Crystal structure analysis of $Ln_2Zr_2O_7$ ($Ln=$ Eu and La) with a pyrochlore composition by high-temperature powder X-ray diffraction

Takeshi HAGIWARA†, Katsuhiro NOMURA* and Hiroyuki KAGEYAMA**

We synthesized Eu$_2$Zr$_2$O$_7$ and La$_2$Zr$_2$O$_7$ using high purity ZrO$_2$ of extremely low Hf content. The crystal structures of Eu$_2$Zr$_2$O$_7$ and La$_2$Zr$_2$O$_7$ were refined by the Rietveld analysis of the powder X-ray diffraction data (indexed as a cubic pyrochlore-type structure, space group: No.227, Fd3m) measured from 1173 to 298 K in a dry condition and from 1173 to 323 K in a wet condition. The crystal structure of La$_2$Zr$_2$O$_7$ is near to an ideal pyrochlore-type structure, whereas that of Eu$_2$Zr$_2$O$_7$ is a distorted pyrochlore-type structure. The thermal expansion coefficients of Eu$_2$Zr$_2$O$_7$ were larger than those of La$_2$Zr$_2$O$_7$. The value of the equivalent isotropic atomic displacement parameters ($B_{eq}$) calculated from the anisotropic atomic displacement parameter for the Zr in Eu$_2$Zr$_2$O$_7$ at 298 K was around 1.4 Å$^2$, and the increase of this value in Eu$_2$Zr$_2$O$_7$ with increasing temperature was smaller than that in La$_2$Zr$_2$O$_7$.©2017 The Ceramic Society of Japan. All rights reserved.

Key-words : High-Temperature XRD, Rietveld analysis, Pyrochlore-type structure, Oxide-ion conductivity, Oxygen vacancy

1. Introduction

Oxide-ion conductors have been used in solid oxide fuel cells as solid electrolytes because of increasing demand for clean generation of electric energy to reduce CO$_2$ formation. The rare-earth doped ZrO$_2$ systems have been widely studied, since fluorite-type oxides can accommodate large amounts of oxygen vacancies by hopping aliovalent cations. However, the highly rare-earth doped ZrO$_2$ systems have low oxide-ion conductivities, because the oxygen vacancies are ordering in the lattice. Yamamura et al.\textsuperscript{1) }reported the electrical conductivity of the $(L_2)_2Zr_2O_7$ and $(Ln_1,_,Ln''_1)_2Zr_2O_7$ ($Ln, Ln'' = La, Nd, Gd, Eu, Sm, Y and Yb)$ systems while maintaining a constant oxygen vacancy concentration. Their results revealed that the electrical conductivity increased with increasing ionic radius ratio ($Ln^{3+}/Zr^{4+}$) in the fluorite phase range, showed the sharp maximum in the vicinity of the phase boundary in the pyrochlore phase range [Eu$_2$Zr$_2$O$_7$ (abbreviated EZO) showed the highest conductivity], and then decreased [La$_2$Zr$_2$O$_7$ (abbreviated LZO) had the lowest conductivity]. They also observed that the oxide-ion conductivity was influenced by the ordering of the oxygen vacancies in the crystal lattice. Xia et al.\textsuperscript{2) }investigated the electrical conductivity of the (Gd,_,Eu$_2$)$_2Zr_2$O$_7$ system. They reported that EZO had the highest electrical conductivity and the lowest activation energy in this system, which was in agreement with the results obtained by Yamamura et al.

The mechanism of oxide-ion conduction in ZrO$_2$-based systems with the pyrochlore composition is influenced by various factors such as the number of oxygen vacancies and their degree of ordering. Therefore, it is important to obtain information of long-range and short-range structures of the pyrochlore compounds with $Ln_2Zr_2O_7$ system.

