

Thermal properties of the optically transparent pore-free nanostructured yttria-stabilized zirconia

S. Ghosh,¹ D. Teweldebrhan,¹ J. R. Morales,² J. E. Garay,^{2,a)} and A. A. Balandin^{1,3,a)}

¹*Nano-Device Laboratory, Department of Electrical Engineering, University of California-Riverside, Riverside, California 92521, USA*

²*Department of Mechanical Engineering, University of California-Riverside, Riverside, California 92521, USA*

³*Materials Science and Engineering Program, University of California-Riverside, Riverside, California 92521, USA*

(Received 21 September 2009; accepted 18 October 2009; published online 3 December 2009)

The authors report results of investigation of thermal conductivity of nanocrystalline yttria-stabilized zirconia. The optically transparent pore-free bulk samples were prepared via the spark plasma sintering process to ensure homogeneity. Thermal conductivity K was measured by two different techniques. It was found that the pore-free nanostructured bulk zirconia is an excellent thermal insulator with the room-temperature $K \sim 1.7\text{--}2.0$ W/m K. It was also shown that the “phonon-hopping” model can accurately describe specifics of K dependence on temperature and the grain size. The obtained results are important for optimization of zirconia properties for specific applications in advanced electronics and coatings. © 2009 American Institute of Physics.
[doi:10.1063/1.3264613]

I. INTRODUCTION

Yttria-stabilized zirconia (YSZ) has been widely used as the high-temperature corrosion-resistive coating and thermal barrier coating in spacecraft and jet turbine engines¹ and as material in solid oxide fuel cells.² The high melting point makes YSZ desirable for electromechanical applications.³ It was also suggested that zirconia oxide (ZrO₂) layers have potential as gate dielectrics in Si complementary metal-oxide-semiconductor technology, owing to their marked stability against silicate formation.⁴ The wide band gap of nanocrystalline zirconia ($E_G \sim 5.62$ eV) provides transparency in a broad spectral range (visible and UV), allowing its application in the optically addressed memory and solar cells.⁵

Most recently there was a notable increase in interest in YSZ for possible new applications in future electronics. The need for integrating conventional semiconductor electronics with the low-noise high-speed superconducting electronics,⁶ which operate at cryogenic temperatures, stimulated the search for optically transparent thermally insulating (OTTI) materials. The devices, which are kept at distinctively different temperatures, can be more efficiently linked optically rather than electrically since electrical conductors would also provide a thermal cross-talk following the Wiedemann–Franz law. Continuing efforts in developing optical interconnects and chip-to-chip links as well as the need, in some cases, to limit heat spreading to certain regions of a chip increase the interest to YSZ as an OTTI material. The needs for the thermally insulating high-temperature materials for protecting precision electronic devices are also growing. Such materials should exhibit high insulating ability in a limited space and withstand high temperatures. YSZ shows promises for this type of applications as well.

In this paper we report the results of our investigation of correlation between the thermal conductivity (K) and grain size in nanostructured YSZ with bulk sizes, produced by a new sintering process. For many novel applications of YSZ it is important to find an optimum grain size, which would provide an optical window in a right spectral range, while simultaneously keeping K at minimum. It is known that the absorption edge in YSZ increases with decreasing grain size⁷ and that dense fully stabilized zirconia made from nanostructured powder has improved light transmittance.⁸ Unlike previously measured nanocrystalline YSZ,^{9,10} our samples are large pore-free ceramics (versus thin films or porous samples). The latter allows us to separate the effect of the grain size from that of pores and microcracks on the thermal conductivity. We also offer an accurate description of the thermal conductivity of YSZ using the phonon-hopping model (PHM). PHM fits well YSZ as a granular material, which is neither completely crystalline nor completely disordered.

