# Internal friction of polycrystalline $Zr_{0.8}R_{0.2}O_{1.9}$ (R = Nd, Y)

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### ARTICLE INFO

### ABSTRACT

The oxygen relaxation in two cubic zirconias, $Zr_{0.8}R_{0.2}O_{1.9}$ where R = Nd and Y, was compared with internal friction in the temperature range of 300–685 K using forced torsion pendulum method. The internal friction of $Zr_{0.8}Nd_{0.2}O_{1.9}$ was shown as a single peak at around 350–450 K at frequencies of 0.32–9 Hz. The activation enthalpy of relaxation in $Zr_{0.8}Nd_{0.2}O_{1.9}$ was determined to be $1.12 \pm 0.1$ eV. The amplitude of the high-temperature peak in Y-doped zirconia was not observed for $Zr_{0.8}Nd_{0.2}O_{1.9}$. The result suggests that the relatively lower mobility of oxygen is due to the doping of larger Nd cation to $ZrO_2$ lattice.

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## 1. Introduction

Rare earth stabilized cubic zirconia has found widespread application as a solid electrolyte including fuel cells and sensors. Zirconia can be stabilized in its cubic phase by forming complexes of dopant cations with lower valence in the range of about 10 mol% as oxide $R_2O_3$. The relaxation, i.e. local jump of oxygen around the cations should be observed as internal friction and dielectric loss peaks. Since ionic conduction occurs by migration of oxygen in the fluorite structure, this process is important to examine in details the basic process of conduction. Long-range migration of the charged oxygen leads ionic conduction under the electric field, so that the internal friction measurement provides the basic information of diffusion process in the local structure and dynamics [1–7]. The internal friction method as well as the mechanical evaluation is useful if applied with the frequency-dependent data at various temperatures to a sample. It is known that ionic radius affects the conduction and mobility in zirconia-based ionics, however the local process or jumping phenomenon itself has been less investigated. In this work, we provide the internal friction of Nd-doped zirconia ($Zr_{0.8}Nd_{0.2}O_{1.9}$), compared to ordinal $Zr_{0.8}Y_{0.2}O_{1.9}$ ceramics, at ordinary temperature region. The effect of a large cation of Nd is examined by a series of low frequency internal friction measurements.

## 2. Experimental

The raw powder was synthesized by coprecipitation method of aqueous metal nitrates with ammonia solution for compositions of $Zr_{0.8}Nd_{0.2}O_{1.9}$ and $Zr_{0.8}Y_{0.2}O_{1.9}$. The precipitate was filtered, washed with distilled water, and heat-treated at 1173 K for 3 h in air, and ground after cooling. The ceramic piece was prepared by the sintering of the pressed bodies at 1873 K for 3 h in air. Specimens with dimensions of $40\,mm \times 4\,mm \times 0.5\,mm$ were cut from them. The internal friction and modulus measurements in the temperature range of 300–685 K were carried out with a forced torsion pendulum method at the frequencies of 0.32–9 Hz using a lab-made apparatus. The internal friction was obtained from the phase shift of strain to stress for each frequency and temperature. X-ray powder diffractometer (Rigaku rint 2000, Japan) was used for identifying the phases in samples.

## 3. Results and discussion

The internal friction of polycrystalline $Zr_{0.8}Nd_{0.2}O_{1.9}$ ceramic is shown in Fig. 1, where three frequencies of 0.32, 3.2 and 9 Hz were applied at 310–720 K. The data show almost the single peaks. Fig. 2 demonstrates the comparison of internal friction of cubic $Zr_{0.8}Nd_{0.2}O_{1.9}$ and $Zr_{0.8}Y_{0.2}O_{1.9}$ at 3.2 Hz. The spectrum of $Zr_{0.8}Y_{0.2}O_{1.9}$ is clear double peaks, however that of $Zr_{0.8}Nd_{0.2}O_{1.9}$ shows a single IF (internal friction) peak. X-ray powder diffractometer has indicated that both cubic $Zr_{0.8}Nd_{0.2}O_{1.9}$ and $Zr_{0.8}Y_{0.2}O_{1.9}$ are in cubic phase, thus have the same amount of oxygen defects in a fluorite-structured crystal. Weller [3,4] reported that the height of internal friction in Y-doped zirconia increases with dopant content reaching a maximum value for 12 mol% $Y_2O_3$ ($Zr_{0.76}Y_{0.24}O_{1.9}$), where the second maximum at higher temperature become larger than the maximum at lower temperature. In this work, the Nd-doped zirconia, $Zr_{0.8}Nd_{0.2}O_{1.9}$ has the internal friction amplitude, the same as the first peak of $Zr_{0.8}Y_{0.2}O_{1.9}$ at the same temperature. Lacking of the other peak as a feature of $Zr_{0.8}Nd_{0.2}O_{1.9}$ is clear