Previously, Hagiwara et al.\textsuperscript{3) }used neutron diffraction to investigate the relationship between crystal structures and oxide-ion conductivity in Nd$_2$Zr$_2$O$_7$ (abbreviated NZO) and LZO. They found that LZO has the ideal pyrochlore-type (P-type) structure, and NZO has a disordered P-type structure with the oxygen vacancies distributed over 8d and 4f sites at room temperature. The oxide-ion conductivities of LZO were found to be lower than those of NZO, which was in agreement with the results of Wuensch et al.\textsuperscript{4) }

Hagiwara et al.\textsuperscript{5) }have also investigated the relationship between the crystal structure and oxide-ion conductivities of Eoz, NZO, and LZO by the Rietveld refinement of high-temperature powder X-ray diffraction (HT-XRD) data in air and dc electrical conductivity measured by the conventional four-probe method. In this paper,\textsuperscript{5) }they reported the thermal expansion ratios estimated from the temperature dependence of the lattice constants of Eoz and LZO selected as representative examples with high oxide-ion conductivity and with low oxide-ion conductivity, respectively. However, they measured the HT-XRD without controlling the atmosphere in this paper.\textsuperscript{5) }The predominant charge carrier of compounds such as LZO changes depending on temperature, oxygen partial pressure and hydrogen partial pressure.\textsuperscript{6) }For example, in a wet atmosphere around 1200 K, water molecules are often inserted into the oxygen vacancies of the compound such as LZO, and those release

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protons then. In this case, the occupancy of oxygen site and the lattice constant of that may change. Therefore, it is important to control the atmosphere for investigation to the crystal structures of compounds such as LZO. Furthermore, the adjustments of XRD optical system at high-temperatures were not carried out in this paper. Therefore, we made HT-XRD measurements of EZO and LZO under controlled atmospheres again. Furthermore, commercial ZrO$_2$ often includes Hf as an impurity. Actually, EZO and LZO prepared in previous studies included Hf as impurity, Hf$^{4+}$ is substituted in Zr$^{4+}$ sites in EZO or LZO, because Hf$^{4+}$ has the chemical properties similar to Zr$^{4+}$. Therefore, it is difficult to get precise values of the factors like an atomic displacement parameter of Zr$^{4+}$ sites in EZO or LZO under the existence of Hf. In this study, we used high purity ZrO$_2$ with extremely low Hf content and attempted the syntheses of EZO and LZO. We refined the crystal structures of EZO, which was difficult to measure neutron diffraction data because of the high absorption cross section value of Eu, and LZO by Rietveld refinement of the HT-XRD data from 1173 to 298 K under dry 21% N$_2$ conditions could be indexed to a cubic pyrochlore-type (P-type) structure. The general P-type structure belongs to the Fd$ar{3}$m space group (No. 227) ($Z = 8$). For an origin choice of 2 with Zr atoms placed at the origin, i.e., 16c site (0, 0, 0), the Ln atoms are located at the 16d site (1/2, 1/2, 1/2) and the O atoms at the O1(4f) site (x, 1/8, 1/8) and O2(8b) site (3/8, 3/8, 3/8). The O3(8a) site (1/8, 1/8, 1/8) is vacant in the completely ordered P-type structure. To investigate the temperature dependence of the crystal structure parameters for EZO and LZO, we refined the crystal structure using a Rietveld analysis of the XRD data. In the present study, we adopted the base crystal structure model suggested by Tabira et al. which consists of a split atom model for Ln sites (Ln atoms are located at the 96 site (1/2 + x, 1/2 – x, 1/2) with an occupancy of 1/6). Furthermore, Whittle et al. reported the Rietveld refinement of neutron diffraction data for a La$_{2-x}$Y$_x$Zr$_2$O$_7$ system. They suggested a crystal structure model with an anion site mixing P-type structure for the oxygen vacancy distributed over 8h and 48f sites (Note: Ln atoms are located at the origin, i.e., 16c site (0, 0, 0), Zr atoms are located at the 16d site (1/2, 1/2, 1/2), O atoms are located at the 8a site (1/8, 1/8, 1/8) and 48f site (x, 1/8, 1/8), and the 8b site (3/8, 3/8, 3/8) is vacant). Therefore, we adopted this disordered P-type structure with an oxygen vacancy as the crystal structure model (Note: In previous studies, Ln atoms were located at the origin, i.e., 16c site (0, 0, 0), Zr atoms were located at the 16d site (1/2, 1/2, 1/2), and O atoms were located at the O1(8a) site (1/8, 1/8, 1/8) and O3(4f) site (x, 1/8, 1/8), which is the same crystal structure model as that proposed by Whittle et al.).

