JOURNAL OF MATERIALS SCIENCE **38** (2003) 3689–3694

Frequency dispersion of the internal friction in tetragonal and cubic zirconia polycrystals stabilized with yttria

J. KONDOH*, H. SHIOTA
Department of Mechanical and Systems Engineering, Faculty of Engineering,
Gifu University, Gifu 501-1193, Japan
E-mail: junya@mat.usp.ac.jp

A forced vibration method for measuring the frequency dispersion of internal friction under cyclic-tensile-compressive stress on the single axis was developed so that various mechanical tests can be conducted using a specimen having the same shape, machining, and sintering conditions. With this new method, frequency dispersions of the internal friction for tetragonal and cubic zirconia polycrystals stabilized with yttria were measured. The activation energy for the relaxation time was determined. As a result of comparison with the activation energy for the relaxation time measured by a conventional method, we conclude that the results of the internal friction measured in this study are valid. The activation energy for the ionic conductivity was determined, and compared with that for the relaxation time. The activation energies for the relaxation time in 2.6YSZ, 3YSZ, and the lower temperature peak of 10YSZ are very similar to those for the conductivity. As a result, we conclude that the internal friction peaks of 2.6YSZ and 3YSZ, and the lower temperature peak of 10YSZ are derived from rearrangement of point defects associated with oxygen ion vacancies.

---

1. Introduction

Yttria-stabilized Zirconia (YSZ), because of its high strength and high ionic conductivity, is used as both a structural material and a solid electrolyte. Recently, it has been reported that the internal friction in YSZ is closely correlated with the ionic conductivity [1]. Therefore, to clarify the mechanism of the ionic conduction, the mechanical properties and the behavior of the point defects, it is important to measure and analyze the internal friction in YSZ.

Conventionally, the internal friction is measured with the flexural resonance method or a free-decay procedure using an inverted torsion pendulum. However, the frequency dispersion of the internal friction is impossible to measure using these methods. Thus, the internal friction is usually measured as a function of the temperature. However, because a change in the temperature changes the distribution and the species of the defects that cause the anelastic relaxation, the frequency dispersion of the internal friction must be measured to analyze the anelastic properties. Nevertheless, the frequency dispersion of the internal friction for YSZ has never been reported for a wide range of yttria concentrations [2].

On the other hand, since forced vibrations apparatus using torsion pendulum was developed by Woirgard [3], many measurements have been currently performed at constant teperature as a function of frequency [4]. Moreover, a testing system for measuring the frequency dispersion of the internal friction under the torsional loading was developed and recently came onto the market [5]. However, because of the required intricate sample shape, this apparatus is not suitable for ceramics. Moreover, the relationship between the microstructure and the anelastic properties cannot be examined due to the measurement under the torsional loading [4, 5]. In addition to such problems, in these methods many kinds of specimens, having various shapes, are necessary for examining all the mechanical properties: the fracture strength, fatigue, and Young's modulus. The influence of the difference in machining and sintering conditions on the mechanical properties cannot be neglected, which makes interpretation of the mechanical properties complicated. Therefore, all the tests must be conducted using a specimen having the same shape, machining, and sintering conditions, under the identical loading axis. Furthermore, to examine the relationship between the mechanical properties and the microstructure, all the experiments should be conducted under a single axial loading.

In the present study, we developed a forced vibration method for measuring the frequency dispersion of

---

*Author to whom all correspondence should be addressed.
Present address: Department of Materials Science, The University of Shiga Prefecture, 2500 Hassaka-cho, Hikone 522-8533, Japan.

0022–2461

TABLE I Sintering temperature and density of each specimen

Specimen (ID)	Sintering temperature (K)	Sintered density (g/cm^3)
2.6YSZ (HSY-2.6W)	1723	6.016
3YSZ (HSY-3)	1723	6.063
10YSZ (HSY-10)	1723	5.770

the internal friction under a cyclic-tensile-compressive stress on the single axis. The internal friction of tetragonal and cubic zirconia polycrystals stabilized with yttria was measured with this method, and the activation energy for the relaxation time was determined. As a result of comparison with the values of the internal friction measured by conventional methods, we indicate that the results of the internal friction measured in this study were reasonable. Moreover, the activation energy for the ionic conductivity was determined, and compared with the activation energy for internal friction.

