic resin and resin-coated balls, and ethanol as a dispersion reagent. After drying, the powder mixtures were calcined at 1373 K for 5 h in air. The powder samples were molded uniaxially under the pressure of 5 MPa and subjected to rubber press at 200 MPa, after sieving under 53 μm in mesh size. Compacts thus obtained were sintered at 1873 K for 10 h in air. These sintered samples were then crushed and ground into powder for submicron.

The neutron powder diffraction measurements were conducted in the IBARAKI Materirals Design Diffractometer, iMATERIA, installed at the J-PARC. The neutron powder diffraction data were collected with wide-*d* mode on the high resolution bank at room temperature. The collected data were refined by Rietveld method using a cmputer program Z-Rietveld.

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

The Pyrochlore-type structure belongs to a space group of $Fd\bar{3}m$ ($Z = 8$), where Ln^{3+} ions are located at the 16*c* site, Zr^{4+} ions at the 16*d* site, and O^{2-} ions at the 8*a* and 48*f* sites. The 8*b* site is vacant in the completely ordered Pyrochlore-type structure. Therefore, the Rietveld analyses were carried out assuming the following two structure-models: Model 1 was assumed to be a perfect pyrochlore structure, where the oxygen 8*b* site was vacancy, i.e. oxygen-8*b* site occupancy was fixed to be 0.0, and Model 2 to be an oxygen-disordered pyrochlore structure, where the oxygen-8*b* site was partially occupied by oxide-ions. Figure 1 shows the final results of the Rietveld analysis of $Nd_2Zr_2O_7$ on the basis of the two models. The R_{wp} values on the basis of model 1 and 2 were 7.39 and 6.37%, respectively. This fact shows that the Model 2 has higher reliability than the Model 1. Therefore, we adopted the model 2 as the crystal structure model in this study.

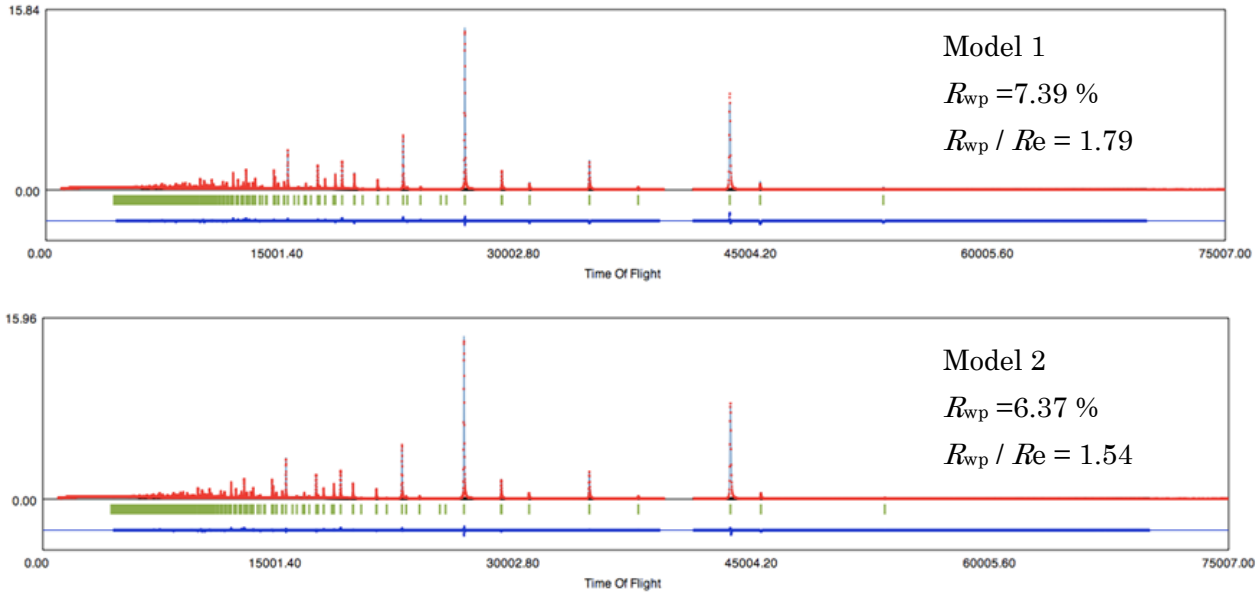

Figure 1 Rietveld analysis of $Nd_2Zr_2O_7$ on the basis of two models.

