

Thermal Properties of Stabilized Zirconia at Low Temperatures

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Abstract

The linear thermal expansion coefficient α from 2 to 100 K and heat capacity per gram c_p from 0.3 to 30 K are reported for fully-stabilized zirconia containing a nominal 16 wt.% (9 mol.%) of yttria. The heat capacity below 7 K has been analysed into a linear (tunnelling?) term, a Schottky term centred at 1.2 K, a Debye term ($\Theta_0 = 540$ K), and a small T^5 contribution. The expansion coefficient is roughly proportional to T^3 from 5 to 20 K and gives a limiting lattice Grüneisen parameter $\gamma_0 \approx 5$, which agrees with that calculated from elastic data.

1. Introduction

The cubic or fluorite form of ZrO_2 may be stabilized by the addition of calcia, magnesia, yttria etc. The fully stabilized and partially stabilized zirconias (PSZ) are of considerable technical importance as high-strength ceramics (Garvie 1984) and as oxygen sensors (Subbarao 1980). They have also been shown to have some glass-like properties at liquid helium temperatures: the heat capacity C_p and thermal conductivity λ show temperature dependences that are characteristic of vitreous materials (Lawless 1980*a*, 1980*b*; Ackerman *et al.* 1981) and are usually attributed to tunnelling states. Recently Ackerman *et al.* (1984) measured the linear expansion coefficient α from about 0.6 to 6 K for $\text{ZrO}_2 + 16 \text{ mol.}\% \text{ Y}_2\text{O}_3$ using a sensitive SQUID detector. They analysed their data at the lowest temperatures to give a linear term $\alpha_T = 0.95 \times 10^{-10} T \text{ K}^{-1}$ from which an associated Grüneisen parameter γ_T is calculated to be +7. This is in contrast to the very large negative values of γ observed in some vitreous solids, notably vitreous silica, and ascribed to the strain-sensitive nature of the tunnelling processes (Barron *et al.* 1980).

We have now measured the linear expansion of $\text{ZrO}_2 + 9 \text{ mol.}\% \text{ Y}_2\text{O}_3$ over the range 2–100 K, and can compare $\gamma(T)$ as T approaches zero with the limiting value for the acoustic modes of lattice vibration calculated from pressure derivatives of the elastic moduli (Hailing and Saunders 1982). We have also measured the specific heat capacity c_p from 0.3 to 30 K for the same material and find a Schottky bump near 1.2 K as well as T , T^3 and T^5 terms.

2. Measurements

The samples were made in the form of cylindrical rods about 60 mm long by 15 mm diameter.* Hafnia-free zirconia was first calcined for 10 hours at 1400°C, then milled and mixed with 16 wt.% Y₂O₃, pressed with some added water to 0.2 GPa (2 kbar), and fired to 1800°C for four hours and refired to 1900°C for four hours. The measured density ρ was 5.2 g cm⁻³.

A cylinder 51 mm long was cut, lapped and silvered (by evaporation) before being mounted in the capacitance dilatometer (White and Collins 1972) where thermal expansions were measured between 2 and 100 K, and 273 and 293 K. Values of α were obtained with probable errors of $\pm 0.01 \times 10^{-8}$ K⁻¹ at 4 K, increasing to $\pm 0.5 \times 10^{-8}$ K⁻¹ at 30 K and $\pm 5 \times 10^{-8}$ K⁻¹ above 50 K. The heat capacity of the same cylinder was measured in an adiabatic calorimeter (Collocott 1983) between 0.3 and 30 K with an inaccuracy of less than 1%.

The sample was later analysed by the Australian Atomic Energy Commission Research Establishment and showed the following impurities by weight:

Hf 2 ppm, Mn 5 ppm, Co 60 ppm,
Fe 300 ppm, Cr 30 ppm, Ni 30 ppm.