2. Experimental procedure

2.1. Materials

Y_2O_3 stabilized ZrO_2 polycrystals with the following compositions were used in this study: 2.6 mol% Y_2O_3-97.4 mol% ZrO_2 (hereinafter called 2.6YSZ, HSY-2.6W made by Daiichi Kigenso Kagaku Kogyo Co., Ltd.), 3 mol% Y_2O_3-97 mol% ZrO_2 (3YSZ, HSY-3 made by Daiichi Kigenso Kagaku Kogyo Co., Ltd.), and 10 mol% Y_2O_3-90 mol% ZrO_2 (10YSZ, HSY-10 made by Daiichi Kigenso Kagaku Kogyo Co., Ltd.). Table I shows sintering temperature, and density of each specimen.

2.2. Measurements of the internal friction

Fig. 1 shows a schematic illustration of the apparatus used for internal friction measurement. The closed-loop-type hydraulic test machine was employed for loading. Ordinarily, the load is measured by a single load cell installed over the upper specimen chuck. However, it takes some time for the load to be transmitted from the specimen to the load cell through the upper specimen chuck. This time lag between the load detected in the load cell and the load applied to the specimen must be compensated for in this measurement. For measurements at high frequencies, this time lag is not negligible. In the present study, two load cells were installed, one over the upper chuck and one under the lower chuck, each located equidistant from the specimen, as shown in Fig. 1. The accurate load-time relation applied on the specimen was determined by averaging the two load-time relations measured from these load cells. The average value of two data at a certain time can be regarded as an accurate load-value of the specimen at the time. The shape and dimensions of the specimen are the same as those of the specimen used for the tensile test reported in another paper [6].

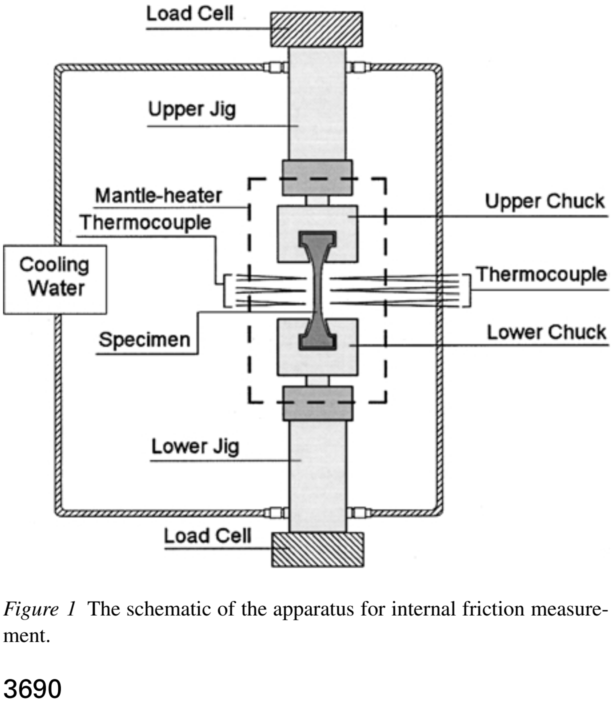


Figure 1 The schematic of the apparatus for internal friction measurement.

The measurement was conducted at atmospheric pressure, in air. The stress was applied, in the form of a sine curve with frequencies in the range of 0.0002 to 1.5 Hz, amplitude 200 MPa for 2.6YSZ and 3YSZ, and 60 MPa for 10YSZ. Measurement of temperature dependence was from room temperature to 523 K. No measurements were made for cases of decreasing temperature. Four strain gauges were attached to the four sides of the specimens to examine the bending component of the strain. The bending component of the strain was always kept below 5% of the average strain. As a result of the decrease in the bending component, the background of the internal friction successfully exhibited a significant decrease. These strain gauges were also used to measure the strain for calculating the internal friction. The specimen was heated in a mantle-heater. The variation in temperature was kept to less than ±3 K of the specified temperature over the gauge length of the specimen, 10 mm.

