Soft phonon modes and the monoclinic-tetragonal phase transformations in zirconia and hafnia

The oxides, zirconia (ZrO_2) and hafnia (HfO_2), together with their crystalline solid solutions undergo a reversible , crystallographic transformation at temperatures ranging from about 1100° C for pure zirconia (forward direction) to about 1600° C for pure hafnia [1]. Data on the transformation temperatures (reverse direction) of the oxides and their solid solutions taken from the work of Ruh and his colleagues are given in Fig. 2 [2]. Conventional crystallographic and kinetic studies have shown that the transformation between the high temperature tetragonal and low temperature monoclinic modifications in zirconia is martensitic, in both directions [1]. In view of the great chemical, physical and crystallographic similarity of these oxides it is likely that this is also the case of hafnia and the solid solutions. Furthermore, as zirconia and hafnia are isostructural (bond lengths, angles, ionic radii and atomic co-ordinates are identical to within one standard deviation), to a first approximation the oxides may be regarded as identical, varying only in cation mass [3]. In this note we propose that soft lattice modes may be implicated in the tetragonal–monoclinic transformation and on the basis of cation mass differences between the oxides, a simple microscopic argument is presented to explain the variation in transformation temperature across the solid solution.

Grain and Garvie suggested earlier that the conventional nucleation and growth mechanism of phase transformations was probably not applicable to the transformation in zirconia [4]. Rather, they suggested, a significant fraction of the ion population will always have amplitudes of vibration great enough to cause spontaneous formation of the new phase, when the temperature is in the transition region. This primitive notion is expressed elegantly in the form of soft phonon mode theories which have been used successfully in recent years to interpret the mechanisms of displacive phase transformations in general and martensitic transformations in particular [5, 6]. This approach may be used to qualitatively account for the transformations occurring in ZrO_2 and HfO_2.

Following Axe, we define a generalized displacive transformation by reference to the idea of an order parameter [5]; i.e. some quantity which is non-zero in one of the phases, but vanishes in the other. In this case the order parameter is the amplitude of the soft mode, Q. The oscillatory displacement of an atom from its equilibrium position can be represented by a sum of all the dynamic modes of vibration of the lattice, expressed in normal co-ordinates, as follows:

$$u_{l,k}(t) = \sum_{\mu=(q,j)} \boldsymbol{\epsilon}_{k\mu} Q_{\mu}(t) \exp iqR_l \qquad (1)$$

where u is the displacement of the kth atom in the lth unit cell, from some reference position, $\boldsymbol{\epsilon}$ is the polarization vector of the wave, Q the amplitude of the μth mode, and q the wave vector. A displacive phase transformation results when one of the vibrational normal modes becomes unstable; i.e. the phonon frequency, ω, tends towards zero and part of Equation 1 will describe a static displacement of the lattice as the soft mode effectively "condenses out" when the temperature, T, approaches the transformation temperature, T_c. In many cases the temperature dependence of the soft mode frequency may be described as

$$\omega_{\mu}^{2}(T) = \beta(T - T_c). \qquad (2)$$

Physically, the frequency of a particular mode is a measure of the restoring force for the displacement and if this restoring force (a subtle balance of harmonic and anharmonic contributions to the inter-atomic potential) tends towards zero, the displacements become free to incorporate themselves into the static structure.

There is some experimental evidence that special soft modes are involved in the zirconia transformations. Patil and Subbarao identified two distinct regions in the forward monoclinic–tetragonal transformation, namely a pre-transformation region (930 to 1100° C) and a co-existence region (1100 to 1220° C [7]. In the former range, these authors observed an anomalous increase in the X-ray intensities of the monoclinic reflections with increasing temperature which they attributed to movements of Zr atoms to become more in phase with each other. These shifts, along with anomalous changes in the lattice parameter in the pre-transformation region, were thought by Patil and Subbarao to be due to the existence of special vibrational modes. A recent esr study of Mn-doped monoclinic crystals and tetragonal ZrO_2 microcrystals shows that the origin of the transformation may be sought in an ionic interaction, which in a special case may lead to a softening of some modes [8].

It is now possible to estimate the transformation temperature for this series of oxides using the following assumptions:

(1) the oxides are identical in every respect except cation mass, as discussed previously;

(2) the soft mode frequency has a temperature dependence according to [2];

(3) to a first approximation, the soft mode frequency is inversely proportional to the square root of cation mass (in the case of pure oxides.)

