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The Elastic Constants and Interatomic Binding in Yttria-Stabilised Zirconia

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Zirconia (ZrO_2) can be forced into a cubic fluorite structure by the addition of more than 7 mol % yttria (Y_2O_3). The elastic stiffness constants of cubic zirconia single crystals containing 8 and 12 mol % yttria have been determined between 77 and 300° K by an ultrasonic pulse echo technique. Elastic constants are almost temperature-independent and at 77° K are for the 8 and 12 mol % respectively: $C_{11} = 2.04$, $C_{12} = 0.87$, $C_{44} = 1.58$; $C_{11} = 2.23$, $C_{12} = 0.973$, $C_{44} = 1.54$ (units: 10^{12} dynes cm^{-2}). Compressibilities and elastic compliances are also presented. The data provide a basis for discussion of crystalline stability and the nature of the interatomic forces. The decreasing cubic lattice stability as the yttria content is reduced is demonstrated quantitatively. An ionic model closely characterises the binding forces. The repulsive energy is about 12% of the Madelung attractive energy. Debye temperatures calculated from the elastic constant data extrapolated to 0° K are 595 and 604° K for the 8 and 12 mol % respectively.

1. Introduction

Zirconium oxide, ZrO_2, is of great importance as a refractory. However, it is polymorphic [1]. The normal monoclinic modification (space group $P2_1/C$) [2] transforms at about 1000° C into a tetragonal form; a considerable volume contraction of about 9% ensues: zirconia itself cannot be fired into a strong, stable, sintered ceramic. But when certain cubic oxides, including yttria (Y_2O_3), form solid solutions with zirconia, a stabilised cubic structure with a fluorite type of lattice is assumed. Such materials can be fired; no transformations at elevated temperatures take place in the stabilised alloys. Valency requirements indicate that oxygen vacancies are now present, due to the replacement of tetravalent Zr^{4+} ions by trivalent Y^{3+} ions; in consequence, electrical conductivity is enhanced. Zirconia-yttria solid solutions are of technical importance as refractory conductors, especially in connection with high temperature electrodes in magneto-hydrodynamic generators and for fuel cell applications. One unfortunate result of high temperature current passage through the stabilised zirconia is a marked tendency for fragmentation of both sintered, polycrystalline electrodes and single crystal specimens. Studies of the way in which electrical currents alter the bulk properties of single crystals are in progress in an attempt to solve this problem. To back up this work, detailed knowledge of the mechanical properties and the nature of the bonding is required.

The elastic constants of single crystals furnish basic mechanical and lattice thermodynamic information. The present concern is to report elastic constant measurements, made using the ultrasonic pulse-echo technique, for yttria-stabilised zirconia. Data are used as a basis for discussion of the stability of the crystals and the nature of the interatomic forces in them.

2. Experimental Details

Two compositions of the solid solutions of yttria with zirconia have been studied, one of 8 mol % Y_2O_3 and the other 12 mol % Y_2O_3, the former because it is close to the stability edge (~ 7 mol % Y_2O_3) [3] of the cubic phase. Single crystals were grown by electrofusion from pure powdered zirconia and yttria. Samples were cut from the crystallised melts and oriented from back-reflection Laue photographs. X-ray examinations showed high crystal perfection, there being no evidence for mosaic imperfections, and that the material was in the cubic phase. The chemical purity was high. Optical spectrographic analysis showed that the only impurities, present at trace level, were silicon, hafnium, magnesium and tin. This result was substantiated by the absence of observable electron spin resonance spectra (sought at 9 GHz and 4.2° K), which also indicated freedom from other paramagnetic impurities.

Crystals were aligned to within 1° of the prerequisite [1 1 0] crystallographic axis, then two (1 1 0) faces were cut by a diamond wheel and lapped flat and parallel to each other to better than 0.001 cm to avoid ultrasonic diffraction and phase sensitivity effects. Ultrasonic wave transit times along the crystal were measured to an accuracy of ± 1% by the single-ended, pulse-echo technique at carrier frequencies between 10 MHz and 50 MHz. Velocities were independent of frequency over this range. Identical results, within experimental error, were obtained from different crystals of the same composition. Resonant, gold-plated quartz transducers, X-cut for longitudinal and Y-cut for shear waves, were used to excite the ultrasound. For Y-cut transducers, the bonding material used (10^6 cs silicone fluid) was unsatisfactory above 200° K, limiting the range of experiment. However, the velocities were not very temperature-dependent. Further experimental details may be found elsewhere [4].