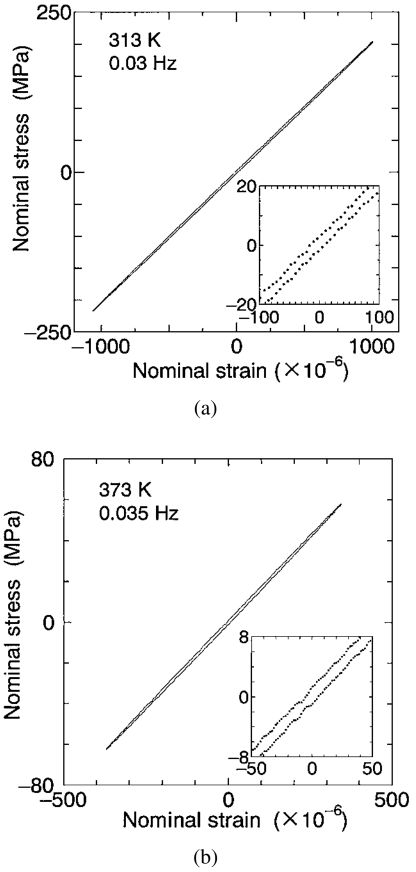
The internal friction was calculated by two different procedures [7]. The internal friction is defined as the loss angle by which the strain lags behind the stress when periodic stress is applied to the specimen. The loss angle ϕ was obtained by fitting the stress-time curve and the strain-time curve to the sine curve with the same frequency. In another method, the internal friction was calculated from the ratio of the energy per unit of volume, dissipated in a full cycle, ΔW, to the maximum stored energy per unit volume, W. On the stress-strain diagram, W and ΔW are the area under the stress-strain curve measured during the tensile loading and the area bounded by the stress-strain curve in a cycle, respectively. Accordingly, we can obtain the internal friction value Q^{-1} as $\tan\phi \cong \phi(\Delta W/W)/(2\pi)$.

2.3. Determination of the activation energy for the conductivity

The DC four-probe technique was used to measure the conductivity, and the activation energy was determined from those results. Each sample was a prism measuring 40 mm × 4 mm × 3 mm. The distance between the two potential probes was 10 mm. All measurements were made at atmospheric pressure, in air. Before each measurement, the sample was heated to 1773 K, near the typical sintering temperature, then cooled to a given temperature in an electric furnace. This procedure prevented samples from aging during the cooling down period after sintering and heating [8]. To ensure that the activation energy was determined without the influence of aging, the conductivity used to determine the activation energy must be measured at 1573–1773 K, that is, at temperatures much higher than the transition temperature. This avoids the effects of aging during measurement [8]. However, in this study, the conductivity used to determine the activation energy was measured at 1073–873 K, which was the lowest possible temperature range in the DC four-probe technique. This was done to reduce the difference in the temperature ranges between internal friction and conductivity measurements.

