MLF Experimental Report	提出日 Date of Report
課題番号 Project No. 2012B0211 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 Prof. Toru Ishigaki 装置名 Name of Instrument/（BL No.） iMATERIA/(BL 20) 実施日 Date of Experiment 2012/12/23-25 (48h)

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) $La_2Zr_2O_7$, sintered body.
2) $Nd_2Zr_2O_7$, sintered body.
3) $Eu_2Zr_2O_7$, submicrometer 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.

Samples of $Ln_2Zr_2O_7$ (Ln = La, Nd, and Eu) were synthesized by a solid-state reaction method, using ZrO_2 (99.2%, Tosoh Corporation), Eu_2O_3 (99.9%, Mitsuwa Chemicals Co.,Ltd.), Nd_2O_3 (99.9%, Mitsuwa Chemicals Co.,Ltd.) and La_2O_3 (99.99%, Wako Pure Chemical Industries, Ltd.) as starting materials.

Weighed powders were wet ball-milled for 20 h using a milling pot made of synthetic resin and resin-coated balls, and ethanol as the dispersion reagent. After drying, the powder mixtures were calcined at 1373 K for 5 h in air. The powder samples were uniaxially-compacted 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. The relative densities of sintered body, which were estimated from geometric dimensions and weights, were 95.3-98.1 % of the true densities. The sintered sample of $Eu_2Zr_2O_7$ was then crushed and ground into powder for submicron.

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

2-1) The results of $Nd_2Zr_2O_7$ and $La_2Zr_2O_7$

The time-of flight (TOF) neutron diffraction (ND) data for $Ln_2Zr_2O_7$ (Ln = Nd and La) were taken using a high throughput neutron diffractometer, iMATERIA, in BL-20 installed at the Material and Life Science Experimental Facility (MLF) of the Japanese Proton Accelerator Research Complex (J-PARC). The ND data of $La_2Zr_2O_7$ and $Nd_2Zr_2O_7$ were collected with a wide-d mode on the high resolution bank at 298, 1076, 1202, 1329, and 1455 K using a vanadium furnace in vacuum (ca. 0.1Pa). The measurement temperatures were calibrated on the basis of lattice constants of $Ln_2Zr_2O_7$ (Ln = Nd and La) obtained by high temperature X-ray diffractometry reported in "*J. Fuel Cell Sci. and Technol.*, **8**, 051020-051024 (2011)". The measurement time for data collection in the 300 kW beam power was about 20 min for about 1.5g samples (sintered bodies) contained in a 6mm diameter cylindrical vanadium cell. Rietveld refinements for TOF-ND data (d spacings between 0.5 and 4.0Å) were performed using the program Z-Rietveld.

The pyrochlore(P)-type structure belongs to a space group of $Fd\bar{3}m$ (NO.227)(Z= 8). For origin choice 2 and placing Ln^{3+} ions at the origin, i.e., 16c site (0, 0 ,0), Zr^{4+} ions are located at the 16d site (1/2, 1/2, 1/2), and O^{2-} ions at the O1(8a) site (1/8, 1/8, 1/8) and O3(48f) site (x, 1/8, 1/8). The O2(8b) site (3/8, 3/8, 3/8) is vacant in the completely ordered P-type structure. The diffraction data were analyzed by using a multi-phase (i.e. $Ln_2Zr_2O_7$ (Ln = Nd or La) with the completely ordered P-type structure and V) model. Figure 1 shows the result of the Rietveld analysis of $Nd_2Zr_2O_7$ at 1455 K. The structural parameters estimated by Rietveld analysis of powder ND data for $Nd_2Zr_2O_7$ and $La_2Zr_2O_7$ at 1455 K are summarized in Table 1.