II. EXPERIMENTAL TECHNIQUES AND SAMPLE PREPARATION

In order to reduce the systematic error we performed our measurements using two distinctively different experimental techniques. Specifically, we used the transient planar source (TPS) technique, also referred to as the “hot-disk” method, and the optical “laser flash” technique (LFT). In the TPS technique (hot disk),^{11,12} a thin spiral heater sensor made of Ni and covered with a thin electrically insulating kapton layer was sandwiched between two pieces of YSZ samples. The samples were heated by short electrical current pulses with the power of 0.5 W for 10 s. The temperature rise in response to the dissipated heat was determined from the

^{a)}Authors to whom correspondence should be addressed. Electronic addresses: jegaray@enr.ucr.edu and balandin@ee.ucr.edu.

change in the resistance of the sensor. The time dependence of the temperature rise was used to extract the thermal conductivity from the equation

$$\overline{\Delta T(\tau)} = P(\pi^{3/2}rK)^{-1}D(\tau), \quad (1)$$

where τ is the parameter related to the thermal diffusivity α and the transient measurement time t_m through the expression $\tau = (t_m \alpha / r^2)^{1/2}$, r is the radius of the sensor, P is the input power for heating the sample, and $D(\tau)$ is the modified Bessel function. The TPS instrument was coupled with the “hot bath” (Haake) to change the sample temperature from 263 to 363 K. The sample in the metal holder was inserted to the bath with 50% ethylene glycol used as the circulating fluid.

In the LFT (Netzsch) measurement, a xenon flash lamp produced shots with an energy of 10 J/pulse on the sample surface while the temperature rise was measured at the other end with the nitrogen-cooled InSb infrared detector.¹³ The thermal-wave travel time allowed us to measure the thermal diffusivity α . The thermal conductivity was determined as $K = \alpha \rho C$, where ρ and C are the mass density and specific heat of the material, respectively.

The YSZ samples were prepared using the spark plasma sintering process. The nanocrystalline powder (Tosoh, Japan) with a crystallite size of ~ 50 nm was placed in graphitic dies with the inner diameter of 19 mm and subjected to the electrical current-assisted pressure-activated densification process. The resulting samples were dense and pore-free. The high dc flux used in this processing potentially enhances mass transport in the samples and helped in achieving better homogeneity.^{14,15} The YSZ samples with a mass of 1.5 g and thickness $H \sim 1$ mm were processed using two pressure ramps and one temperature ramp. All powders were pre-pressed at 70 MPa for 1 min in order to ensure a consistent initial density. The pressure was then raised to 106 MPa at room temperature (RT) followed by the temperature increase to selected targets ranging from 1175 to 1250 °C. Upon reaching the final temperature the pressure was raised to 141 MPa. This second load ramp is effective in removing residual porosity and increasing density. Details of the synthesis were reported by some of us elsewhere.⁸ The sample density was $>99\%$ of the theoretical in all cases. The lack of porosity in the samples was further confirmed by their optical transparency. It is known that only extremely dense samples can transmit light well due to the fact that pores are efficient light scatterers. The outlined technique allowed us to synthesize bulk sizes of the pore-free YSZ as opposed to the thin films normally achievable with other techniques.

The samples selected for the thermal study had the grain size variation from $d = 55$ to 180 nm and were made from powders of zirconia stabilized by 8 mol % of yttria (8-YSZ). Figure 1 shows a scanning electron microscopy (SEM) image of a fracture surface of the YSZ sample. The grain size was determined using x-ray diffraction and SEM image analysis. The sample composition was verified with the micro-Raman spectroscopy. Figure 2 shows typical spectra of YSZ excited with 488 nm laser. The most pronounced peak for all samples is seen at ~ 600 cm^{-1} . It originates from F_{2g} -symmetry Brillouin zone (BZ) center phonons.^{16,17} The

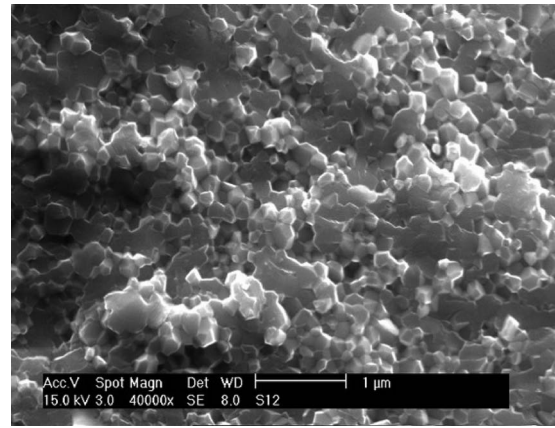


FIG. 1. SEM micrograph of a fracture surface of the pore-free nanostructured YSZ sample processed at 1522 K.

broadening of F_{2g} peaks is explained by contributions from non-BZ center phonons due to the disorder-induced relaxation of the selection rules. A_{1g} and E_{2g} peaks are also present between ~ 100 and 450 cm^{-1} .