The oxygen site occupancies (g of O1(4f) and O3(8a)) were refined together. The occupancies of cation sites were calculated from the ICP-AES results (EZO: EuZr = 49.1 mol%:50.9 mol%, LZO: LaZr = 51.4 mol%:48.6 mol%). In other words, the 96h site of EZO contained Eu$^{3+}$+Zr$^{4+}$ (Eu$^{3+}$+Zr$^{4+}$ = 0.164:0.003), and the 16c site of LZO contained Zr$^{4+}$ and La$^{3+}$ (Zr$^{4+}$+La$^{3+}$ = 0.970:0.03). LZO prepared in this work contained small amounts of La$_3$O$_7$ and La$_{10}$Si$_4$Al$_2$O$_{26}$ (La$_3$O$_7$ and La$_{10}$Si$_4$Al$_2$O$_{26}$ = 0.50:0.1; the mole fractions (%) were estimated from the Rietveld refinement of the XRD data at 298 K). As La$_3$O$_7$ and La$_{10}$Si$_4$Al$_2$O$_{26}$ was a small amount, we carried out a Rietveld analysis of the HT-XRD data for LZO using a two-phase model (pyrochlore and La$_3$O$_7$). EZO prepared in this work contained a small amount of Eu$_{45}$O$_{60}$(SiO$_4$)$_{10}$ (EZO:Eu$_{45}$O$_{60}$(SiO$_4$)$_{10}$ = 99.8:0.2; the mole fractions (%) were estimated from the Rietveld refinement of the XRD data at 298 K). We carried out a Rietveld analysis of the HT-XRD data for EZO using a one-phase model (pyrochlore). At the initial stage of the refinement, the atomic displacement parameters of each site were refined as isotropic parameters (EZO at 1173 K in dry conditions: $R_{wp}$ = 8.31, $R_B$ = 3.32, $R_F$ = 3.29). In the next stage, the atomic displacement parameters of the Zr sites were refined as anisotropic parameters (EZO at 1173 K in dry conditions: $R_{wp}$ = 8.28, $R_B$ = 3.22, $R_F$ = 3.03). The isotropic atomic displacement parameters ($B$) of each oxygen site were refined together.

Although the HT-XRD were carried out under dry and wet conditions, no differences were practically observed in the lattice constants and the crystal structure parameters of EZO and LZO between dry and wet conditions when the standard deviations were considered. Therefore, we showed only the results of a dry condition in this paper. Figures 1 and 2 show the final results of the Rietveld analyses of EZO and LZO, respectively, at 1173 K in a dry condition. The structural parameters estimated from the Rietveld analysis of the XRD data of EZO at 298 and 1173 K in a dry condition are summarized in Table 1. Those of LZO at 298

### 3. Results and discussion

The XRD data of EZO and LZO from 1173 to 298 K under dry 21% O$_2$–79% N$_2$ and from 1173 to 323 K under wet 21% O$_2$–
et al.17) reported that the end-member LZO pyrochlore unit cell of Eu₂Zr₂O₇ at 1173 K after the completion of Rietveld refinement. The vertical bars just below the background level indicate calculated positions of Kₐ₁ and Kₐ₂ components of Bragg peaks of Eu₂Zr₂O₇. The curve in the bottom part of the plots represents the difference between observed and calculated intensities (i_{obs} - i_{calc}).

The observed (+) and calculated (solid line) XRD patterns of Eu₂Zr₂O₇ at 298 K in a dry condition, the second set indicates those of impurity phases of La₂O₃. The curve in the bottom part of the plots represents the difference between observed and calculated intensities (i_{obs} - i_{calc}).

Fig. 1. The observed (+) and calculated (solid line) XRD patterns of Eu₂Zr₂O₇ at 298 K and 1173 K in a dry condition are summarized in Table 2.

