

Internal Friction in ZrO_2 Containing CaO

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Internal friction was measured on polycrystalline ZrO_2 containing 4, 7, 10, 13, 16, and 20 mole percent CaO. In the range 10 to 20 percent a symmetrical internal friction peak occurs with its maximum at about 300 °C at 1 kHz; below 10 percent a nonsymmetrical peak occurs at somewhat higher temperature which may be associated with the presence of two phases. The symmetrical peak in as-sintered specimens has the same dependence on CaO content as that reported for electrical resistivity at 1000 °C and is probably caused by motion of oxygen vacancies. Annealing at 1000 °C for 1000 hours causes reduction of the peak height but with a different composition dependence from that reported for annealing of electrical resistivity. The results suggest that oxygen vacancies in calcia stabilized zirconia exist in several states of binding but that detailed models are likely to be complex.

1. Introduction

Ceramics high in ZrO_2 are of considerable technological importance; an extensive bibliography on structural and physical properties of zirconia has recently been published [1].¹ Many applications of zirconia rely upon the presence of additives to produce partial or complete stabilization in the cubic phase and so avoid difficulties caused in pure ZrO_2 by the transformation which occurs in the range 1200 to 1000 °C from the high temperature tetragonal phase to a low temperature monoclinic phase. Various additives have been tried, but CaO appears to be the most successful and widely studied. The phase diagram of the ZrO_2 -CaO system remains a subject of discussion; it is generally agreed that a cubic phase exists for compositions neighboring 15 percent CaO (mole percent rather than weight percent is used throughout this paper). The reported limits of the one phase region vary considerably; Carter and Roth [2] take them to be 10 and 20 percent. Below the lower limit a mixture of two phases exists.

The cubic phase is usually regarded as a fluorite structure with Zr^{4+} and Ca^{2+} distributed at random over the cation sites and with enough oxygen vacancies to provide charge compensation distributed at random over the oxygen sites. This model is in accord with x-ray diffraction evidence and the high diffusion rate for oxygen but is generally thought to be oversimplified in not allowing for the association or ordering of defects or even the possibility of additional phases not yet detected. The variation of electrical resistivity with composition and heat treatment has been interpreted as indicating ordering of vacancies [3, 2]. Neutron diffraction patterns [2] are consistent with this interpretation.

Homogeneous stress or electric field acting upon a point defect can, under certain conditions, cause reorientation of the defect and produce a corresponding mechanical or electrical relaxation. Measurements of the internal friction peak or dielectric loss peak can then be used to study the variation of point defect concentration with composition and heat treatment.

An internal friction peak was found by Dew [4] in commercial zirconia partially stabilized with CaO and its existence was confirmed in two subsequent investigations [5, 6]. All workers used polycrystalline specimens. Interpretation of this peak is difficult because the specimens probably contained some of the tetragonal phase as well as the cubic phase. Dew suggested plastic deformation as a possible cause; Chang suggested the motion of twin boundaries; and Wachtman et al., suggested the motion of oxygen vacancies.

A dielectric relaxation process which occurs in the same frequency and temperature range as the internal friction peak has been found by Carter [7] in both single crystal and polycrystalline zirconia stabilized with 14.2 percent CaO. This relaxation process appears to involve motion of oxygen vacancies because its dependence on heat treatment parallels that of the electrical conductivity at 1000 °C which is known to take place by oxygen vacancy motion. The observed dielectric relaxation probably arises from the series combination of two regions with different oxygen mobility either on an atomic scale (such as a vacancy constrained to the sites neighboring a relatively immobile point defect) or on a somewhat larger scale (such as a small region of a second phase or a surface layer under the electrode). The composition of Carter's specimen places it within the single, cubic phase area of conventional phase diagrams, but Carter and Roth present neutron diffraction and x-ray diffraction evidence that annealing at 1000 °C results in the formations of small ordered regions of a preprecipitate which are epitaxially related to the host lattice.

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¹ Figures in brackets indicate the literature references at the end of this paper.

Investigation of the composition and heat treatment dependence of the internal friction peak has been undertaken to test the similarity of its behavior with the electrical conductivity and dielectric relaxation.