Table 1. Smoothed values of the linear coefficient of expansion α , heat capacity per gram c_p and $\gamma = 3\alpha B_s/\rho c_p$
Here $B_s = 192$ GPa and $\rho = 5.2$ g cm⁻³ are used

<i>T</i> (K)	10 ⁸ α (K ⁻¹)	c_p (mJ g ⁻¹ K ⁻¹)	γ	<i>T</i> (K)	10 ⁸ α (K ⁻¹)	c_p (mJ g ⁻¹ K ⁻¹)	γ
3	0.06	0.021	3	24	23.0	7.9	3.2
4	0.12	0.031	4.2	26	28.1	9.7	3.2
5	0.18	0.052	3.8	28	33.7	11.6	3.2
6	0.31	0.087	3.9	30	39.7	13.4	3.2
7	0.52	0.140	4.1	35	56		
8	0.80	0.216	4.1	40	74		
10	1.65	0.460	3.9	55	138		
12	2.99	0.864	3.8	65	183		
14	4.89	1.40	3.8	75	224		
16	7.36	2.23	3.6	85	272		
18	10.4	3.23	3.5	95	307		
20	14.0	4.5	3.4	283	778	490	1.7
22	18.2	6.0	3.3				

3. Results

Thermal Expansion

Smoothed values of the linear coefficient α are shown in Table 1. Raw data below 30 K are plotted in Fig. 1 in the form of α/T^3 against T , together with an approximate curve taken from Fig. 10 of Ackerman *et al.* (1984). Our error bars are large below 5 K but the values are not inconsistent with the Ackerman data. The

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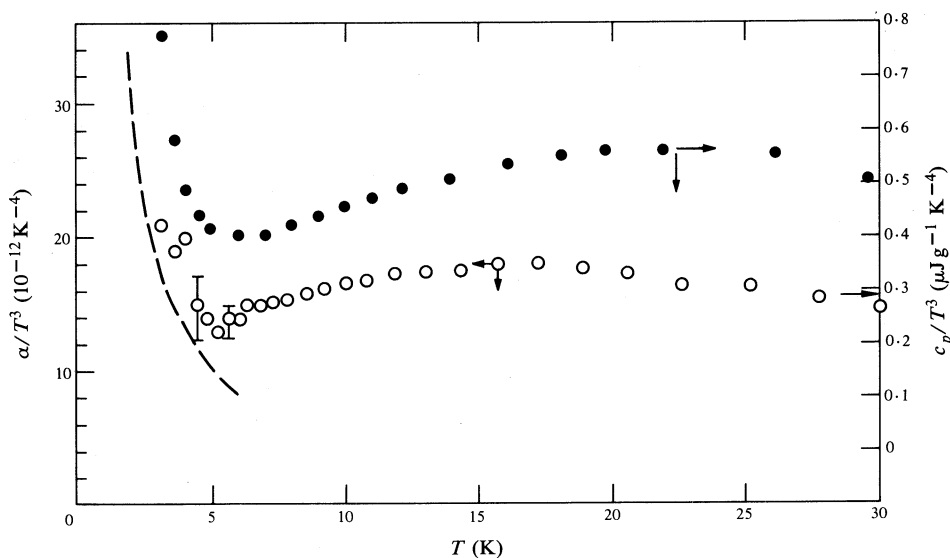


Fig. 1. Values of α/T^3 (open circles) and c_p/T^3 (filled circles) for stabilized zirconia below 30 K. For c_p/T^3 only a few representative points are shown. The dashed curve is α/T^3 from Ackerman *et al.* (1984), while the arrow shows the Debye contribution to c_p/T^3 for $\theta_0 = 540$ K.

