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Citation: *Appl. Phys. Lett.* **98**, 211906 (2011); doi: 10.1063/1.3593383

View online: <http://dx.doi.org/10.1063/1.3593383>

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The grain size and temperature dependence of the thermal conductivity of polycrystalline, tetragonal yttria-stabilized zirconia

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(Received 15 April 2011; accepted 1 May 2011; published online 24 May 2011)

The thermal conductivity of optically transparent, yttria-stabilized tetragonal zirconia having a range of grain sizes from 100 to 180 nm has been measured from just below its approximate Debye temperature up to 1000 °C. It is found that the grain size dependence is most marked at room temperature, decreasing with increasing temperature until being indistinguishable at the highest temperatures. The Kapitza thermal resistance of the grain boundaries is found to be almost independent of temperature, with a value of $R_k = 4.5 \pm 0.5 \times 10^{-9}$ m²K/W and an estimated grain boundary phonon transparency of ~ 0.9 . © 2011 American Institute of Physics. [doi:10.1063/1.3593383]

Considerable research has been devoted in recent years to investigate the thermal conductivity of nanocrystalline materials and determining how the thermal conductivity depends on grain size. In the cases reported to date for single-phase materials, the thermal conductivity is reduced below that of large grain or single crystal material.¹ With few exceptions, the majority of measurements on nanocrystalline materials have been made at temperatures below or near room temperature but for many practical applications it is desirable to also know how the thermal conductivity varies with both grain size and temperature up to considerably higher temperatures. In this letter we report on the grain size and temperature dependence of the thermal conductivity of tetragonal zirconia, stabilized with 3 m/o Y₂O₃ (3YSZ), from room temperature up to 1000 °C. This composition is very similar to that used in thermal barrier coatings to provide thermal protection in gas turbines.² In contrast to most polycrystalline YSZ materials prepared by either sintering or phase deposition, which are white due to entrained porosity, reducing their thermal conductivity, the material fabricated and measured in this work was transparent indicating the absence of porosity. The methodology adopted in this work was to produce 3YSZ disks, appropriate in size for bulk thermal diffusivity measurements by the laser flash technique³ and after measurements anneal the disks to increase the grain size and then remeasure the thermal diffusivity. The material investigated remained tetragonal as assessed by Raman spectroscopy even after the longest annealing treatments (Fig. 1). The most closely related previous work was by Yang *et al.*,⁴ who measured the temperature dependence of vapor-deposited, nanocrystalline cubic zirconia films from 6 to 480 K and over a range of grain sizes from 10 to 100 nm. By virtue of the method they used to produce their films, they contained 10% of porosity as determined by small angle neutron diffraction scattering.

The fully dense and transparent 3YSZ material in this work was produced in bulk from commercial 3YSZ powders (Tosoh Corporation, Japan) densified using a current assisted densification system of our own design for 5 min at 1200 °C at an applied load of 140 MPa using graphite dies. The conditions are similar to those used by Alaniz *et al.*⁵ to produce

optically transparent cubic zirconia. Subsequent annealing treatments in air for various times between 1 and 200 h at a temperature of 1200 °C were used to increase the grain size up to 180 nm. Although considerably greater grain growth occurs at higher annealing temperatures, the material is susceptible to phase partitioning above 1200 °C. The grain sizes were measured from calibrated scanning electron microscope images using the linear intercept method. The densities of all the samples were measured by the Archimedes method and each was in excess of 99.9% crystallographic density. The thermal diffusivities from 100 to 1000 °C were recorded after each annealing treatment using the laser flash technique (LFA 457, Netzsch Instruments, Burlington, MA). The specific heat as a function of temperature was calculated using the Kopp–Neumann rule⁶ from literature values of pure zirconia and pure yttria. Previously, measurements of specific heat for 3YSZ were, within experimental error, the same as those calculated this way.

The thermal conductivity, κ , derived from the measured thermal diffusivity, the measured density, and the calculated

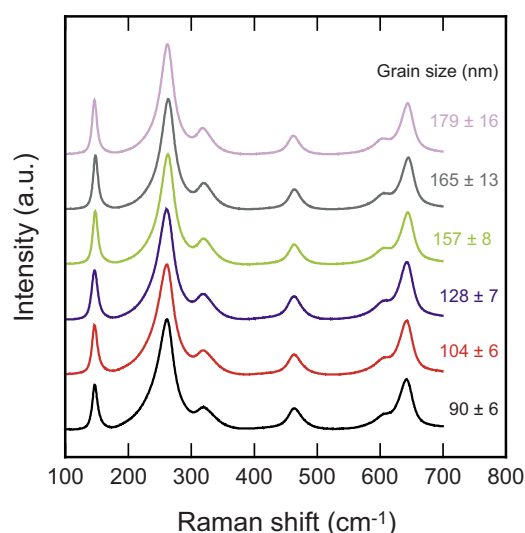


FIG. 1. (Color online) Raman spectra as a function of grain size indicating that the material's crystal structure remained tetragonal. All the lines are distinctive of the tetragonal phase with no indication of monoclinic phase whose most distinctive lines are a strong doublet at 181 and 192 cm⁻¹.