2. Specimens

Single crystals suitable for internal friction measurements were not available. Polycrystalline specimens were prepared from ZrO_2 powder containing 0.15 percent SiO_2 , 0.02 percent HfO_2 , and 0.03 percent MgO as the major impurities: mixtures were made up using CaO powder produced by calcining "chemically pure" calcium carbonate at 1000 °C. Specimens were cold pressed in a steel bar-mold, isostatically pressed, and sintered for 1 hr at 1800 °C in a gas fired furnace. The porosity and grain size of the resulting bars are given in table 1; the dimensions were about 6 by 0.5 by 0.25 in.

TABLE 1

Additive	Porosity	Grain size	Frequency at peak	Temperature at peak	Peak height, Q^{-1}	Apparent activation energy
% CaO		Microns	c/sec	°C	10 ⁻²	kcal/mole ^b
4		19	1115	455	1.7	
4 ^a			397			
7		29	1362	427	1.8	
7 ^a			366		1.8	
10	0.18	28	1983	315	1.2	42±7
10 ^a			628	297	1.0	
13	.28	22	1883	319	2.2	29±7
13 ^a			486	290	2.1	
16	.24	32	1913	305	1.5	43±9
16 ^a			582	290	1.6	
20	.27	24			1.1	

^a Specimen thinned to reduce resonance frequency.

^b kcal=4184 joules. Standard errors are based on peak temperatures obtained by curve fitting through twenty points.

3. Experimental Procedure

The variation of internal friction with temperature was determined by Forster's method in which a bar is suspended horizontally from two fiberglass threads tied near the nodes of flexural vibration. One thread was driven by a magnetic record-cutting head and the other was attached to a piezoelectric pickup. The driving frequency was varied until the resonance frequency, f_1 , was found and measured on a crystal controlled counter. The frequencies f_2 and f_3 (on either side of f_1) at which the amplitude of vibration is half that at resonance were also measured. The internal friction was calculated from [8]

$$Q^{-1} = 0.5773(f_3 - f_2)/f_1. \quad (1)$$

Measurements of Q^{-1} as a function of temperature up to 650 °C were first made on as-sintered specimens of all the compositions made (ZrO_2 containing 4, 7, 10, 13, 16, and 20% CaO). All of the specimens were

then thinned over the central third of their length by diamond grinding to lower the resonance frequency and all were then remeasured except for the 20 percent CaO specimen which was broken in grinding. The activation energy, E , was calculated from [8]

$$E = \frac{RT_{p1}T_{p2} \ln f_{p1}/f_{p2}}{T_{p1} - T_{p2}} \quad (2)$$

where T_{p1} is the absolute temperature at which the quantity TQ^{-1} was largest and f_{p1} is the corresponding resonance frequency; T_{p2} and f_{p2} are the corresponding quantities for the same specimen after thinning.

Three additional unthinned specimens (containing 10, 13, and 16 percent CaO) were then held at 1000 °C in air for 1000 hr and subsequently measured; we refer to these as annealed specimens.

4. Results

The curves of internal friction as a function of temperature are shown in figure 1; for each composition the lower solid curve (shown dashed for the 4% specimen because of scatter) refers to the thinned specimen. Results obtained on the annealed specimens after the 1000 hr heat treatment are shown by dot-dash curves. A marked contrast is evident between the results for the 4 and 7 percent specimens, on the one hand, and the specimens completely stabilized in the cubic phase, on the other hand.

The partially stabilized specimens show an unsymmetrical peak with a shoulder on the high temperature side. Grinding these specimens apparently produced internal cracking leading to wide scatter in results, particularly for the 4 percent specimen.