3. Results and discussion

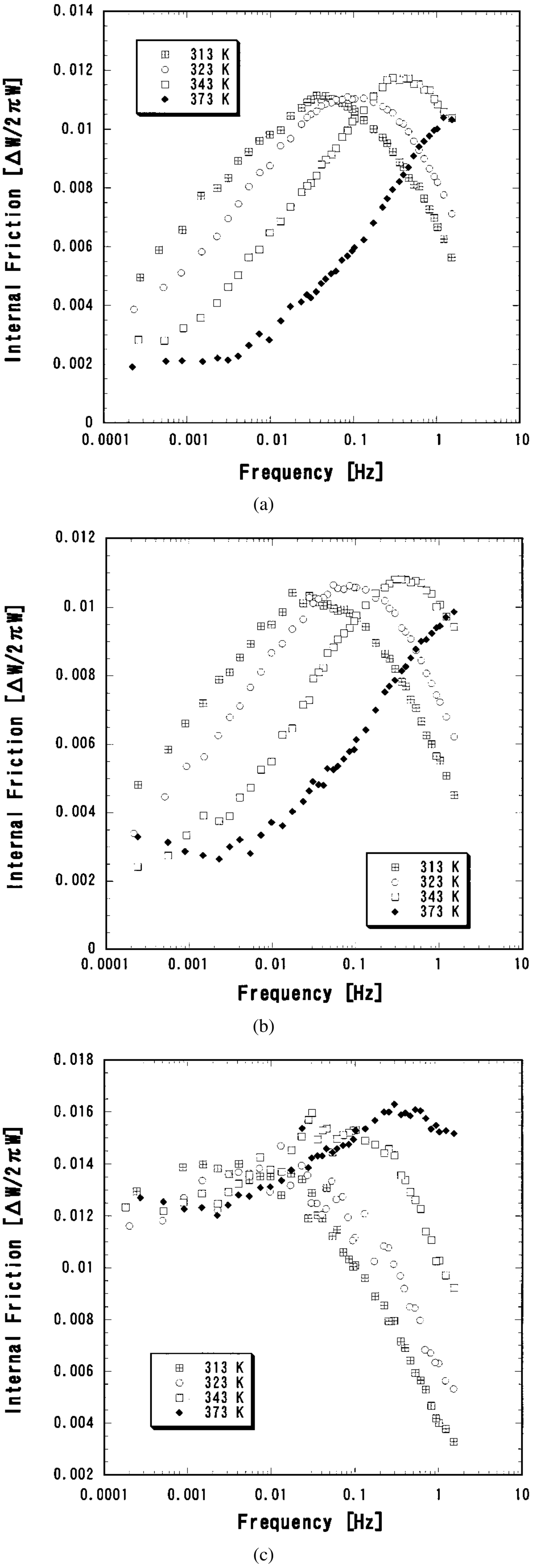
Fig. 2a and b show the relationship between the stress and the strain during a given cycle, for 3YSZ at 313 K and 0.03 Hz and for 10YSZ at 373 K and 0.035 Hz, respectively. Both stress-strain responses exhibited a hysteresis loop, obviously derived from the internal friction. Fig. 3a–c show the frequency dispersions of $\Delta W/2\pi W$ for 2.6YSZ, 3YSZ, and 10YSZ at 313, 323, 343, and 373 K, respectively. The frequency dispersions of ϕ exhibited the same tendency as those of $\Delta W/2\pi W$ shown in Fig. 3a–c. In all the specimens, the peaks of $\Delta W/2\pi W$ shifted toward higher frequency as the temperature increased. Because the frequency dispersions of 10YSZ were too broad to indicate the whole of the



(a)

(b)

Figure 2 (a) Stress-strain response measured at 313 K and 0.03 Hz. A magnified portion is also shown. (b) Stress-strain response measured for 10YSZ at 373 K and 0.035 Hz. A magnified portion is also shown.



(a)

(b)

(c)

Figure 3 Frequency dispersions of the internal friction at 313, 323, 343, and 373 K. (a) 2.6YSZ, (b) 3YSZ, and (c) 10YSZ.

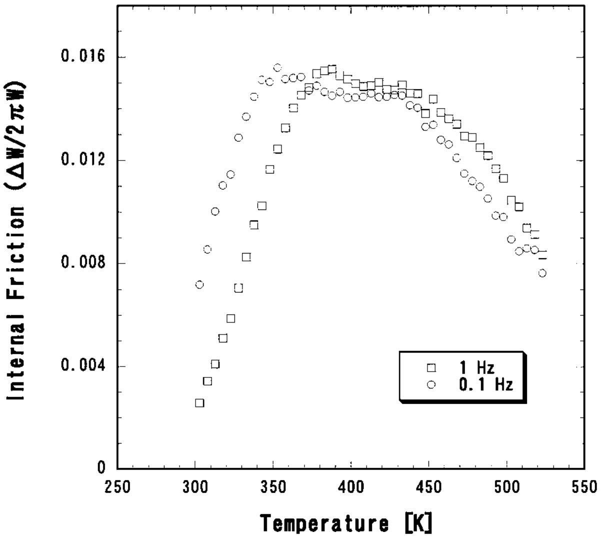


Figure 4 Temperature dependence of the internal friction measured for 10YSZ at 0.1 and 1 Hz.

internal friction peaks within the frequency range in this study, temperature dependence of the internal friction was measured at 0.1 and 1 Hz, as shown in Fig. 4. Temperature dependence of the internal friction for 10YSZ apparently had two peaks, which seem to overlap.