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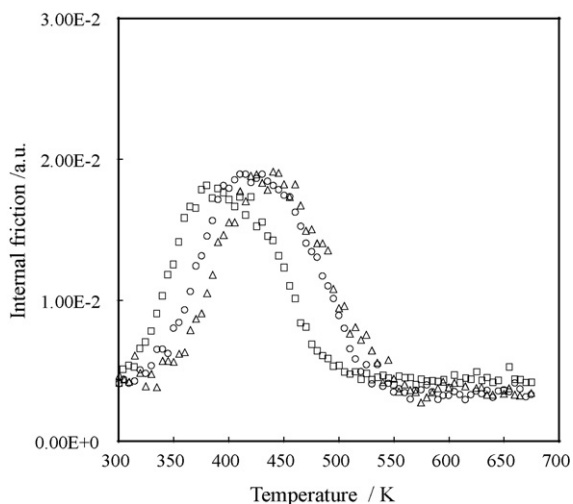  E-mail address: ozawa@nitech.ac.jp (M. Ozawa).

**Fig. 1.** Internal friction of polycrystalline $Zr_{0.8}Nd_{0.2}O_{1.9}$ at 0.32 Hz($\square$), 3.2 Hz($\bigcirc$), and 9 Hz($\square$). The apparatus background is not reduced.
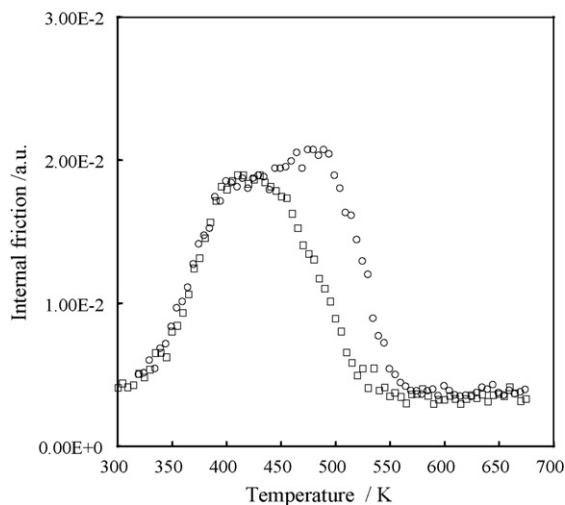


**Fig. 2.** Internal friction of polycrystalline $Zr_{0.8}Nd_{0.2}O_{1.9}$ ($\square$) and $Zr_{0.8}Y_{0.2}O_{1.9}$ ($\bigcirc$) at 3.2 Hz. The apparatus background is not reduced.

when we superimpose it with peaks of $Zr_{0.8}Y_{0.2}O_{1.9}$ as in Fig. 2, which was measured by the same condition and apparatus as well as the same preparation process. These data suggest the mechanical relaxation or jump of oxygen in the local structure is critically different between two zirconias. Table 1 lists the parameters of peak temperature and amplitude at each frequency. The activation enthalpy $H$ of maximum was determined from the frequency shift as in Fig. 3. For $Zr_{0.8}Y_{0.2}O_{1.9}$, in our previous and this work, the activation enthalpies $H$ were $1.24 \pm 0.1$ eV for a low-temperature peak, and $2.28 \pm 0.2$ eV for a high-temperature peak. This time, newly, we determined $H = 1.12 \pm 0.1$ eV for $Zr_{0.8}Nd_{0.2}O_{1.9}$ from a single peak. Nd- or Y-doped zirconia has the same relaxation process at low temperature around 400 K at 0.3–9 Hz, regarding the activation enthalpy within experimental error. However, there is

**Table 1**
Parameters for internal friction peaks of $Zr_{0.8}Nd_{0.2}O_{1.9}$.

| Frequency (Hz) | Peak temperature (K) | Amplitude[a] |
|---|---|---|
| 0.32 | 376 | 0.03 |
| 3.2 | 402 | 0.03 |
| 9.0 | 416 | 0.03 |

[a]The amplitude was obtained after apparatus background was reduced.
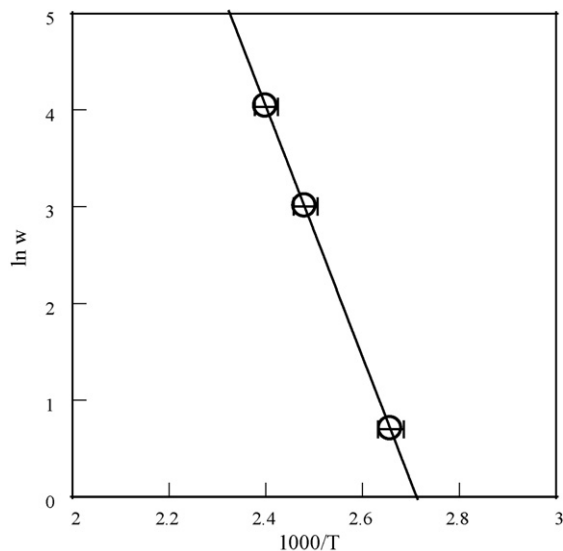