The latter assumption requires some discussion. This is the case if one considers that the only vibrations to consider are the cations (the observations of Patil and Subbarao support this view) and that they behave as simple harmonic oscillators. On a more sophisticated level it is clear that the frequency is a complicated function of both the cation and anion masses, elastic constants and lattice parameters. However, as only differences in T_c are to be calculated, and as in (1) the oxides are presumed identical except in cation mass, only the contribution due to the cation mass need be isolated. In the limit of vanishingly small anion masses the contribution due to cation mass will be according to (3), and as the ratio of anion to cation mass is small for these oxides it is expected that, to first order at least, this will still be the case for non-zero anion masses [9]. There may be more merit to (3) than the crudeness of the assumption indicates at first glance. Recent work on the far infra-red spectroscopy of solids has shown that changing the isotopic mass changes the frequency of absorption bands by nearly the (mass) $^{-1/2}$ factor expected [10]. Furthermore, Table I lists infra-red absorption data for ZrO_2 and HfO_2 [11]. Two of the HfO_2 and ZrO_2 peaks are identical, whilst two are shifted in the direction expected for an increase in mass. Finally, some years ago Keyes showed that the longitudinal optical frequencies in Si, Ge and 111-V compounds were linked by a similar rule involving the reduced mass [12, 13].

TABLE I Infra-red absorption data for ZrO_2 and HfO_2 [11]

Oxide	Wave number (cm^{-1})			
	ν_1	ν_2	ν_3	ν_4
ZrO_2	425	525	685	760
HfO_2	425	535	685	770

Using these assumptions yields the following relation between transformation temperature and cation mass:

$$T_H - T_Z = \frac{\kappa}{\beta}(1/M_Z - 1/M_H) \qquad (3)$$

where T is the transformation temperature and the subscripts H, Z refer to hafnium or zirconium. κ is some effective force constant according to (3), and M is the cation mass.

To deal with the solid solutions of hafnia and zirconia, where cation masses are distributed randomly on the lattice, an effective cation mass is defined as follows:

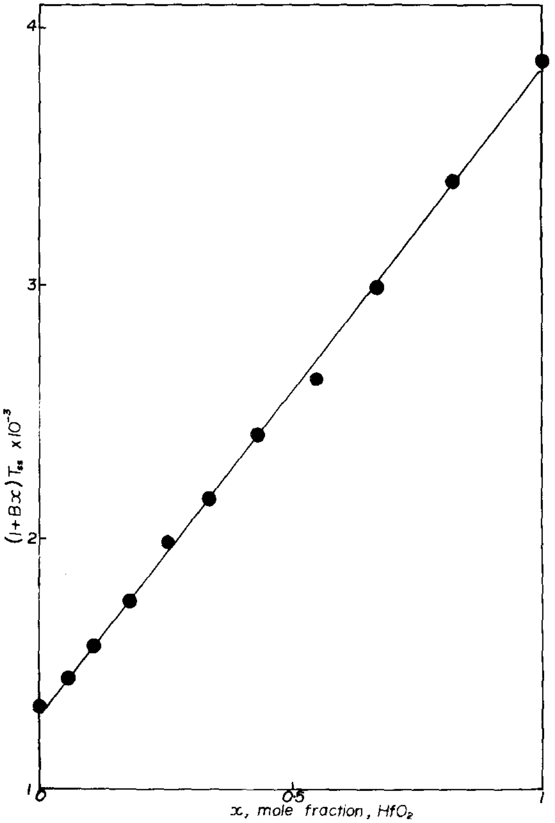

Figure 1 $(1 + Bx)T_{SS}$ plotted as a function of mole fraction hafnia, x.

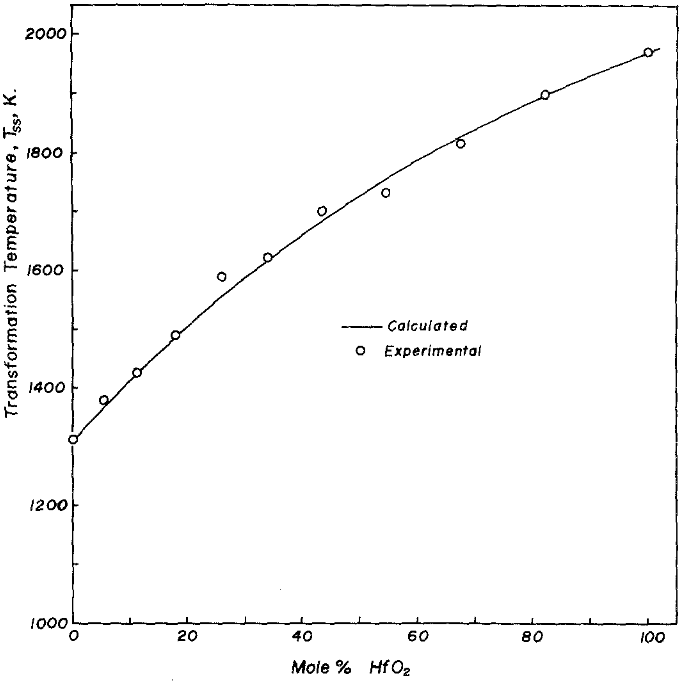

Figure 2 DTA data of Ruh *et al.* on the start of the tetragonal-monoclinic transformation [3].