The peaks for specimens in the 10 through 20 percent range of compositions are symmetrical, but are much too broad to result from a relaxation process with a single relaxation time. For comparison, the curve calculated for a single relaxation time process (Debye type process) has been drawn under the lower curve for the specimen containing 13 percent CaO . The height of the Debye peak was chosen equal to the experimental peak and the activation energy calculated from eq (2) was used. The experimental curve is about three times as wide as the Debye curve. The variation of peak height with composition for the as-sintered specimens (greatest at 13%, decreasing toward 10% or toward 20%) parallels the variation of electrical conductivity found for comparable specimens [2, 3]. The heat treatment at 1000 °C has somewhat similar results on electrical conductivity at 1000 °C and on internal friction in that both properties decrease for certain compositions and remain unchanged for others. The composition dependence is different, however. Carter and Roth report that the electrical conductivity of ZrO_2 containing 14 percent CaO remains unchanged with time at 1000 °C but the conductivity of compositions less than 13 or more than 16 percent decreases. In contrast, the internal friction peak

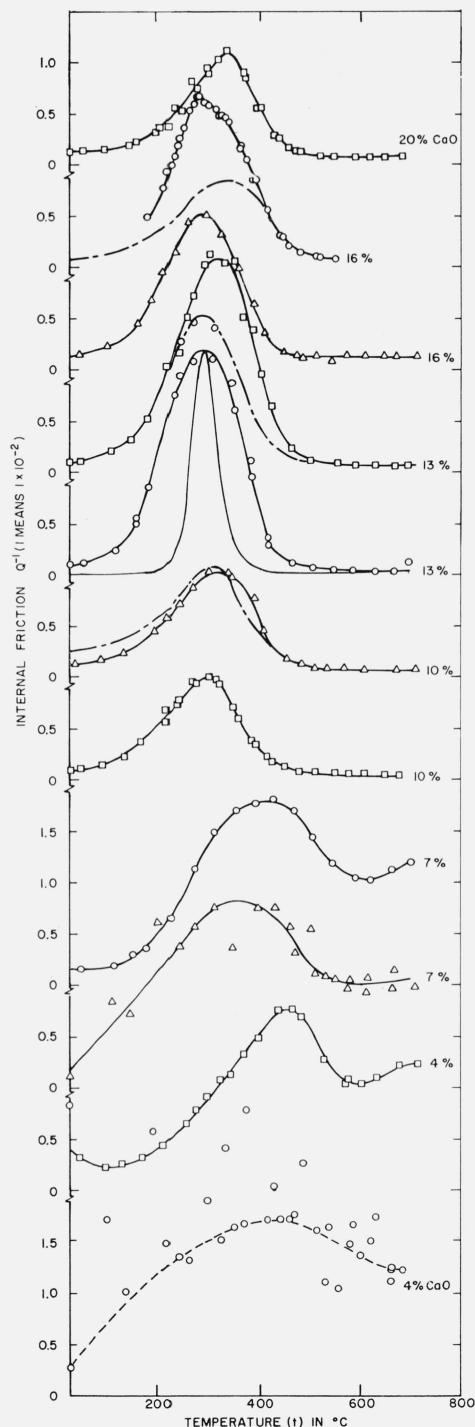


FIGURE 1. Internal friction of ZrO_2 containing stated amounts of CaO .

The dot-dash curves were determined after 1000 hr at 1000 °C in air. The other curves were obtained on as-sintered specimens; where more than one such curve is given the lower one was obtained after machining the specimen to lower its resonance frequency.

height for the specimen containing 10 percent CaO was not changed but the peak for the specimen with 13 percent CaO was decreased and that for the specimen with 16 percent CaO was reduced even more.

5. Discussion

The unsymmetrical peak occurring in partially stabilized ZrO_2 might be associated with Chang's mechanism of twin boundary motion in tetragonal grains, but the symmetrical peak occurring in the range of 10 to 20 percent CaO can not be associated with tetragonal grains. The similarity of peak height dependence and electrical conductivity dependence on CaO content suggests that the symmetrical peak is associated with oxygen vacancy motion.

The concentration of oxygen vacancies and of Ca^{2+} ions is so high that many complex groupings probably occur. We discuss three defect models that might be appropriate at very low concentrations in order to illustrate certain qualitative features which may be valid even at high concentrations.

First, consider a single oxygen vacancy in an otherwise perfect fluorite structure (see fig. 2). This vacancy would move under electric field but not under homogeneous stress [9]. It would contribute to the frequency independent part of the electrical conductivity but would not contribute to internal friction or dielectric relaxation.