Table 2. The results of Rietveld analysis of XRD data for Eu₂Zr₂O₇ at 298 K and 1173 K in a dry condition.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Site</th>
<th>Occupancy (g)</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>B (Å²)</th>
<th>U (Å²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eu1</td>
<td>96h</td>
<td>0.164</td>
<td>0.5086(8)</td>
<td>0.4914(8)</td>
<td>1/2</td>
<td>0.39(8)</td>
<td>0.0049(8)</td>
</tr>
<tr>
<td>Zr1</td>
<td>96h</td>
<td>0.003</td>
<td>0.5086(8)</td>
<td>0.4914(8)</td>
<td>1/2</td>
<td>0.39(8)</td>
<td>0.0049(8)</td>
</tr>
<tr>
<td>Zr2</td>
<td>16c</td>
<td>1.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>1.39(2)*</td>
<td>0.0176(3)**</td>
</tr>
<tr>
<td>O1</td>
<td>48f</td>
<td>0.955(3)</td>
<td>0.3414(4)</td>
<td>1/8</td>
<td>1/8</td>
<td>1.7(1)</td>
<td>0.021(1)</td>
</tr>
<tr>
<td>O2</td>
<td>8b</td>
<td>1.0</td>
<td>3/8</td>
<td>3/8</td>
<td>3/8</td>
<td>1.7(1)</td>
<td>0.021(1)</td>
</tr>
<tr>
<td>O3</td>
<td>8a</td>
<td>0.27(2)</td>
<td>1/8</td>
<td>1/8</td>
<td>1/8</td>
<td>1.7(1)</td>
<td>0.021(1)</td>
</tr>
</tbody>
</table>

Lattice parameter = 1.0546(1) nm, R_θ = 3.10%, R_p = 2.68%, R_α = 8.19%, S = 1.29.

Table 2. The results of Rietveld analysis of XRD data for Eu₂Zr₂O₇ at 298 K and 1173 K in a dry condition.

<table>
<thead>
<tr>
<th>Atom</th>
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<th>B (Å²)</th>
<th>U (Å²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eu1</td>
<td>96h</td>
<td>0.164</td>
<td>0.5103(8)</td>
<td>0.4987(8)</td>
<td>1/2</td>
<td>1.4(1)</td>
<td>0.018(1)</td>
</tr>
<tr>
<td>Zr1</td>
<td>96h</td>
<td>0.003</td>
<td>0.5103(8)</td>
<td>0.4987(8)</td>
<td>1/2</td>
<td>1.4(1)</td>
<td>0.018(1)</td>
</tr>
<tr>
<td>Zr2</td>
<td>16c</td>
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<td>0.0</td>
<td>0.0</td>
<td>1.67(3)*</td>
<td>0.0212(4)**</td>
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<tr>
<td>O1</td>
<td>48f</td>
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<td>0.3386(4)</td>
<td>1/8</td>
<td>1/8</td>
<td>2.9(1)</td>
<td>0.037(1)</td>
</tr>
<tr>
<td>O2</td>
<td>8b</td>
<td>1.0</td>
<td>3/8</td>
<td>3/8</td>
<td>3/8</td>
<td>2.9(1)</td>
<td>0.037(1)</td>
</tr>
<tr>
<td>O3</td>
<td>8a</td>
<td>0.17(2)</td>
<td>1/8</td>
<td>1/8</td>
<td>1/8</td>
<td>2.9(1)</td>
<td>0.037(1)</td>
</tr>
</tbody>
</table>

Lattice parameter = 1.0650(1) nm, R_θ = 3.22%, R_p = 3.03%, R_α = 8.28%, S = 1.27.

Fig. 2. The observed (+) and calculated (solid line) XRD patterns of La₂Zr₂O₇ at 1173 K after the completion of Rietveld refinement. The first set of vertical bars just below the background level indicate calculated positions of Kₐ₁ and Kₐ₂ components of Bragg peaks of La₂Zr₂O₇. The second set indicates those of impurity phases of La₂O₃. The curve in the bottom part of the plots represents the difference between observed and calculated intensities (i_{obs} - i_{calc}).

The observed (+) and calculated (solid line) XRD patterns of La₂Zr₂O₇ at 298 K in a dry condition were almost 1.0 and 0.0, respectively, indicating that the crystal structure of LZO is near to an ideal P-type structure when the standard deviation in the values was considered, the occupancies of O₁(48f) and O₃(8a) at 298 K in a dry condition were almost 1.0 and 0.0, respectively. Furthermore, those at 273 K in a dry condition, the occupancies of O₁(48f) and O₃(8a) at 298 K in a dry condition were almost 1.0 and 0.0, respectively. On the other hand, in the case of LZO at 1173 K in a dry condition, the occupancies of O₁(48f) and O₃(8a) at 298 K in a dry condition were almost 0.995(2) and 0.03(1), respectively. When the standard deviation in the values was considered, the occupancies of O₁(48f) and O₃(8a) at 298 K in a dry condition were almost 1.0 and 0.0, respectively, indicating that the crystal structure of LZO is near to an ideal P-type structure when the standard deviation in the values was considered, the occupancies of O₁(48f) and O₃(8a) at 298 K in a dry condition were almost 1.0 and 0.0, respectively.