III. THERMAL CONDUCTIVITY DATA AND DISCUSSION

Most of the thermal conductivity measurements have been carried out with TPS technique, which is better suited for the large size YSZ samples. The noncontact optical LFT approach works better for films and was used for cross-checking the thermal data to make sure that the systematic error is within acceptable limits. Figure 3 shows the thermal conductivity measured by TPS technique as a function of temperature for four YSZ samples with the grain sizes ranging from 55 to 180 nm. The gradual increase in K value with T is characteristic for the disordered materials. This dependence is in sharp contrast with that for crystalline materials where the thermal conductivity scales inversely proportional to temperature, $K \sim 1/T$, due to the phonon umklapp scattering. For a variety of polycrystalline materials, an empirical relationship can be written as $K \sim 1/T^\sigma$ near RT.¹⁸ For the YSZ samples σ is ~ 0.04 . The RT value of K reduces from

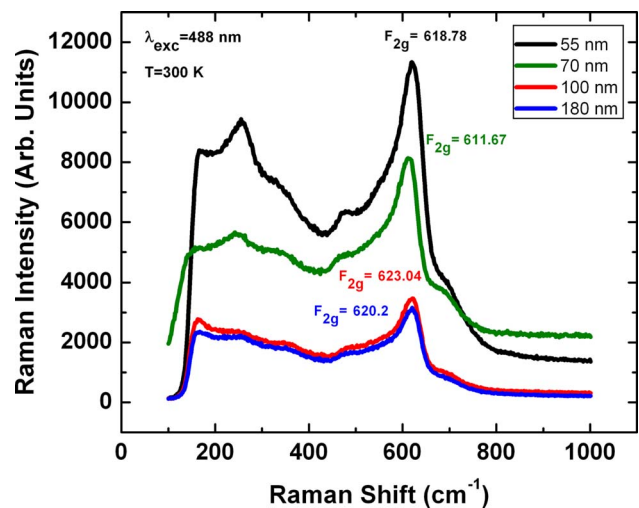


FIG. 2. (Color online) Raman spectra of four nanostructured YSZ samples with different grain sizes.

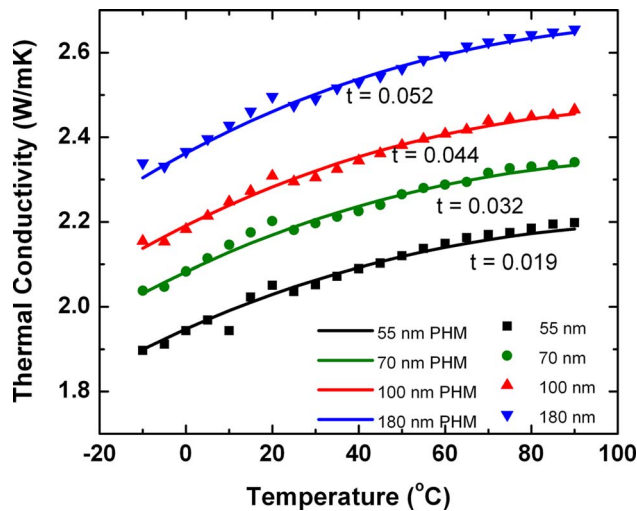


FIG. 3. (Color online) Thermal conductivity of the high-density pore-free nanostructured YSZ as a function of temperature shown for bulk-size YSZ samples with the grain diameter ranging from $d=55$ nm to $d=180$ nm. The experimental data points were obtained with the “hot-disk” technique. The solid lines were calculated using the PHM.

2.47 to 2.03 W/m K with the decreasing grain size. As the grains become smaller the number of grain boundaries increases, causing stronger phonon scattering. The phonon scattering on oxygen vacancies adds to the overall reduction in the thermal conductivity.