As the strains induced by ultrasonic waves are only of the order of 10^{-7}, Hooke's law is valid and each stress component T_{ij} can be considered as a linear homogeneous function of the strain components ϵ_{kl}:

$$T_{ij} = C_{ijkl}\,\epsilon_{kl}\,(i, j, k, l = 1, 2, 3)\,, \qquad (1)$$

where the connecting components are the elastic stiffnesses or moduli C_{ijkl}. The usual matrix notation giving these constants as C_{ij} is achieved by replacing 11 by 1, 22 by 2, 33 by 3, 23 by 4, 13 by 5 and 12 by 6. Symmetry in cubic crystals reduces the 6 × 6 array for C_{ijkl} in equation 1 so that only three independent elastic constants remain.

In the present work, velocities v, of longitudinal and slow and fast shear waves propagated along the [1 1 0] direction were measured. In this case

$$\begin{aligned}&\rho v_1^2 = \rho v^2{}_{\text{long}} = (C_{11} + C_{12} + 2C_{44})/2 = C_n\,;\\ &q \text{ along } [1\,1\,0];\\ &\rho v_2^2 = \rho v^2{}_{\text{shear (1)}} = C_{44};\ q \text{ along } [0\,0\,1];\\ &\rho v_3^2 = \rho v^2{}_{\text{shear (2)}} = (C_{11} - C_{12})/2 = C'\,;\\ &q \text{ along } [1\,\bar{1}\,0]\,, \end{aligned} \qquad (2)$$

where q is the polarisation vector and ρ is the sample density. All three elastic constants C_{11}, C_{12} and C_{44} are obtainable from this set of measurements. However, the three elastic constants C_n, C_{44} and C' can also be used to define the three independent stiffnesses and have direct physical significance. For the [1 1 0] direction a normal stress T_n, as applied through the longitudinal sound wave inserted onto the (1 1 0) face, produces a strain S_n parallel to [1 1 0] and T_n/S_n is C_n. For shear waves propagating down and with atomic motion perpendicular to the [1 1 0]direction, two physical situations occur, as shown by equation 2; first, for atoms vibrating in the [0 0 1] direction, the ratio of the shear stress to shear strain is C_{44}, second, for tractions parallel to $[1\,\bar{1}\,0]$ the ratio is $(C_{11} - C_{12})/2$.

Ultrasonic wave velocities at 77 and 196° K are given in table I, together with sample densities (measured by Archimedes' principle) and lattice spacings (obtained from Debye-Scherrer powder photographs taken with Cu Kα radiation applying the Nelson-Riley extrapolation formula).

3. Results and Discussion

The linear combinations of the elastic constants C_n, C_{44} and C' derived from the velocity data, using equation 2, are given as a function of temperature in fig. 1. Calculated values of C_{11}, C_{12} and C_{44} at 77 and 196° K are presented in table II. Another simple deformation is a pure volume dilation without shear, expressed as the bulk modulus K, the measure of stiffness to volume dilation.

$$K = -V\frac{\mathrm{d}P}{\mathrm{d}V} = \frac{C_{11} + 2C_{12}}{3}\,. \qquad (3)$$

The bulk modulus data are also given in table II. In addition to the stiffnesses C_{ijkl}, tabulations usually include the elastic compliances defined by

$$\epsilon_{ij} = S_{ijkl}\,T_{ij}\,. \qquad (4)$$

S_{ijkl} is the reciprocal tensor of C_{ijkl}. The compliances of cubic crystals are given by

TABLE I Velocities of ultrasonic waves propagating down the [110] axis in zirconia-yttria solid solutions, the measured density and the lattice spacing