Second, consider an oxygen vacancy neighboring a Ca^{2+} ion at $(0, 0, 0)$ and constrained by electrostatic attraction to the eight nearest neighbor oxygen sites at $(\pm \frac{1}{4}, \pm \frac{1}{4}, \pm \frac{1}{4})$. Either homogeneous stress or electric field will cause a preferred distribution so that this oxygen vacancy will make no contribution to the frequency independent electrical conductivity but will contribute both to

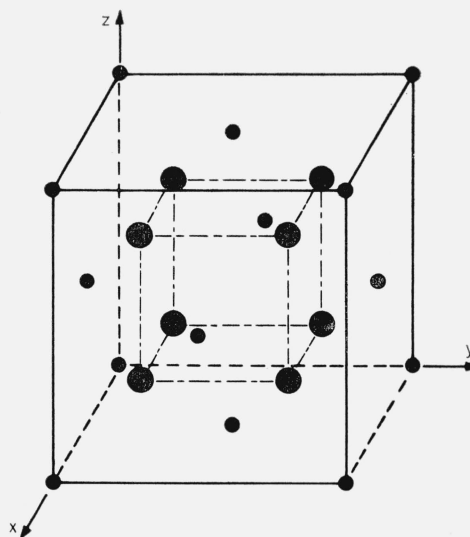


FIGURE 2. The fluorite structure.

internal friction and to dielectric relaxation. Each should be characterized by a single relaxation time. This type of defect is thought to be responsible for a dielectric relaxation process and internal friction peak observed in ThO_2 containing small amounts of CaO [10].

Third, consider two oxygen vacancies at $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ and $(\frac{1}{4}, \frac{1}{4}, -\frac{1}{4})$ neighboring two Ca^{2+} ions at $(0, 0, 0)$ and $(\frac{1}{2}, \frac{1}{2}, 0)$. Two defects of the second type should have electrostatic attraction of the dipole-dipole type tending to cause this defect to form. The oxygen vacancies in this defect will make no contribution to the frequency independent part of the electrical conductivity, to dielectric relaxation, or to internal friction.

It is tempting to interpret the as-sintered specimens as having defects of all three types with quenched in concentrations corresponding to thermal equilibrium at some temperature above 1000°C at which the Ca^{2+} ion motion was frozen out during furnace cooling. Subsequent long time heat treatment at 1000°C would cause slow diffusion of Ca^{2+} and produce a slow increase in the concentration of defects of the third type accompanied by a decrease in the concentrations of the first and second type. This would account for the observed decrease of measured properties for some concentrations with 1000°C heat treatment. We can hardly expect, however, to take such a model literally at concentrations so high that one cation in five is Ca^{2+} and the model cannot account for several features of the data. This model predicts a single relaxation time for the internal friction peak in contrast to the broad peak observed. The model gives no indication why some compositions (10% CaO for the internal friction peak and 14% CaO for the electrical conductivity) are unaffected by heat treatment at 1000°C . Nevertheless, the model is probably correct in attributing the 1000°C annealing effect to Ca^{2+} diffusion and the accompanying changes in the binding of oxygen vacancies. The model is also probably correct in assuming some defect similar to type three in which the oxygen vacancies are too tightly bound to move, but some features of defects of the first and second type might be combined. An oxygen vacancy making successive jumps in the same direction may encounter several sites with an equal number of Ca^{2+} neighbors before coming to one which has fewer Ca^{2+} neighbors and so requires some energy of dissociation.

The jump involving dissociation would be rate limiting for the electrical conductivity while motion back and forth along the equally favored sites would correspond to dielectric relaxation. The initially equally favored sites may become inequivalent under stress if permitted by symmetry [9] and so cause an internal friction peak. Various arrangements of Ca^{2+} ions can be visualized which fit these conditions so that the existence of a distribution of relaxation times is not surprising.

It does not appear fruitful to attempt more detailed interpretation. Measurements of orientation dependence of internal friction might be helpful if suitable single crystals become available, but progress in understanding probably depends primarily on diffraction studies of single crystals of various compositions.

6. References

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