For the standard anelastic solid, or when the real and imaginary parts of the dynamic compliance and the internal friction are expressed by the Debye equations, the activation energy for the relaxation time in mechanical relaxation was determined as follows [9]. The relaxation time τ generally obeys the Arrhenius equation;

$$\tau = \tau_\infty \exp(H/kT), \tag{1}$$

where H is the activation energy, τ_∞ is the pre-exponential factor, k is Boltsmann's constant, and T is the absolute temperature. For the case of a Debye peak, the condition that $\ln \omega\tau = 0$ at the peak gives

$$0 = \ln \omega\tau_\infty + (H/k)(1/T_\mathrm{P}), \tag{2}$$

where T_P is the temperature in frequency dependence of the internal friction or the temperature at the peak top in temperature dependence, and ω is the angular frequency in temperature dependence or the angular frequency at the peak top in frequency dependence. According to Equation 2, when the internal friction peak is expressed by the Debye equations, the activation energy can be obtained from the slope of $\ln \omega$ plotted relative to $1/T_\mathrm{P}$.

However, because the concentration of point defects is very high in any stabilized zirconia, especially in 10YSZ, the relaxation peaks of 10YSZ are much broader than the Debye peak, and the relaxation time clearly indicates continuous distributions. Therefore, the activation energies can not be determined simply by the above method using Equation 2. The distribution function of YSZ is different from the symmetrical function with respect to the mean relaxation time such as the Gaussian distribution, the Fuoss-Kirkwood distribution which are well-known as a distribution function of the relaxation time, and the box distribution, and is not symmetrical. In YSZ, the distribution function is expressed by the Lévy distribution function [10], which shows extremely asymmetric distribution [11]. This means that the creep function of YSZ is expressed by Kohlausch-Williams-Watts's equation, which is very famous equation in dielectric relaxation. Assuming that the distribution function of the pre-exponential factor is followed by the Lévy distribution, when the peak fitting was carried out, the simulated peaks completely correspond with the experimental peaks in all internal friction data for YSZ. The details of the distribution function are shown in another paper [10].

However, according to Nowick and Berry, in such a case, a precise value of the activation energy can be easily determined without knowing a detailed distribution function and carrying our a complicated peak fitting calculation, as follows [12]. The occurrence of a distribution in the relaxation times may reflect the existence of a distribution in τ_∞, in H, or in both of these quantities, in Equation 1. To know which or both parameters in Equation 1 contribute to the occurrence of a distribution, in other words, which parameters show a continuous distribution, the degree of the temperature shift with frequency change $\delta(1/T)$ ought to be examined. As known in Fig. 5, the internal friction peak shown in Fig. 5 consists of two peaks, and the degree of the shift with frequency $\delta(1/T)$ is the same over the entire curve in both lower and higher temperature peaks, respectively. Therefore, it is clear that only the pre-exponential factor τ_∞ shows a continuous distribution and this result is characteristic of a unique activation energy for each peak. A continuous distribution of times is derived only from a continuous distribution of the pre-exponential factor τ_∞, and activation energies H are constant in each peak. The degree of the temperature shift with frequency change $\delta(1/T)$ indicate the difference between the lower and higher temperature peaks, and this shows that parameters of a continuous distribution function of the pre-exponential factor τ_∞ are different between two peaks.

Therefore, using the method explained by Nowick and Berry [12], the activation energy can be determined

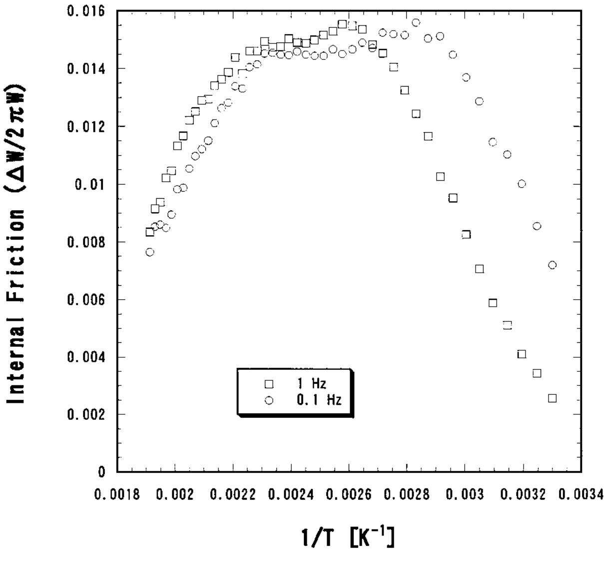


Figure 5 The internal friction versus $1/T$ measured for 10YSZ at 0.1 and 1 Hz.