**Fig. 3.** A plot of log-angular frequency versus reciprocal temperature for $Zr_{0.8}Nd_{0.2}O_{1.9}$.

a clear difference about the second relaxation at higher temperature. They suggest the difference of defect-complexes, which are assumed between $Zr_{0.8}Nd_{0.2}O_{1.9}$ and $Zr_{0.8}Y_{0.2}O_{1.9}$. In the temperature range at this work, the mechanical relaxation is induced by oxygen relaxation, which is not due to diffusion of cations, grain boundary and/or dislocations.

Defect formation can be described by the following reactions in classical Kroger–Vink notation.

$$2Zr_{Zr}{}^{x} + O_{O}{}^{x} + Nd_2O_3 = 2Nd'_{Zr}V_O{}^{\bullet\bullet} + 2ZrO_2 \qquad (1)$$

Actually, the defect complex $(Nd'_{Zr}V_O{}^{\bullet\bullet})^{\bullet}$ and $(2Nd'_{Zr}V_O{}^{\bullet\bullet})^{x}$ should form in Nd-doped zirconia crystal. Weller [4] has also discussed on Y-doped zirconia that the trigonal symmetry of the defects causing maximum directly to their assignment to simple $(Y'_{Zr}V_O{}^{\bullet\bullet})^{\bullet\bullet}$ complexes like according to Eq. (1). This defect model for the fluorite lattice of zirconia is valid for present $Zr_{0.8}Nd_{0.2}O_{1.9}$ too, however lacking of the second peaks cannot be explained. The oxygen vacancies can essentially jump (reoriented) on the eight [1 1 1]-oriented, nearest neighboring site. Although the second peak probably requires the other relaxation pass in the lattice, it is practically difficult to realize the different route of oxygen movement with one nearest pass around cations. Possibility is of a few atoms due to its higher activation enthalpy of 2 eV or a simple relaxation with high potential barrier for hopping. The former means that a dominating high-temperature peak in $Y_2O_3$–$ZrO_2$ for higher Y dopant levels is assigned to relaxation of oxygen vacancies within a cluster of two or more Y ions. The latter is assumed when the simplest defect may consist of two Y ions and an oxygen vacancy forming a large complex such as $(2Nd'_{Zr}V_O{}^{\bullet\bullet})^{x}$. The local structure inducing anelastic relaxation of zirconia has been discussed elsewhere by several workers [2–4,7]. If a large complex defect, e.g. $(2Y'_{Zr}V_O{}^{\bullet\bullet})^{x}$ and its relaxation, gives the anelastic relaxation peak, the doping of larger cation of Nd is not preferred to form a complex, because the two large cations are closing each other. With the cation sizes (the ionic size, $Nd^{3+}$(0.10 nm) > $Y^{3+}$(0.09 nm) > $Zr^{4+}$(0.08 nm)), a large complex $(2Y'_{Zr}V_O{}^{\bullet\bullet})^{x}$ has much strain and stabilized as a local structure without relaxation of oxygen. Actually, the mobility of oxygen has been partially lost by the local structural character in Nd-doped $ZrO_2$. The relaxation is a phenomenon of oxygen movement under elastic field, however it affects the essential property of transport of oxygen under electric field. The lower ionic conductivity

of $Nd_2O_3$–$ZrO_2$, compared to $Y_2O_3$–$ZrO_2$ ceramics, must be closely related with the defect complex structure [8]. A tentative figure for the effect of doping larger Nd cation on oxygen relaxation was discussed in this work. More work is required for comparison with other techniques to investigate the local structure.

## 4. Summary

The oxygen relaxation in two cubic zirconias, $Zr_{0.8}R_{0.2}O_{1.9}$ where R = Nd and Y, was compared with internal friction in the temperature range of 300–685 K using forced torsion pendulum method. The internal friction of $Zr_{0.8}Nd_{0.2}O_{1.9}$ was shown as a single peak at around 350–450 K at frequencies of 0.32–9 Hz. The activation energy of relaxation in $Zr_{0.8}Nd_{0.2}O_{1.9}$ was $1.12 \pm 0.1$ eV with dif-

ferent peak temperatures. The amplitude of the high-temperature peak in Y-doped zirconia was not observed for $Zr_{0.8}Nd_{0.2}O_{1.9}$, lacking a large complex in zirconia lattice.

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