In the refined results of EZO at 1173 K in a dry condition, the occupancies of O₁(48f) and O₃(8a) were 0.971(3) and 0.17(2), respectively. On the other hand, in the case of LZO at 1173 K in a dry condition, the occupancies of O₁(48f) and O₃(8a) were 0.995(2) and 0.03(1), respectively. When the standard deviation in the values was considered, the occupancies of O₁(48f) and O₃(8a) at 1173 K in a dry condition were almost 1.0 and 0.0, respectively. Furthermore, those at 273 K in a dry condition were almost 1.0 and 0.0, respectively, indicating that the crystal structure of LZO is near to an ideal P-type structure when the standard deviation in the values was considered, the occupancies of O₁(48f) and O₃(8a) at 1173 K in a dry condition were almost 1.0 and 0.0, respectively.

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ed by Maram et al.14) [0.339(2)]. When the ZrO$_6$ sublattice in a
positions [0.3416(4)] was slightly larger than the re
position of O1(48
 positions of O1(48
 positions of O1(48
 positions of O1(48

In Eu$_3$

et al.9) [0.3306(2)] and Wittle et al.10) [0.3311(2)] [Note: Wittle
et al. adopted a crystal structure model with
positions of O1(48
positions of O1(48
positions of O1(48
positions of O1(48

et al.16) sites. Furthermore, the XRD data reported
by Kutty et al. was substituted
et al. as shown by ICP-AES, EZO prepared in this work was rich
in Zr (Eu:Zr = 49.1 mol %: 50.9 mol %). We thought that Zr$^{4+}$
has a small cation radius (0.084 nm),16) was substituted
in Eu$^{2+}$ which has a smaller cation radius (0.084 nm),16) was substituted
in Eu$^{2+}$. Furthermore, the XRD data reported
by Kutty et al. was substituted

Although the lattice constant of EZO at 298 K in dry conditions
[1.0546(1) nm] agreed with that reported by Maram et al.14)

et al.9) [0.3306(2)] and Wittle et al.10) [0.3311(2)] [Note: Wittle
et al. adopted a crystal structure model with
positions of O1(48
positions of O1(48
positions of O1(48
positions of O1(48

Figure 3 represents the temperature dependence of the lattice
constants of EZO estimated from the Rietveld analyses. The results of Kutty et al.,18) Maram et al.14) and Hagiwara et al.9) are also shown in the
figure for comparison. As compared with previous results,9) the slope of EZO prepared in this work was larger than that. The results of lattice constants of previous study9) without the adjustments of XRD optical system at high-
temperatures would probably be incorrect. While, as compared with
that of Kutty et al.,10) the slope of EZO prepared in this work was similar to that. However, the lattice constants of EZO prepared in this work were smaller than those reported by Kutty et al. as shown by ICP-AES, EZO prepared in this work was rich
in Zr (Eu:Zr = 49.1 mol %: 50.9 mol %). We thought that Zr$^{4+}$
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in Eu$^{2+}$ which has a smaller cation radius (0.084 nm),16) was substituted
in Eu$^{2+}$. Furthermore, the XRD data reported
by Kutty et al. was substituted

Figure 3. Lattice constants of Eu$_2$Zr$_2$O$_7$ as a function of temperature. *: calculated values from Table 1 in Ref. 18
**: calculated values from Table IV in Ref. 14
***: read values from Fig. 3 in Ref. 5

Table 2. The results of Rietveld analysis of XRD data for La$_2$Zr$_2$O$_7$ at 298 and 1173 K in a dry condition

<table>
<thead>
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<th>Atom</th>
<th>Site</th>
<th>Occupancy (g)</th>
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<th>y</th>
<th>z</th>
<th>B (Å$^2$)</th>
<th>U (Å$^2$)</th>
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<td>0.00</td>
<td>0.59(1)*</td>
<td>0.0074(2)**</td>
</tr>
<tr>
<td>La2</td>
<td>16c</td>
<td>0.03</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.59(1)*</td>
<td>0.0074(2)**</td>
</tr>
<tr>
<td>O1</td>
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<td>1/8</td>
<td>1/8</td>
<td>0.99(8)</td>
<td>0.013(1)</td>
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<td>O2</td>
<td>8b</td>
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<td>3/8</td>
<td>3/8</td>
<td>3/8</td>
<td>0.99(8)</td>
<td>0.013(1)</td>
</tr>
<tr>
<td>O3</td>
<td>8a</td>
<td>0.01(1)</td>
<td>1/8</td>
<td>1/8</td>
<td>1/8</td>
<td>0.99(8)</td>
<td>0.013(1)</td>
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La$_2$Zr$_2$O$_7$ 1173 K