from Fig. 5 by Equation 3 shown below.

$$\delta\left(\frac{1}{T}\right) = \frac{k}{H}\ln\frac{\varpi_2}{\varpi_1} \tag{3}$$

This equation has the advantage that a precise value of the activation energy can be determined withot knowing a detailed distribution function of the pre-exponential factor. Therefore, we insist that the accuracy of the activation energies of the internal friction determined in the present study is very high.

2.6YSZ and 3YSZ consist of both the tetragonal and cubic phases [1]. Thus, the internal friction peaks for these specimens consist of at least two peaks. However, because the quantity of the cubic phase in 2.6YSZ and 3YSZ is small, the measured peaks were regarded as a single peak derived from the tetragonal phase in the present study. Actually, in temperature dependence of the internal friction for 3YSZ, the internal friction peak due to the cubic phase in partially-stabilized zirconia (PSZ) appears as a slight broadening of the right shoulder of the tetragonal peak [1]. As a result of the calculation, the activation energy of 3YSZ is about 0.854 eV. This value is very similar to the activation energies for 3YSZ, reported using conventional methods [13, 14].

Therefore, we conclude the following from these results: Using the method developed in this study,it is possible to measure the frequency dispersion of the internal friction for ceramics under single axial loading, utilizing the identical specimen and test system as those used in the tensile and fatigue tests.

Table II shows the activation energies for the ionic conductivity and the relaxation time of each specimen. Because 10YSZ apparently shows two peaks, the activation energy was determined for each peak. The activation energies for the relaxation time in 2.6YSZ, 3YSZ, and the lower temperature peak of 10YSZ are very similar to those for the conductivity. This indicates that the internal friction peaks of 2.6YSZ and 3YSZ, and the lower temperature peak of 10YSZ are derived from rearrangement of point defects associated with oxygen ion vacancies.

On the other hand, because the activation energies for self-diffusion of magnesium and calcium ions in zirconia are 2.95 and 4.35 respectively [15, 16] and the short range migration is observed in phase transformation due to cooling, for example c-t' phase transformation, and slight displacement of cations occurs even in a low temperature range (Though this type of phase transformation is called diffusionless phase transformation or displacive phase transformation generally, as a matter of fact, displacement and shuffling of cations occur necessarily [17–21].), the activation energy for the relaxation time in the higher temperature peak of 10YSZ can be presumed to be similar to that for the diffusion of the dopant cation.

TABLE II The activation energies for relaxation time and ionic conductivity

	Activation energy (eV)	
Specimen	Conductivity	Relaxation time
HSY-2.6	0.889	0.821
HSY-3	0.830	0.854
HSY-10	0.938	0.894[a], 3.114[b]

[a] The activation energy obtained from the lower temperature peak.

[b] The activation energy obtained from the higher temperature peak.

Therefore, it is likely that the higher temperature peak is derived from rearrangement of point defects associated with dopant cations (yttrium ions). However, to know details of the species and symmetry of the point defects causing each internal friction peak, analysis of internal friction spectra, or the decomposition of the peaks, for single crystalline YSZ and the following examination of orientation factor dependence of the relaxations of the reciprocal torsional torsional or Young's modulus are needed [22]. A detailed analysis of the internal friction for single crystalline 10YSZ is reported in another paper [10].

4. Summary

In the present study, we developed the forced vibration method for measuring the frequency dispersion of the internal friction under the cyclic-tensile-compressive stress on the single axis so that various mechanical tests can be conducted using the specimen having the same shape and machining and sintering conditions, under the single axial loading. Frequency dispersions of the internal friction for tetragonal and cubic zirconia polycrystals stabilized with yttria (2.6YSZ, 3YSZ, and 10YSZ) were measured with this method. For 10YSZ, temperature dependence of the internal friction was also measured by the same method. From these results, the activation energy for the internal friction was determined. As a result of comparison with the activation energy for the internal friction measured by a conventional method, we conclude that the results of the internal friction measured in this study are valid.