To cross-check the experimental data we measured the YSZ sample with 55 nm grain size using LFT. The obtained RT value was $K \sim 1.56$ W/m K ($\rho=6.056$ g/cm³ and $C=0.460$ J/g⁻¹ K⁻¹). The K increase with T was analogous to the one shown in Fig. 3 and, over the examined T range, was described approximately by the linear scaling law as $K=1.52069+0.00164T$ (W/m K). The values and T dependence obtained by TPS and LFT were consistent. Some discrepancy, within the typical range for different thermal measurement techniques, is explained by the thermal boundary resistance effects, which vary in the noncontact optical, LFT, and contact electrical, TPS, methods.

Traditionally the thermal conductivity in YSZ, like in many other nanophase materials, is described within Callaway–Klemens¹⁹ model. In this approach the scattering on grain boundaries is treated as just one additional scattering mechanism added to scattering on point defects and other imperfections. The problem with such an approach is that it was initially developed for the low-disorder crystalline materials with the phonons described by the extended plane waves.²⁰ The considered YSZ samples hardly fall into such a category. From the opposite side, the thermal conductivity of completely disordered materials was calculated using so-called minimum thermal conductivity model, which gives the low bound for thermal conductivity of amorphous and disordered materials.²¹ The 8-YSZ samples are crystalline inside the grains and cannot be considered completely disordered. For this reason, we propose to use an alternative phonon-hopping model, recently developed for granular materials,²² for description of the thermal conductivity of YSZ. PHM works surprisingly well for YSZ and can present a valuable alternative to treatment of heat transport in this class of materials.

PHM assumes that inside a crystalline granular material the phonon transport can be described by the conventional Klemens formulas while phonon transfer, i.e., hopping, from grain to grain is defined by some transparency parameter t . This parameter can be calculated from the first principles in the simplest cases while in others it is found via fitting to the experimental data. The thermal conductivity is then found as²²

$$K = k_B T \int_0^{T_D/T} K_i F(x) t A \varphi [\hbar k_B^{-1} K_i a^2 d + k_B T_D F(x) t A \varphi] dx, \quad (2)$$

where k_B is Boltzmann’s constant, $K_i=(1/3)C_v v \Lambda$ is the “bulk” thermal conductivity inside the grain, A is the mean area of the grain-grain interface, \hbar is Plank’s constant, φ is the grain size disorder factor, $a=0.5084$ nm is the lattice constant, d is the diameter of the grain, $F(x)=(9/2) \times (T/T_D)^4 x^4 e^x (x-T_D/T)^2 (e^x-1)^{-2}$, Λ is the phonon mean free path (MFP), v is the phonon velocity, and T_D is the effective Debye temperature. The phonon MFP inside the grain can be obtained by calculating the scattering rates^{19,20} or, as it was done here, from the semiempirical relation $\Lambda=(20T_M a)/(\gamma^2 T)$, where $T_M=2973$ K is the melting point and $\gamma=1.403$ is the Grüneisen parameter for YSZ.²³ The calculated PHM curves for the thermal conductivity are shown in Fig. 3 by solid lines, which match the experimental data very closely. The transparency parameter for 8-YSZ samples reduces with the decreasing grain size. The effective Debye temperature extracted for our samples is $T_D=1300$ K, which is somewhat larger than values in the range 600–963 K reported for YSZ.²⁴ The latter is likely related to the pore-free nature of our samples. The density of our samples was close to the theoretical limit (~ 5.9 g/cm³).

We now compare our results with previous studies reported for YSZ, which were prepared by different techniques and had some structural and morphological differences from our samples. First, it is interesting to note that the absence of pores in our samples does not lead to a noticeable increase in the thermal conductivity. A variety of porous YSZ films were reported to have K in the range of ~ 1.5 – 3 W/m K.²⁵ It is likely that the smaller grain size and intergrain boundaries can be responsible for comparable K in our samples. The latter is good news for the proposed nanostructured pore-free YSZ applications as thermal barrier materials in advanced electronics. Bisson *et al.*²⁶ showed that the thermal conductivity of single crystal zirconia strongly depends on yttria content. They found that pure zirconia has a RT thermal conductivity of 8.1 W/m K and in the fully cubic (8 mol % Y₂O₃) modification it reduces to 2.3 W/m K. Our samples of fully stabilized samples with 8 mol % Y₂O₃ have RT value range of ~ 2.45 – 2 W/m K. Thus, our results are consistent with the previous studies: the K values for the single crystals are understandably higher. The thermal conductivity of our YSZ samples with the largest grain size approaches that of the single crystals. Raghavan *et al.*⁹ measured the thermal conductivity of bulk YSZ nanocrystalline ceramics with a wide range of porosity, grain sizes, and composition content. In contrast to our results, they observed no