<table>
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<th>Site</th>
<th>Occupancy (g)</th>
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<th>B (Å$^2$)</th>
<th>U (Å$^2$)</th>
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<tr>
<td>La1</td>
<td>96h</td>
<td>1/6</td>
<td>0.5122(4)</td>
<td>0.4878(4)</td>
<td>1/2</td>
<td>1.24(6)</td>
<td>0.0157(8)</td>
</tr>
<tr>
<td>Zr2</td>
<td>16c</td>
<td>0.97</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>1.40(3)*</td>
<td>0.0177(3)**</td>
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<tr>
<td>La2</td>
<td>16c</td>
<td>0.03</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>1.40(3)*</td>
<td>0.0177(3)**</td>
</tr>
<tr>
<td>O1</td>
<td>48f</td>
<td>0.995(2)</td>
<td>0.3296(3)</td>
<td>1/8</td>
<td>1/8</td>
<td>2.61(1)</td>
<td>0.033(1)</td>
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<td>O2</td>
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<td>3/8</td>
<td>3/8</td>
<td>3/8</td>
<td>2.61(1)</td>
<td>0.033(1)</td>
</tr>
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<td>O3</td>
<td>8a</td>
<td>0.03(1)</td>
<td>1/8</td>
<td>1/8</td>
<td>1/8</td>
<td>2.61(1)</td>
<td>0.033(1)</td>
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</tbody>
</table>

La$_2$Zr$_2$O$_7$ 1173 K

<table>
<thead>
<tr>
<th>Atom</th>
<th>Site</th>
<th>Occupancy (g)</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>B (Å$^2$)</th>
<th>U (Å$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr2, La2</td>
<td></td>
<td>0.0126(3)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-0.0017(7)</td>
</tr>
</tbody>
</table>

Lattice parameter = 1.0816(1) nm, $R_B = 2.66\%$, $R_f = 2.67\%$, $R_{av} = 7.87\%$, $S = 1.41$.

Lattice parameter = 1.0904(1) nm, $R_B = 2.69\%$, $R_f = 2.88\%$, $R_{av} = 7.76\%$, $S = 1.34$.

[1.0546(16) nm], the lattice constants of EZO prepared in this
work between 873 and 1173 K were smaller than those reported
by Maram et al. The previous study14) used an unconditioned
beam from a 250 W CO$_2$ laser for sample heating and an optical
pyrometer for measuring samples temperatures. It is di
cult to compare simply the results of the lattice constant of EZO because
of the differences in the measuring conditions and methods. The
difference of the lattice constants of EZO might also be related to
using high purity ZrO$_2$ with extremely low Hf content.

Figure 4 represents the temperature dependence of the lattice
constants of LZO estimated from the Rietveld analyses. The
results of Kutty et al.,18) Han et al.19) and Hagiwara et al.5) are also shown in the figure for comparison. As compared with previous results,5) the lattice constants of LZO clearly disagreed with those prepared in this work. Since the adjustments of XRD optical system at high-temperatures were not carried out, the results of lattice constants of previous study5) would probably be incorrect. The lattice constants of LZO prepared in this work were larger than those reported by Kutty et al.18) and Han et al.19) As shown by ICP-AES, LZO prepared in this work was rich in La (La:Zr = 51.4 mol%:48.6 mol%). We thought that La3+ which has a large cation radius (0.118 nm)16) was substituted in Zr (0.084 nm)16) sites.