$$M_{ss} = (1-x)M_Z + xM_H, \quad (4)$$

where x is the mole fraction of hafnia. Such a choice of effective mass will give the correct wave velocity in the continum limit. (Recall that velocity varies as the reciprocal root of the density.) Then the transformation temperatures of solid solutions, T_{ss}, will be given by

$$T_H - T_{ss} = \frac{\kappa}{\beta}(1/M_{ss} - 1/M_H). \quad (5)$$

This relation may be tested in the following way. Simplifying Equation 5 yields the expression:

$$(1+Bx)T_{ss} = (BT_H + A)x + (T_H - A) \quad (6)$$

$$\text{where } B = \frac{M_H}{M_Z} - 1 \text{ and } A = \frac{\kappa}{\beta}\left(\frac{1}{M_H} - \frac{1}{M_Z}\right).$$

Fig. 1 shows a graph of $(1+Bx)T_{ss}$ as a function of mole fraction of hafnia (x). The predicted linear dependence is clearly evident. The value of the constant, κ/β, derived from this plot is self-consistant and equal to $1.25 \pm 0.04 \times 10^5$. This constant may be used to calculate the transformation temperatures of the solid solutions as a function of hafnia content. Calculated transformation temperatures are shown as a solid line in Fig. 2. The good agreement between the calculated and experimental values of T_{ss} allows some credence to be placed in the notion that the phase transformations of zirconia and hafnia are manifestations of soft lattice modes.

We suggest that detailed experimental and theoretical soft lattice mode studies of these interesting oxides should be rewarding.

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S. BURKE
R. GARVIE
Division of Tribophysics,
CSIRO,
PO Box 4331, Melbourne,
Victoria, Australia

Effect of post sinter cooling rates on manganese zinc ferrites

It is well known that the important technical and commercial parameters of soft ferrites are the permeability, the quality factor, hysteresis loss, temperature factor and disaccommodation factor. To satisfy requirements all these parameters must simultaneously be within certain well defined limits. Unfortunately due to the inter-dependence of these parameters and their conflicting requirements during powder preparation and heat-treatment, it is extremely difficult to obtain a sintered ferrite with all five components fully maximized. In practice some degree of optimization must occur e.g. a high quality factor (μQ) requires that MnZn ferrites be sintered under an atmosphere giving approximately 96% stoichiometry [1], while to obtain a low temperature factor (TF) a somewhat higher oxygen content is necessary in the sintering atmosphere [2] resulting in a lower stoichiometry in the sintered ferrite [3]. This in turn can produce quite high values for the disaccommodation. The temperature factor and disaccommodation factor (DF) have sometimes been regarded as secondary factors and many workers have concentrated on the other three parameters. Unfortunately, once these parameters have been brought into line, there is no guarantee that the TF and DF will be within limits. The only existing method of controlling the latter is to alter either the firing conditions, or the basic composition of the powder and, as outlined earlier, this could invalidate the earlier maximization of the primary parameters. Quite clearly any technique which enables the separate control of any of these parameters is particularly welcome.

A number of workers [4–7] have shown that in MnZn ferrites the DF depends on the Fe^{2+} ion concentration and the vacancy concentration. The TF, however, has been shown to depend on Fe^{2+} content and also on the degree of cation order–disorder in the final sintered samples [8]. Thus it may be possible to vary one of these parameters by varying the degree of cation order–disorder. A MnZn ferrite having an initial chemical composition of 53.00 mol. % Fe$_2$O$_3$, 30.10 mol. % MnO$_x$, 16.30 mol. % ZnO, 0.60 mol. % TiO$_2$ was prepared by standard ceramic processing methods and toroidal specimens were dry pressed at 155 x 10^6 Pa (10.05 tons in.$^{-2}$). Two sintering schedules were carried out by means of a programmable furnace. Initially the specimens were heated from room temperature at a rate of 100° C^{-1} under an atmosphere of air and then sintered for 5 h at 1255° C under an atmosphere of 95% N$_2$ and 5% O$_2$. As the furnace cooled the oxygen level was continuously decreased according to the equation log P (O$_2$) = KT^{-1}. At a temperature of 960° C the oxygen content of the furnace atmosphere was less than 0.001% and the remainder of the cooling schedule took place under pure nitrogen. This "phase rule" cooling maintains the Fe^{2+} level at the value dictated by the oxygen/nitrogen ratio and the temperature in the sintering stage [9, 10]. In the first schedule the toroids were cooled at 300° C h^{-1}, while in the second the cooling rate was 150° C h^{-1}. In both cases the oxygen content of the atmosphere was monitored using a high accuracy semiconductor probe [11]. The inductance of a toroidal specimen was measured with a Boonton Inductance Bridge at a frequency of 100 kHz and a field of 0.5 mT. In the case of the DF, measurements were made 1 min and 10 min after demagnetization. In all cases the results quoted are the mean of those obtained on 10 specimens.