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specific heat is shown in Fig. 2. (At the grain sizes we are considering, it is assumed that the specific heat is not grain size dependent.) At relatively low temperatures, there is a clear dependence of conductivity on grain size which becomes less pronounced as the temperature is raised until at 1000 °C, the highest temperature at which we could make measurements, there is no discernable grain size dependence. This is in qualitative agreement with the expectations of the Klemens–Callaway model^{7,8} where the thermal conductivity depends on the sum of the phonon relaxation times associated with anharmonic phonon-phonon scattering, τ_p , point defect scattering, τ_{pd} , and grain boundary scattering, τ_d , from grain boundaries an average distance, d , apart.

$$\kappa(T, d) = \frac{k_B}{2\pi\nu_s} \left(\frac{k_B T}{\hbar} \right)^3 \int_0^{T_D/T} \tau(x, \omega, d) \frac{x^4 e^x}{(e^x - 1)^2} dx, \quad (1)$$

where $x = \hbar\omega/k_B T$, $\tau_d = d/\nu_s$, and ν_s is the speed of sound. The fundamental constants k_B and \hbar have their usual meaning. The Debye temperature, T_D , for zirconia has been reported to be 475 K.⁹

In the Klemens–Callaway model, the thermal conductivity decreases with increasing temperature above the Debye temperature and approaches a constant value independent of the presence of defects at temperatures several multiples of the Debye temperature. The model and the more recent phonon hopping model¹⁰ for polycrystalline materials both have a functional dependence on grain size that has the same form as the macroscopic heat conduction formalisms¹¹ based on the Kapitza resistance of grain boundaries, namely,

$$\kappa(T, d) = \frac{\kappa_i}{1 + \frac{R_k \kappa_i}{d}}. \quad (2)$$

In this formulation it is assumed that the grain boundaries have a temperature dependent thermal resistance, R_k , and the grains have an intrinsic, grain size-independent, but temperature dependent thermal conductivity, κ_i . By fitting Eq. (2) to the data in Fig. 2, the intrinsic thermal conductivity and Kapitza resistance shown in Fig. 3 are calculated. Although the uncertainties in the derived Kapitza resistance are relatively large, the data suggest that, for this material at least, the Kapitza resistance is temperature independent above room temperature. Recasting the thermal resistance in Eq. (2) in terms of a characteristic length, $L_k = R_k \kappa_i$, that length is found to be 15 nm at 100 °C and 10 nm at 1000 °C. We note that the value of the Kapitza resistance is comparable to the value derived by Yang *et al.*⁴ for a compositionally related but crystallographically distinct cubic YSZ material containing 8–15 mol % Y_2O_3 . They found that the Kapitza resistance increased with temperature up to about room temperature and then was constant at a value of $R_k = 4.5 \pm 0.5 \times 10^{-9}$ m²K/W up to ~200 °C (approximately the Debye temperature). The temperature dependence of the intrinsic thermal conductivity derived using Eq. (2) satisfies the general form^{8,12} derived for a dielectric material together with an additional term asymptoting to a constant high-temperature limit, κ_{\min}

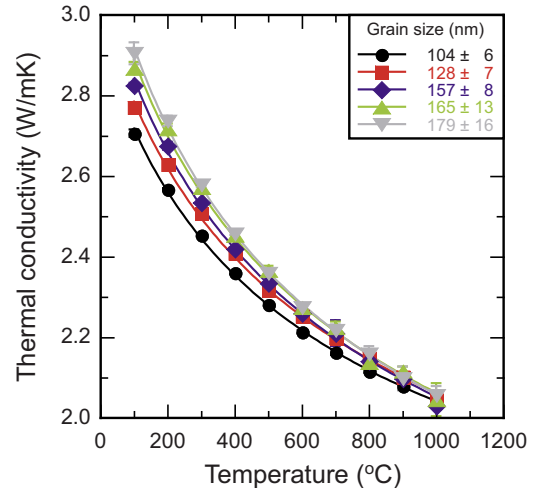


FIG. 2. (Color online) Thermal conductivity as a function of temperature for tetragonal zirconia stabilized with 3 mol % Y_2O_3 for samples aged at the times indicated at 1200 °C to increase the average grain size. The error bars are smaller than the size of the symbols. The lines through the data points are the best fits to the empirical equation: $\kappa(T) = A + BT^{-C}$, where T is temperature and A , B , and C are fitting parameters.

$$\kappa_i(T) = \kappa_{\min} + \frac{k_B \nu_s^{1/2}}{\pi^{3/2}} \frac{1}{\sqrt{\Omega_0 C T}} \frac{1}{\sqrt{T}} \tan^{-1} \left[\frac{k_B T_D}{\hbar} \left(\frac{\Omega_0 \Gamma}{4 \pi \nu_s^3 C T} \right)^{1/2} \right], \quad (3)$$

where k_B is Boltzmann's constant, C is a temperature-independent parameter that characterizes the anharmonic scattering as a function of phonon frequency, Γ is a scattering parameter, and Ω_0 is the unit cell volume. As several of the parameters in Eq. (3) are not known for tetragonal zirconia, the intrinsic conductivity was represented by

$$\kappa_i(T) = \kappa_{\min} + \frac{B}{\sqrt{T}} \tan^{-1} \left(\frac{C}{\sqrt{T}} \right), \quad (4)$$

where the fitting parameters have values of: $\kappa_{\min} = 1.39$, $B = 25.1 \pm 4.71$, and $C = 72.2 \pm 269$ (Fig. 3). [Eq. (4) is a very slowly decreasing function at high temperatures and with these parameters, the intrinsic conductivity at 2500 °C is still 1.84 W/mK].