The activation energy for the ionic conductivity was determined, and compared with that for the internal friction. As a result, we conclude that the internal friction peaks of 2.6YSZ and 3YSZ, and the lower temperature peak of 10YSZ are derived from rearrangement of point defects associated with oxygen ion vacancies. On the other hand, we think it likely that the higher temperature peak is derived from rearrangement of point defects associated with dopant cations (yttrium ions).

Acknowledgments

We would like to express our thanks to Prof. Shiomi Kikuchi for his significant assistance in manufacturing the apparatus, and to Mr. Katsuhiro Kawachi and Dr. Toshio Nakatani, Daiichi Kigenso Kagaku Kogyo Co., Ltd., for supplying us with the samples.

References

1. J. KONDOH, S. KIKUCHI, Y. TOMII and Y. ITO, *J. Electrochem. Soc.* **145** (1998) 1550.
2. L. DONZEL and R. SCHALLER, *Acta Mater.* **46** (1998) 5187.
3. J. WOIRGARD, Y. SARRAZIN and H. CHAUMET, *Rev. Sci. Instrum.* **48** (1977) 1322.

4. P. GADAUD, B. GUISOLAN, A. KULIK and R. SCHALLER, *ibid.* **61** (1990) 2671.
5. Y. WEN, Q. SU and M. WUTTIG, *Mech. Work Steel Process* **35** (1997) 271.
6. J. KONDOH, H. SHIOTA, K. KAWACHI and T. NAKATANI, *J. Alloys and Compounds*, in press (2003).
7. A. S. NOWICK and B. S. BERRY, in "Anelastic Relaxation in Crystalline Solids" (Academic Press, New York, 1972) p. 10.
8. J. KONDOH, T. KAWASHIMA, S. KIKUCHI, Y. TOMII and Y. ITO, *J. Electrochem. Soc.* **145** (1998) 1527.
9. A. S. NOWICK and B. S. BERRY, in "Anelastic Relaxation in Crystalline Solids" (Academic Press, New York, 1972) p. 52.
10. J. KONDOH, *Phil. Mag.*, submitted.
11. E. W. MONTROLL and J. T. BENDLER, *J. Statistical Physics* **34** (1984) 129.
12. A. S. NOWICK and B. S. BERRY, in "Anelastic Relaxation in Crystalline Solids" (Academic Press, New York, 1972) p. 109.
13. G. HANECZOK and M. WELLER, *Journal de Physique IV* **6** (1996) C8.
14. K. MATSUSHITA, T. OKAMOTO and M. SHIMADA, *J. Phys. Paris* **C10**(Suppl. 46) (1985) 549.
15. Y. SAKKA, Y. OISHI and K. ANDO, *Bull. Chem. Soc. Jpn.* **55** (1982) 420.
16. W. H. RHODES and R. E. CARTER, *J. Amer. Ceram. Soc.* **49** (1966) 244.
17. A. H. HEUER, R. CHAIM and V. LANTERI, in "Advances in Ceramics," Vol. 24 edited by S. Somiya, N. Yamamoto and H. Yanagida (The American Ceramics Society, Columbus, OH, 1988) p. 3.
18. T. LOG, R. A. CUTLER, J. F. JUE and A. V. VIRKAR, *J. Mater. Sci.* **28** (1993) 4503.
19. T. S. SHEU, T. Y. TIEN and I. W. CHEN, *J. Amer. Ceram. Soc.* **75** (1992) 1108.
20. M. YASHIMA, K. MORIMOTO, N. ISHIZAWA and M. YOSHIMURA, *ibid.* **76** (1993) 1745.
21. M. YASHIMA, K. MORIMOTO, N. ISHIZAWA and M. YOSHIMURA, *ibid.* **76** (1993) 2865.
22. A. S. NOWICK and B. S. BERRY, in "Anelastic Relaxation in Crystalline Solids" (Academic Press, New York, 1972) p. 77.

Received 22 February 2002
and accepted 9 June 2003