Table 1 summarizes the results of Rietveld analysis for $La_2Zr_2O_7$ and $Nd_2Zr_2O_7$ according to the Model 2.

1)$La_2Zr_2O_7$: The 8*a* and 48*f* site occupancies were about 1.00. Therefore, we suggested that $La_2Zr_2O_7$ had perfect pyrochlore structure and the 8b site occupancy was nearly 0.

2) $Nd_2Zr_2O_7$: As the 8*a* site occupancy was 1.00, the oxygen vacancy distributed between the 8b and 48f sites.

3)$Eu_2Zr_2O_7$: We did not get the good fitting for Rietveld analysis because diffraction intensity of $Eu_2Zr_2O_7$ was very weak, although the collecting time of $Eu_2Zr_2O_7$ was 10 times comparing to that of the other samples. Therefore, The result of $Eu_2Zr_2O_7$ (Figure 2) was reference data.

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

Table 1 The results of Rietveld analysis of $Ln_2Zr_2O_7$ (Ln = La, Nd)

$La_2Zr_2O_7$

Atom	Site	Occupancy	x	y	z	B
La	16*c*	1	0.125	0.125	0.125	0.375(4)
Zr	16*d*	1	0.625	0.625	0.625	0.227(3)
O1	8*a*	1.000(2)	0	0	0	0.429(3)
O2	8*b*	0.023(2)	0.5	0.5	0.5	0.429(3)
O3	48*f*	0.996(2)	0.2936(1)	0	0	0.429(3)

Lattice parameter / nm 1.0812(1) R_{wp} = 5.87, R_{wp} / Re = 1.38, R_B = 3.15, R_F = 4.53

$Nd_2Zr_2O_7$

Atom	Site	Occupancy	x	y	z	B
Nd	16*c*	1	0.125	0.125	0.125	0.366(6)
Zr	16*d*	1	0.625	0.625	0.625	0.705(7)
O1	8*a*	1.000(2)	0	0	0	0.862(6)
O2	8*b*	0.195(2)	0.5	0.5	0.5	0.862(6)
O3	48*f*	0.967(1)	0.2865(1)	0	0	0.862(6)

Lattice parameter / nm 1.0631(1) R_{wp} = 6.37, R_{wp} / Re = 1.54, R_B = 4.52, R_F = 8.55

Remarks: The isotropic atomic displacement parameters (B) of all oxide sites used the same value. And the oxygen 8*b* site occupancy is populating with concomitant of depopulation of the 48*f* site.

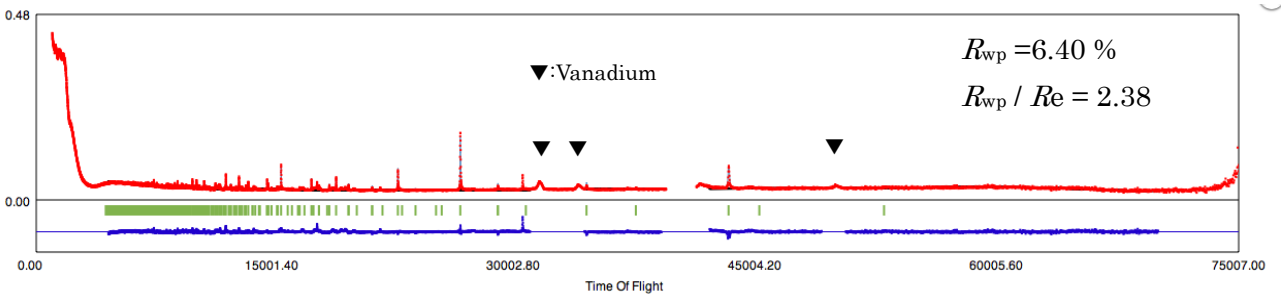

Figure 2 Rietveld analysis of $Eu_2Zr_2O_7$.

The results of this study can be summarized as follows：

1) Rietveld analysis showed that the 8*b* site occupancy increased from 0.023 for $La_2Zr_2O_7$ to 0.195 for $Nd_2Zr_2O_7$. The increase in 8*b* site occupancy means the increase of disordered oxide-ion in the pyrochlore structure.

2) The oxide-ion conductivity increased with an increase in the 8*b* site occupancy which can be recognized as a measure of disordered oxide-ion in the pyrochlore-type structure.