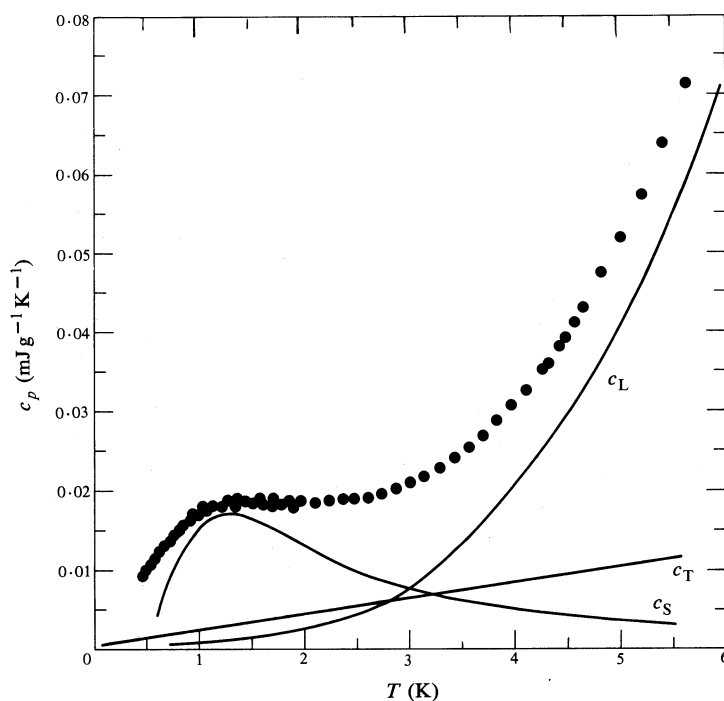


Fig. 2. Heat capacity of stabilized zirconia below 6 K. Filled circles are the observed values, and curves are analysed components as follows: $c_L = c_{\text{Debye}} + 1.4 \times 10^{-3} T^5 \mu\text{J g}^{-1} \text{K}^{-1}$ is the lattice component for a Debye temperature of 540 K; $c_T = 1.9 T \mu\text{J g}^{-1} \text{K}^{-1}$; and c_S is the Schottky term from the best fit to equation (1).

limiting value of the T^3 term is $\approx 13 \times 10^{-12} T^3 \text{ K}^{-1}$. There do not appear to be other data below room temperature for stabilized zirconia. Earlier expansion data at high temperatures (see e.g. Nielsen and Leipold 1964) suggest that $\alpha \approx 8 \times 10^{-6} \text{ K}^{-1}$ at room temperature in agreement with our value of $7.8 \times 10^{-6} \text{ K}^{-1}$.

Heat Capacity

Raw data are plotted in Figs 1 and 2. Plots of c_p/T against T^2 indicate an anomaly of the Schottky type that is important below about 3 K. We have fitted the experimental values below 7 K, after subtracting a Debye (lattice) T^3 term for which $\Theta_0 = 540 \text{ K}$ from elastic data (Pace *et al.* 1969; Farley *et al.* 1972; Chisty *et al.* 1977), to a Schottky term plus a linear term and a T^5 term using a nonlinear least-squares procedure, i.e.

$$c_p = c_{\text{Debye}} + aT + bT^5 + dx^2e^{-x}(1+e^{-x})^{-2}, \quad (1)$$

with

$$x = \delta/T.$$

We find for the level-splitting parameter $\delta = 2.95 \pm 0.003 \text{ K}$, with $a = 1.87 \pm 0.1 \mu\text{J g}^{-1} \text{ K}^{-2}$ ($\approx 10 \mu\text{J cm}^{-3} \text{ K}^{-2}$ for $\rho = 5.2 \text{ g cm}^{-3}$), $b = (1.43 \pm 0.1) \times 10^{-3} \mu\text{J g}^{-1} \text{ K}^{-6}$ and $d = 38.4 \pm 9 \mu\text{J g}^{-1} \text{ K}^{-1}$. The uncertainties quoted are standard errors in the fit and do not take account of estimated experimental errors.

Above 7 K the heat capacity shows the usual increasing departure from a simple Debye continuum limit (see Fig. 2). This arises from dispersion in the lattice spectrum, but it cannot be analysed quantitatively without knowledge of the lattice density-of-states. This has not been measured.

Grüneisen Parameter

This is defined by $\gamma = \beta B_s V/C_p = \beta B_T V/C_V = \beta B_s/\rho c_p$, where the volume coefficient $\beta = 3\alpha$ for cubic solids, B_s (B_T) is the adiabatic (isothermal) value of the bulk modulus, and $C/V = \rho c_p$ is the heat capacity per unit volume, i.e. c_p is the heat capacity per unit mass. Note that γ is a weighted mean of all the individual values $\gamma_i = -(\partial \ln \omega_i / \partial \ln V)_T$ appropriate to different modes ω_i of the crystal lattice and to other energy contributing processes, whether they be magnetic interactions or tunnelling. The thermal expansion data are not sufficiently accurate to allow for quantitative analysis into possible lattice, linear and Schottky terms below 7 K, and the corresponding Grüneisen parameters cannot be estimated.

In order to calculate the γ values in Table 1 we have used $B_s = 192 \text{ GPa}$ (1.92 Mbar) which is taken from elastic data of Farley *et al.* (1972) for single-crystal 8 and 12 mol.% yttria samples. Other elastic measurements by Chisty *et al.* (1977) on $\text{ZrO}_2 + 8, 10, 12, 16 \text{ mol.}\% \text{ Y}_2\text{O}_3$ are in substantial agreement with Farley *et al.* [Note that Ackerman *et al.* (1984) quoted $B = 290 \text{ GPa}$ in their tabulation of data.]