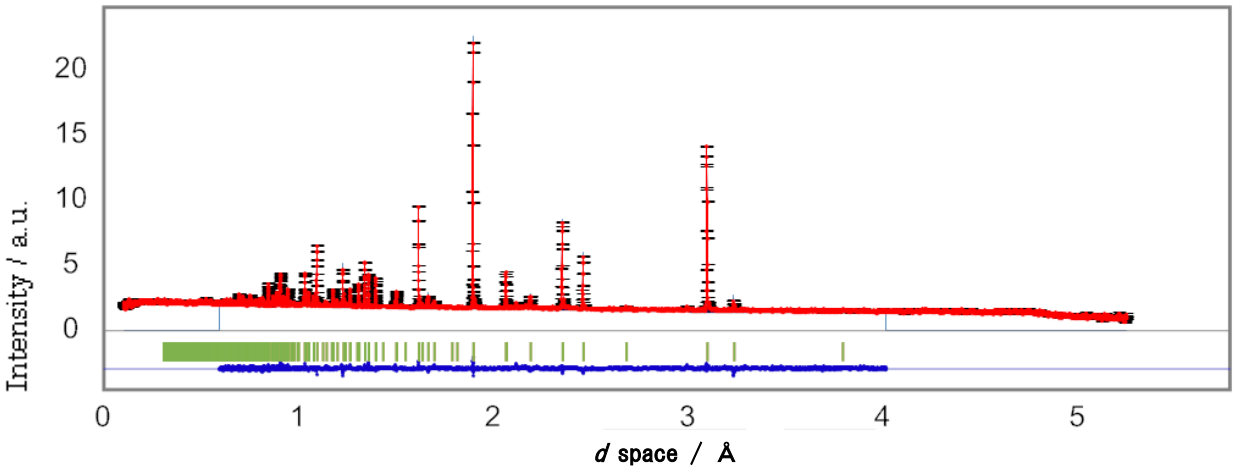

Fig. 1 The observed (+) and calculated (solid line) neutron diffraction patterns of $Nd_2Zr_2O_7$ at 1455 K after the completion of Rietveld refinement. The curve in the bottom part of the plots represents the difference between observed and calculated intensities ($Y_i^{obs} - Y_i^{calc}$).

Table 1. The results of Rietveld analysis of ND data for $Nd_2Zr_2O_7$ and $La_2Zr_2O_7$ at 1455 K.

$Nd_2Zr_2O_7$

Atom	Site	Occupancy	*x*	*y*	*z*	*B* (Å²)
Nd	16*c*	1.0	0.0	0.0	0.0	0.80(2)
Zr	16*d*	1.0	0.5	0.5	0.5	0.49(2)
O1	8*a*	1.0	0.125	0.125	0.125	1.62(1)
O2	8*b*	0	0.375	0.375	0.375	1.62(1)
O3	48*f*	1.0	0.4102(1)	0.125	0.125	1.62(1)

Lattice parameter = 10.739(1) Å, R_B =11.0%, R_F = 13.3%, R_{wp} = 3.03%.

$La_2Zr_2O_7$

	Site	Occupancy	*x*	*y*	*z*	*B* (Å²)
La	16*c*	1.0	0.0	0.0	0.0	1.58(2)
Zr	16*d*	1.0	0.5	0.5	0.5	0.88(2)
O1	8*a*	1.0	0.125	0.125	0.125	1.80(2)
O2	8*b*	0	0.375	0.375	0.375	1.80(2)
O3	48*f*	1.0	0.4189(1)	0.125	0.125	1.80(2)

Lattice parameter = 10.906(1) Å, R_B =8.61%, R_F = 11.7%, R_{wp} = 3.69%.

Although the values of R_{wp} for Rietveld analysis results of $Nd_2Zr_2O_7$ and $La_2Zr_2O_7$ were lower than 4%, the values of R_F of them were higher than 10%. To improve the refinements, we are planning to introduce another crystal structure model, i.e. oxygen vacancies exist not only in O2 (8*b*) site but also in O1 (8*a*) and O3 (48*f*) sites.