	Ultrasonic wave velocity cm/sec × 10^5			Density at room temperature gm cm^{-3}	Lattice spacing at room temperature Å
	Longitudinal	Shear			
		Fast	Slow		
$(ZrO_2)_{0.92}(Y_2O_3)_{0.08}$				6.036 ± 0.001	5.1276 ± 0.0001
77° K	7.09	5.12	3.11		
196° K	7.09	5.12	3.11		
$(ZrO_2)_{0.88}(Y_2O_3)_{0.12}$				5.894 ± 0.001	5.1401 ± 0.0001
77° K	7.30	5.78	3.26		
196° K	7.30	5.78	3.24		

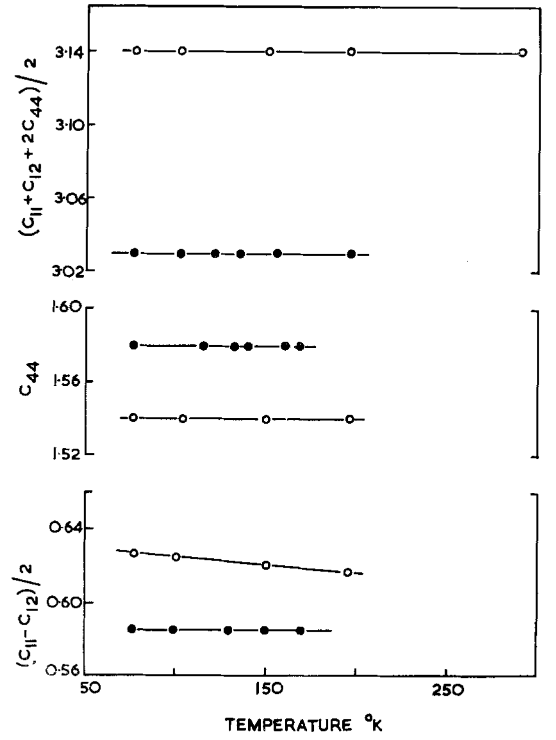

Figure 1 The temperature-dependence of the measured linear combinations of the elastic constants of $(ZrO_2)_{0.88}(Y_2O_3)_{0.12}$ (open circles) and $(ZrO_2)_{0.92}(Y_2O_3)_{0.08}$ (closed circles). The units are 10^{12} dynes cm^{-2}.

$$S_{11} = \frac{-(C_{11}+C_{12})}{(C_{11}+2C_{12})(C_{12}-C_{11})} ;$$

$$S_{12} = \frac{C_{12}}{(C_{11}+2C_{12})(C_{12}-C_{11})} ;$$

$$S_{44} = \frac{1}{C_{44}} . \quad (5)$$

Calculated values of S_{ij} are collected in table II.

The three independent compliances for cubic crystals can also be defined as the two reciprocal shear moduli S_{44} and $2(S_{11} - S_{12})$ and the compressibility $3(S_{11} + 2S_{12})$.

The elastic stiffnesses and compliances for the two compositions of crystals are close: the mechanical properties are similar. Some insight can be gained into the degree of crystal stability: for a crystal lattice to be stable, certain relationships must hold between the elastic constants so that the energy density is positive [5]. Both $\frac{1}{2}(C_{11} - C_{12})$ and $(C_{11} + 2C_{12})/3$ must be positive in cubic crystals. The greatest difference ($\sim 8\%$) between the elastic constants of $(ZrO_2)_{0.88}(Y_2O_3)_{0.12}$ and $(ZrO_2)_{0.92}(Y_2O_3)_{0.08}$, lies in $(C_{11} - C_{12})/2$. And this is significant. A negative value for $(C_{11} - C_{12})/2$ would lead to a spontaneous collapse of the lattice; the composition at which $(C_{11} - C_{12})/2$ becomes zero, represents the absolute stability limit of the fluorite phase. The decrease of 8% in $(C_{11} - C_{12})/2$ found between $(ZrO_2)_{0.88}(Y_2O_3)_{0.12}$ and $(ZrO_2)_{0.92}(Y_2O_3)_{0.08}$ indicates a reduction in lattice stability.

The absence of a substantial temperature-dependence of $(C_{11} - C_{12})/2$ for these crystals is consistent with the vertical phase boundary line at about 7 mol % Y_2O_3 in ZrO_2 in the phase diagram [3]: if the composition at which the phase change occurs did vary with temperature then $(C_{11} - C_{12})/2$ in compositions near the limit would be temperature-sensitive. A further criterion for stability is that $C_{11}^2 - C_{12}^2 > 0$. The parameter $(C_{11}^2 - C_{12}^2)$ decreases by 18% from the 12 mol % to the 8 mol % solution, again confirming the decreasing lattice stability as the yttria content is reduced.