Kutty et al.18) investigated the thermal expansion of Ln2M2O7 (Ln = La, Nd, Sm, Eu and Gd, M = Zr and Hf) systems. Figure 5 shows the temperature dependence of the thermal expansion coefficients of EZO and LZO prepared under a dry condition calculated according to the method of Kutty et al.18) The thermal expansion coefficients at any temperature were calculated by the following formula:

\[
\text{Thermal expansion coefficient} = \frac{1}{a_{298}} \times \frac{da}{dT} \tag{1}
\]

Where \(a_{298}\) is the cubic lattice constant at 298 K and \(\frac{da}{dT}\) is the slope of the curve at temperature \(T\). The results of Kutty et al. and Han et al.19) are also shown in the figure for comparison. As the behavior of the thermal expansion coefficients calculated from the lattice constants for EZO of Maram et al.14) clearly disagreed with that in this work, the results of them are not shown in this figure. Similarly, the results of previous study5) are not shown in this figure too. Although the lattice constants of LZO prepared in this work were larger than those reported by Han et al., the values of the thermal expansion coefficients of LZO prepared in this work almost agreed with that reported by Han et al. The thermal expansion coefficients of EZO and LZO prepared in this work were larger than those reported by Kutty et al.18) As compared with the results of Kutty et al.,18) the slope of EZO prepared in this work was little bit larger than that. They also reported that the thermal expansion coefficients of EZO were larger than those of Eu2Hf2O7. While, the slope of LZO prepared in this work was similar to that by Kutty et al. They also observed that the thermal expansion coefficients of LZO were almost similar to those of La2Hf2O7. This difference in the values of the thermal expansion coefficients seemed to depend on the measuring method and conditions. Further, difference of the slopes might also be related to using high purity ZrO2 with extremely low Hf content. It is very interesting that all the thermal expansion coefficients of EZO were larger than those of LZO, as shown in Fig. 5.

Figures 6 and 7 represent the temperature dependences of the isotropic atomic displacement parameters (\(B\)) of Ln for Eu2Zr2O7 and La2Zr2O7.
EZo with increasing temperature was smaller than that in LZO. As one of these reasons, it is likely that substitution of Hf\(^{4+}\) to a part of Zr\(^{4+}\) sites in EZO. However, we think that Hf\(^{4+}\) is almost not substituted in Zr\(^{4+}\) sites, because we used high purity ZrO\(_2\) with extremely low Hf content. Therefore, the results of \(B_{\text{eq}}\) for Zr in EZO were unrelated in existence of Hf. As another reason, we propose a static disorder of the local structure around Zr\(^{4+}\) sites in EZO. Argyriou\(^{20}\) investigated the temperature factors of both cations and anions in 10 mol\% Y\(_2\)O\(_3\)-ZrO\(_2\) using neutron powder diffraction between 15 and 1323 K, and calculated the static disorder term of the temperature factors for both Zr/Y and O atoms. He reported that the temperature factors of Zr/Y atoms in 10 mol\% Y\(_2\)O\(_3\)-ZrO\(_2\) were large, even at 15 K. He also observed that the values of \(B_{\text{eq}}\) for Zr/Y at 300 and 673 K were 1.33(3) and 1.48(3)\(\AA^2\), respectively, and that Zr/Y atoms in 10 mol\% Y\(_2\)O\(_3\)-ZrO\(_2\) had a static disorder component. In our study, the values of \(B_{\text{eq}}\) for Zr in EZO at 298, 573, and 773 K in dry conditions were 1.39(2), 1.44(2), and 1.53(2)\(\AA^2\), respectively. The results of Argyriou were similar to the values of \(B_{\text{eq}}\) for Zr sites in EZO prepared in this work between 298 and 773 K, as well as the increase in \(B_{\text{eq}}\) with increasing temperature.

4. Conclusion

We summarize the findings of the HT-XRD studies of EZO and LZO using high purity ZrO\(_2\) with extremely low Hf content as follows:

1. As the occupancies of the O1(48f) and O3(8a) sites in LZO are almost 1.0 and 0.0, respectively, LZO has a near ideal P-type structure. On the other hand, EZO has a distorted P-type structure because of the oxygen vacancy distributed between the O1(48f) and O3(8a) sites. Furthermore, the x-positional parameter of O1(48f) in LZO and EZO revealed that the crystal structure of LZO is near to an ideal P-type structure, whereas that of EZO is a distorted P-type structure.

2. The thermal expansion coefficients of EZO were larger than those of LZO.

3. The value of \(B_{\text{eq}}\) for Zr in EZO at 298 K was around 1.4\(\AA^2\), and the increase of this value in EZO with increasing temperature was smaller than that in LZO.

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References