2-2) The results of $Eu_2Zr_2O_7$

Since the absorption cross section of the neutron for Eu is very large (σ_a = 4530 barns), the $Eu_2Zr_2O_7$ sample for ND measurement was prepared by a special method. The cylinder of vanadium foil (diameter: ca.5mm) was put in the cylindrical vanadium cell of diameter 6 mm. The space between the vanadium foil and vanadium cell was filled with about 0.2 g of $Eu_2Zr_2O_7$ powder. The powder ND data of $Eu_2Zr_2O_7$ were collected with a wide-*d* mode on the high resolution bank at 298 K. The measurement time for data collection in the 300 kW beam power was about 14 h for about 0.2 g samples contained in a 6mm diameter cylindrical vanadium cell. Rietveld refinements for TOF powder ND data (*d* spacing between 1.0 and 4.0Å) were performed using the program Z-Rietveld. The Rietveld analyses were carried out assuming the following two structure-models: Model 1 was assumed to be a completely oxygen vacancy ordered P-type structure, where the O2(8*b*) site was vacancy, i.e. O2(8*b*) site occupancy was fixed to be 0.0, and Model 2 to be an oxygen vacancy disordered P-type structure, where the O2(8*b*) site was partially occupied by oxide-ions.

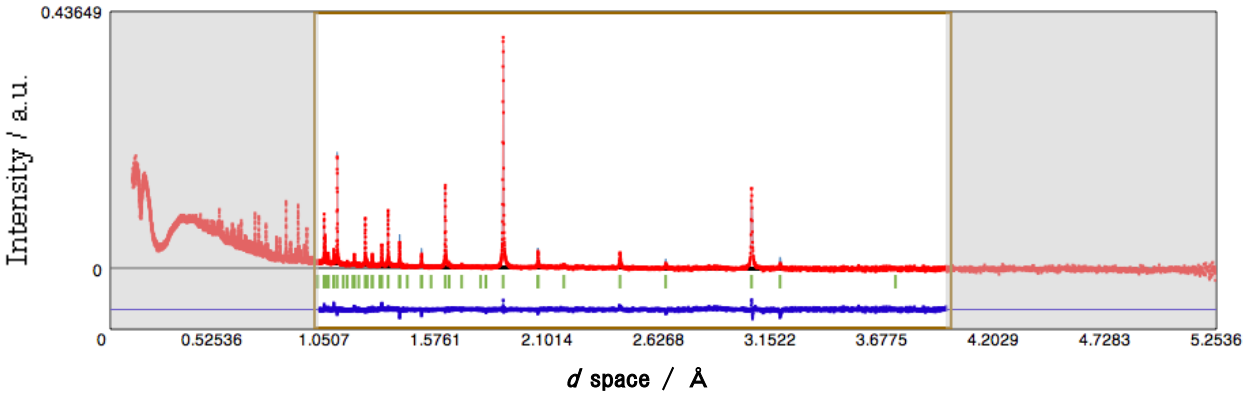

Fig. 2 The observed (+) and calculated (solid line) powder neutron diffraction patterns of $Eu_2Zr_2O_7$ at 298 K. after the completion of Rietveld refinement. The curve in the bottom part of the plots represents the difference between observed and calculated intensities ($Y_i^{obs} - Y_i^{calc}$).

Table 2. The results of Rietveld analysis of ND data for $Eu_2Zr_2O_7$ at 298 K.

$Eu_2Zr_2O_7$

Atom	Site	Occupancy	*x*	*y*	*z*	*B* (Å^2)
Eu	16*c*	1.0	0.0	0.0	0.0	0.2
Zr	16*d*	1.0	0.5	0.5	0.5	0.2
O1	8*a*	1.00(1)	0.125	0.125	0.125	1.18(3)
O2	8*b*	0.480(1)	0.375	0.375	0.375	1.18(3)
O3	48*f*	0.920(2)	0.4045(1)	0.125	0.125	1.18(3)

Lattice parameter = 1.0558(1)nm, R_B =17.0%, R_F = 9.68%, R_{wp} = 11.2%.

Figure 2 shows the final result of the Rietveld analysis of $Eu_2Zr_2O_7$ on the basis of the Model 2. The *B* values of Eu and Zr sites were fixed to 0.2, since they converged to very small values. The R_{wp} values on the basis of Models 1 and 2 were 12.5 and 11.2%, respectively. The R_B and R_F values on the basis of Model 1 were 15.2 and 10.5%, respectively. While the R_B and R_F values on the basis of Model 2 were 17.0 and 9.68%, respectively. The structural parameters estimated by Rietveld analysis of powder ND data for Model 2 is summarized in Table 2. To complete the lower *R* values, we are planning to perform the Rietveld analysis again using the wider *d* range data.