For an isotropic substance $(C_{11} - C_{12})$ equals $2C_{44}$. The extent to which this relation holds good is an indication of the isotropy of a cubic

TABLE II The elastic stiffness and compliance constants of zirconia-yttria solid solutions

Elastic constants 10^{12} dynes cm^{-2}	$(ZrO_2)_{0.92}(Y_2O_3)_{0.08}$ 77° K	$(ZrO_2)_{0.92}(Y_2O_3)_{0.08}$ 196° K	$(ZrO_2)_{0.88}(Y_2O_3)_{0.12}$ 77° K	$(ZrO_2)_{0.88}(Y_2O_3)_{0.12}$ 196° K
$(C_{11} + C_{12} + 2C_{44})/2$	3.03	3.03	3.14	3.14
$(C_{11} - C_{12})/2$	0.585	0.585	0.627	0.617
C_{44}	1.58	1.58	1.54	1.54
C_{11}	2.04	2.04	2.23	2.22
C_{12}	0.870	0.870	0.973	0.983
$\frac{(C_{11} + 2C_{12})}{3}$ bulk modulus	1.26	1.26	1.39	1.40
$\frac{2C_{44}}{(C_{11} - C_{12})}$ anisotropy ratio	2.70	2.70	2.46	2.50
$\frac{C_{12}}{C_{44}}$ Cauchy relation	0.55	0.55	0.63	0.64
$C_{11}^2 - C_{12}^2$	3.305	3.305	4.032	4.052
Elastic compliances 10^{-12} cm^2 dyne^{-1}				
S_{11}	0.658	0.658	0.610	0.619
S_{12}	− 0.197	− 0.197	− 0.185	− 0.190
S_{44}	0.633	0.633	0.649	0.649

crystal. Values of $2C_{44}/(C_{11} - C_{12})$, quoted in table II, for the alloys, are not close to unity: a shear on a $\{100\}$ cube face is resisted rather more than one on a diagonal $\{110\}$ face. If the interatomic lattice forces are central, so that every atom is sited at an inversion point, the Cauchy relation ($C_{12} = C_{44}$) should hold. In the present case the experimental value of C_{12}/C_{44} is ~ 0.6. This is close to that found in MgO but different from the ratios found in the alkali halides in which the Cauchy relations hold quite well. In an alloy consisting of three atomic species and containing vacancies, the central forces model will not hold rigidly.

Knowledge of the bulk modulus can be used to develop an understanding of the type of binding between the atoms in the crystals. One approach is to assume ionic binding in spite of the non-central forces. Then we can write for the potential energy per unit cell

$$\Phi_0 = \frac{-\alpha^2 e^2 \mu A}{r} + \frac{B}{r^n}, \tag{6}$$

where α is the largest common factor in the valencies of the ions (2 in the present case), μ is the number of molecules per unit cell, A is the Madelung constant and n is the repulsive exponent, which can be determined from the bulk modulus. The constant B in the repulsive term can be found in the usual way from the condition that $d\Phi/dr = 0$, when r takes the equilibrium distance R_0. Then

$$\Phi_0 = \frac{-\alpha^2 e^2 \mu A}{R_0}\left(1 - \frac{1}{n}\right) = \Phi_0^{(1)} + \Phi_0^{(n)} \cdot \tag{7}$$

Now writing the lattice energy per mole U_0 as $(-N\Phi_0/\mu)$ we have

$$U_0 = \frac{\alpha^2 e^2 N A}{R_0}\left(1 - \frac{1}{n}\right) \cdot \tag{8}$$

The effect of the presence of oxygen vacancies in the crystals can be taken into account to a first approximation by choosing for R_0 the cube root δ_0 of the molecular volume. The corresponding Madelung constant is then given by

$$\frac{A}{R_0} = \frac{A_{\delta 0}}{\delta_0} \cdot \tag{9}$$

Then substituting 9 into 8 and introducing numerical values for Avogadro's number N and the electronic charge e, we have

$$U_0 = 280.6\, \alpha^2 (\rho/M)^{1/3} A_{\delta 0}\left(1 - \frac{1}{n}\right), \tag{10}$$

where M is the gram molecular weight. $A_{\delta 0}$ for the fluorite lattice is 7.33058 [6, 7]. Calculated values for the Madelung energy, $280.6\, \alpha^2 (\rho/M)^{1/3} A_{\delta 0}$, are collected in table III. The attractive energy in the solid solutions is rather greater than that of pure zirconia.

