 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.

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

<p>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.</p> <p>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.</p> <p>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.</p> <p>The neutron powder diffraction measurements were conducted in the IBARAKI Materials 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 computer program Z-Rietveld.</p>

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 $16c$ site, Zr^{4+} ions at the $16d$ site, and O^{2-} ions at the $8a$ and $48f$ sites. The $8b$ 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 $8b$ site was vacancy, i.e. oxygen- $8b$ site occupancy was fixed to be 0.0, and Model 2 to be an oxygen-disordered pyrochlore structure, where the oxygen- $8b$ 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.

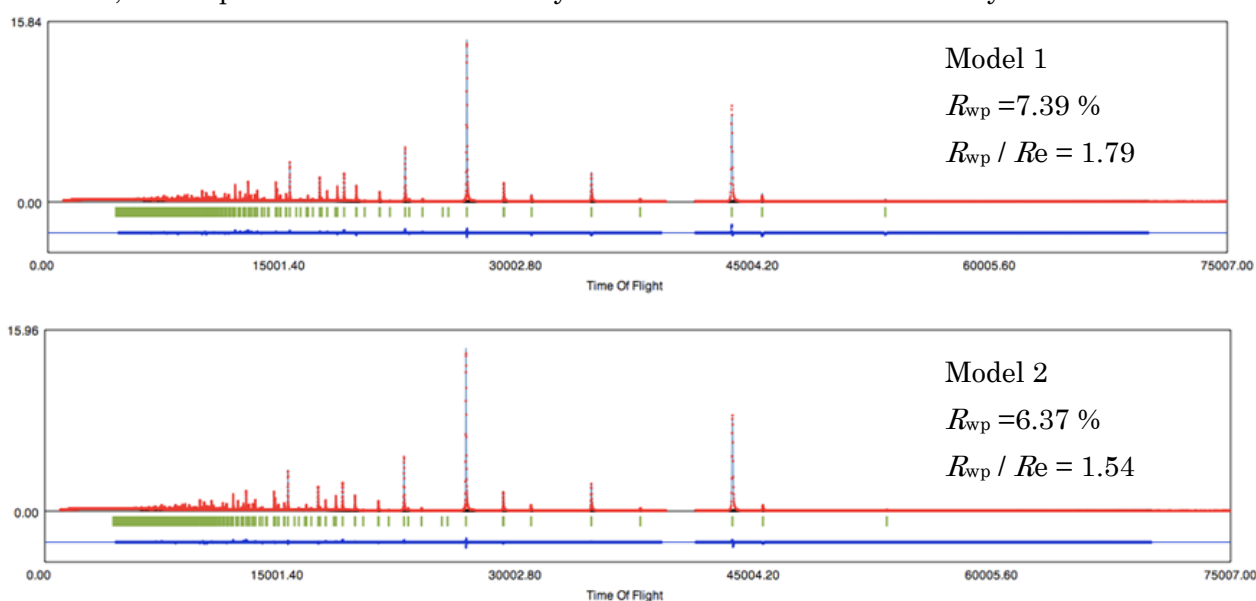


Figure 1 Rietveld analysis of $Nd_2Zr_2O_7$ on the basis of two models.

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 $8a$ and $48f$ 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 $8a$ 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 ₂ Zr ₂ O ₇						
Atom	Site	Occupancy	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
La	16 <i>c</i>	1	0.125	0.125	0.125	0.375(4)
Zr	16 <i>d</i>	1	0.625	0.625	0.625	0.227(3)
O1	8 <i>a</i>	1.000(2)	0	0	0	0.429(3)
O2	8 <i>b</i>	0.023(2)	0.5	0.5	0.5	0.429(3)
O3	48 <i>f</i>	0.996(2)	0.2936(1)	0	0	0.429(3)

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

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

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

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.

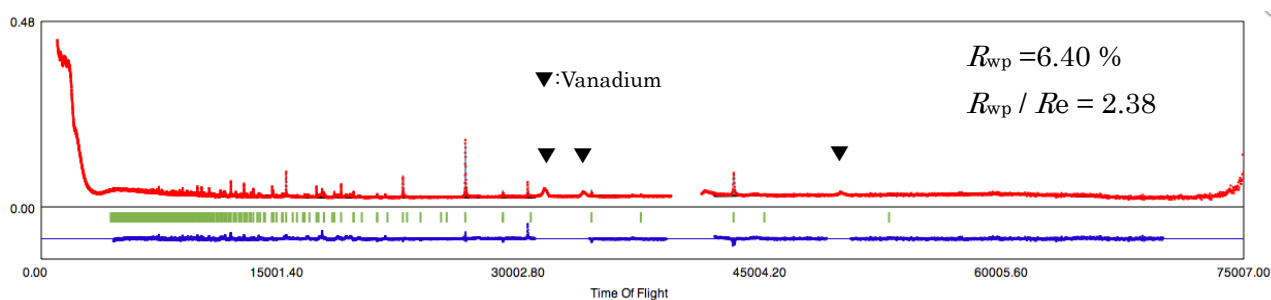


Figure 2 Rietveld analysis of $Eu_2Zr_2O_7$.

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.