Farley *et al.* gave a density of $\rho = 6.0 \text{ g cm}^{-3}$ for their crystals. In the present calculations of γ for sintered material we have used the measured density of 5.2 g cm^{-3} and the single-crystal value for the bulk modulus. Only Young's modulus has been measured for this sintered material. The value of 207 GPa (R. C. Garvie, personal communication) lies within the Voigt (209 GPa) and Reuss (199 GPa) limits calculated from single-crystal elastic moduli and gives support to our use of the single-crystal bulk modulus when calculating γ .

4. Discussion

Expansion Coefficient and Grüneisen Parameter

Above 20 or 30 K, $\alpha(T)$ of stabilized zirconia appears to behave much like that of thoria, ThO_2 (see White and Sheard 1974), which is also a ceramic oxide with fluorite structure. For both of them γ at room temperature is in the vicinity of 2. However, at low temperatures $\gamma(T)$ for the zirconia rises significantly, indicating that γ_i for the dominant acoustic modes in the long-wave limit must be large. Hailing and Saunders (1982) have measured the pressure dependence of the elastic stiffnesses c_i from which they calculate corresponding values of $\gamma_i = -\frac{1}{6} + B \partial \ln c_i / 2 \partial P$, which all lie in the range 4–6. From these measurements we calculate a low temperature limiting value of $\gamma_0(\text{elastic}) = 5.2$. The thermal value of γ_0 obtained from the approximate values of the T^3 terms in C_p and α is 5.0 ± 0.5 , in good agreement with the elastic value. This value is surprisingly high compared with other insulating crystals including alkali halides, alkaline-earth oxides, alkaline-earth fluorides, zincblende crystals, ThO_2 , Al_2O_3 for which $\gamma_0 \leq 2$ (see e.g. Barron *et al.* 1980).

Present measurements of $\alpha(T)$ are not sufficiently sensitive to resolve a T term or Schottky term below 4 K. Suffice to say that our data are generally consistent with those of Ackerman *et al.* in this range (see Fig. 1).

Heat Capacity

It is difficult to compare present data with previous work as the yttria and impurity contents are very different. The first measurements by Lawless (1980*a*) on a sample containing 8 wt.% ZrO_2 and considerable hafnia showed a large anomaly below about 5 K. This was attributed to a quadrupole interaction involving hafnia, and effectively smothered any linear (tunnelling) term. At 10–14 K, values of c_p were comparable with our values.

Lawless (1980*b*) measured another sample of $\text{ZrO}_2 + 8 \text{ wt.}\% \text{Y}_2\text{O}_3$ with reduced hafnia impurity and found that from 3 to 6 K

$$c_p = aT + bT^3,$$

with $a = 1.0 \mu\text{J g}^{-1} \text{K}^{-2}$ and b corresponding to a value $\Theta_0 = 503 \text{ K}$. Below 3 K there was still evidence of an anomaly. Ackerman *et al.* (1984) referred to measurements of $\text{ZrO}_2 + 16 \text{ mol.}\% \text{Y}_2\text{O}_3$ by F. T. Walker (unpublished) which showed no anomaly but a linear term for which $a = 11.5 \mu\text{J cm}^{-3} \text{K}^{-2}$, corresponding to about $2 \mu\text{J g}^{-1} \text{K}^{-2}$ if ρ is between 5 and 6 g cm^{-3} .

Analysis of our data below 7 K indicates an impurity anomaly of the Schottky form with splitting of about 3.0 K, a linear term of about $1.9 T \mu\text{J g}^{-1} \text{K}^{-1}$ and a Debye T^3 term fitted to $\Theta = 540 \text{ K}$. The magnitude of the Schottky term suggests a concentration of about $6 \times 10^{-4} \text{ mol.}^{-1}$ of impurities, which is too large to be attributed to hafnia, but is consistent with the concentration of magnetic ions reported in the crystal analysis. It is idle to speculate further without detailed information about the magnetic energy levels of the individual ions in the cubic zirconia lattice. The existence of a linear term in the heat capacity is confirmed. We have no evidence as to its origin, but its presence in this disordered non-stoichiometric material suggests that it arises from tunnelling processes which occur in glasses at these temperatures.

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