TABLE III Thermodynamic parameters of the zirconia-yttria solid solutions

	$\frac{\rho}{M}$	Madelung attractive energy U_M	Repulsive energy U_n	Total binding energy $U_0 = U_M + U_n$	Debye temperature θ_0
ZrO_2	0.0430	− 2889	—	—	—
$(ZrO_2)_{0.88}\,(Y_2O_3)_{0.12}$	0.0435	− 2892	+ 321	− 2571	604° K
$(ZrO_2)_{0.92}\,(Y_2O_3)_{0.08}$	0.0459	− 2945	+ 348	− 2597	595° K
Energy units: kcal/mol					

The relationship between the bulk modulus

$$K = -\frac{1}{V}\frac{\mathrm{d}P}{\mathrm{d}V} = -V\frac{\partial^2 U}{\partial V^2} = -V\left(\frac{\partial^2 U}{\partial x^2}\right)\left(\frac{\mathrm{d}x}{\mathrm{d}V}\right)^2 \tag{11}$$

and the repulsive exponent can be obtained by differentiating the potential energy expression twice with respect to internuclear distance and substituting into 11. For the fluorite lattice the nearest neighbour distance r_0 is $\surd(3\ a_0/4)$ and the volume V of a gram molecule is $16/(3\surd 3)\ Nr_0{}^3$. The exponent n can be shown to be

$$n = 1 + \frac{9\ \delta_0{}^4\ K}{\alpha^2 e^2 A_{\delta 0}} = 1 + \frac{9\ a_0{}^4\ K}{\alpha^2 e^2 A_{a_0}}\ . \tag{12}$$

Taking the measured lattice spacing (see table I), the appropriate Madelung constant ($A_{a_0} = 11.63$ for the fluorite lattice) [6, 7], and the measured bulk modulus, n is calculated as 9.1 for $(ZrO_2)_{0.88}$ $(Y_2O_3)_{0.12}$ and 8.5 for $(ZrO_2)_{0.92}$ $(Y_2O_3)_{0.08}$. For many ionic crystals, n is approximately equal to 9: the binding in these solid solutions appears to be largely ionic. By putting the values of n into equation 10, the total lattice energy per mole can be calculated (see table III). Repulsive energies are about 12% of the attractive energies. From the values of U_0, many thermochemical parameters become available.

One useful parameter, the Debye temperature θ_0, may be calculated readily from elastic constant data. Here the method of de Launay, based on the Born-von Karman model, has been used [8].
Then

$$\theta_0 = \frac{h}{k}\left(\frac{9N}{4\pi V}\right)^{1/3}\left(\frac{C_{44}}{\rho}\right)^{1/2}\left[\frac{9}{18+\surd 3}f\right]^{1/3},$$

where values of f are tabulated in [6] in terms of the parameters

$$s = \frac{C_{11} - C_{44}}{C_{12} + C_{44}} \text{ and } t = \frac{C_{12} - C_{44}}{C_{44}}\ .$$

Elastic constant data have been extrapolated to 0° K. The values of θ_0 derived in this way are 604° K for $(ZrO_2)_{0.88}$ $(Y_2O_3)_{0.12}$ and 595° K for $(ZrO_2)_{0.92}$ $(Y_2O_3)_{0.08}$. Knowledge of the Debye temperature is important in the interpretation of spin-lattice relaxation behaviour [9] particularly in assessing whether direct or Raman processes should dominate the relaxation at a given temperature and in determining the influence of defect sites. In the studies of the effects of current passage in yttria-stabilised zirconia single crystals, it has been shown that, in electrically reduced samples, electron spin resonance spectra are observable at 77 and 4.2° K (9 GHz); these results will be discussed more fully elsewhere.

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