Further insight into grain boundary scattering can be obtained by comparing our experimental data with the predictions of the phonon hopping model introduced by Braginsky *et al.*¹⁰ in which the Kapitza conductance, G_K , is related to the transparency, t , of the grain boundaries to phonon hopping across them. For the case of fully dense materials having homogeneous grain size and without porosity, Braginsky *et al.*'s equation for the Kapitza conductance can be expressed as

$$G_K = \frac{k_B^2 T_D}{3 \hbar a_0^2} B(\bar{x}) t, \quad (5)$$

where a_0 is the mean interatomic distance and $B(\bar{x})$ is the value of the expression

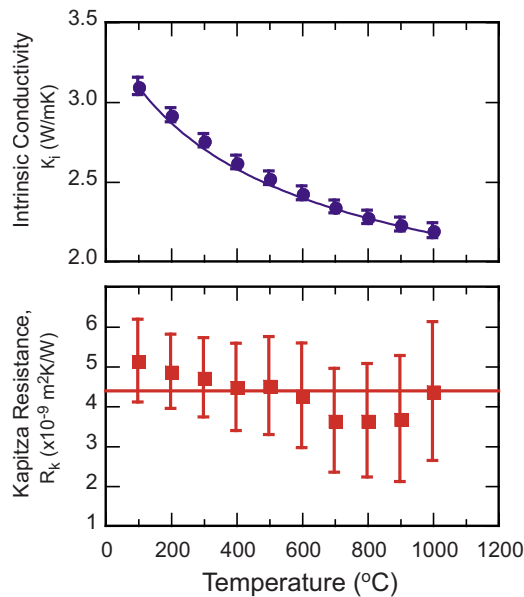


FIG. 3. (Color online) Intrinsic thermal conductivity (top) and grain boundary Kapitza resistance (bottom) derived from the measured thermal conductivity in Fig. 1 using the macroscopic heat conduction model.

$$B(x) = \frac{9}{2} \left(\frac{T}{T_D} \right)^4 \frac{x^4 e^x}{(e^x - 1)^2} \left(x - \frac{T_D}{T} \right)^2 \quad (6)$$

evaluated at a normalized temperature, $\bar{x} = T_D/2T$. At the Debye temperature the grain boundary conductance reduces to the simple expression

$$G_K = \frac{0.735 k_B^2 t T_D}{8 \hbar a_0^2}. \quad (7)$$

Substituting in values for the mean interatomic spacing in zirconia (0.224 nm) and the fundamental constants, and equating to our derived value for the Kapitza resistance, the grain boundary hopping transparency is computed to have a value of 0.89. Given the considerable simplifications made by Braginsky *et al.* in deriving an expression for the Kapitza conductance and evaluating it from the data as well as in assuming that the transparency is independent of the phonon wavelength, it is perhaps surprising that the value is as physically reasonable as it is. It is less than unity which is consistent with there being a boundary resistance. It is also greater than half, the value one might consider for a diffuse interface in which the phonons are absorbed by the boundaries and re-emitted equally in the forward and backward directions. The value of one half would also result if the transparency was solely determined by the ratio of the phonon velocities in the grains on either side of the boundaries.

Our results have important implications for the microstructural design of materials used for high temperature applications, such as thermal barrier coatings and oxide thermoelectrics. While reducing grain size is a viable strategy for reducing thermal conductivity of materials used for room temperature applications, it is evidently ineffective at considerably higher temperatures. In part this is because even in a perfect crystal the phonon mean free path decreases with increasing temperature until it approaches the interatomic spacing. As this occurs, the high temperature conductivity approaches a high-temperature limit, κ_{\min} .¹³ Consequently, unless the grain boundaries are totally opaque to phonon transmission across them, the high-temperature thermal conductivity will be limited by the interatomic spacing and not the grain boundaries. At least for tetragonal zirconia, our analysis also indicates that the grain boundaries are not opaque to phonon transport across them so they have limited thermal resistance.

In summary, although the room temperature thermal conductivity of tetragonal zirconia depends on grain size, there is no grain size dependence at high temperatures ($\sim 1000^\circ\text{C}$), approximately three times the Debye temperature. This suggests that making nanocrystalline materials for high-temperature thermal barrier coatings is not a viable approach to reducing their conductivity at the still higher temperatures where they are generally used to provide thermal protection to turbine blades.

This work was supported by the Office of Naval Research through Grant No. N00014-09-1068.

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