clear effect of grain size. It is likely that grain size dependence in their samples was masked by the residual porosity. Soyez *et al.*¹⁰ measured the thermal conductivity of cubic YSZ thin films with nanocrystalline grains at RT. Their films were porous (estimated $\sim 10\%$ porosity) and had very small grain sizes. The results reported in Ref. 10 show clear grain size dependence and a steep drop in K at the grain sizes less than 30 nm. However, they did not observe the dependence of the thermal conductivity on the grain size for the grains larger than 30 nm. As we discussed previously, thin films are known to have porosity and microcracks. For this reason it is difficult to decouple the effects of the porosity and defects on the thermal conductivity from the effects produced by varying grain sizes. It is again likely that the porosity overshadowed the grain size dependence for the samples with the grain size above 30 nm.

The proposed PHM description of thermal transport in YSZ is expected to work even for much smaller grain sizes. It was shown that PHM is valid for quantum dot superlattices with the quantum dot sizes as small as few nanometers.²⁷

IV. CONCLUSIONS

We measured the thermal conductivity of the optically transparent pore-free nanostructured YSZ by two different techniques. The large size of our bulk samples as well as the absence of pores and cracks allowed us to distinguish the effects of the grain boundaries on YSZ's thermal conductivity. We have shown that the PHM, which can be better justified from the physics point of view, describes the heat conduction in YSZ very well. The obtained experimental results and model description are important due to increasing interest in YSZ for applications in advanced electronics. The PHM with the extracted parameters can be used for YSZ optimization for specific applications.

ACKNOWLEDGMENTS

A.A.B. acknowledges support from the Focus Center Research Program (FCRP) through the Interconnect Focus Center (IFC). J.E.G. gratefully acknowledges the Young Investigator Award from the Army Research Office (ARO).

- ¹D. R. Clarke and C. G. Levi, *Annu. Rev. Mater. Res.* **33**, 383 (2003).
- ²K. W. Chour, J. Chen, and R. Xu, *Thin Solid Films* **304**, 106 (1997).
- ³U. Betz and H. Hahn, *Nanostruct. Mater.* **12**, 911 (1999).
- ⁴M. Copel, M. Gribelyuk, and E. Gusev, *Appl. Phys. Lett.* **76**, 436 (2000).
- ⁵I. Kosacki, V. Petrovsky, and H. U. Anderson, *Appl. Phys. Lett.* **74**, 341 (1999).
- ⁶R. Sobolewski, *Supercond. Sci. Technol.* **14**, 994 (2001).
- ⁷M. M. Mikhailov and A. C. Verevkin, *Russ. Phys. J.* **47**, 600 (2004).
- ⁸S. R. Casolco, J. Xu, and J. E. Garay, *Scr. Mater.* **58**, 516 (2008).
- ⁹S. Raghavan, H. Wang, R. B. Dinwiddie, W. D. Porter, and M. J. Mayo, *Scr. Mater.* **39**, 1119 (1998).
- ¹⁰G. Soyez, J. A. Eastman, L. J. Thompson, G. R. Bai, P. M. Baldo, A. W. McCormick, R. J. DiMeifi, A. A. Elmestafa, M. F. Tambwe, and D. S. Stone, *Appl. Phys. Lett.* **77**, 1155 (2000).
- ¹¹S. E. Gustafsson, *Rev. Sci. Instrum.* **62**, 797 (1991).
- ¹²M. Shamsa, S. Ghosh, I. Calizo, V. Ralchenko, A. Popovich, and A. A. Balandin, *J. Appl. Phys.* **103**, 083538 (2008).
- ¹³R. Ikkawi, N. Amos, A. Lavrenov, A. Krichevsky, D. Teweldebrhan, S. Ghosh, A. A. Balandin, D. Litvinov, and S. Khizroev, *J. Nanoelectron. Optoelectron.* **3**, 44 (2008).
- ¹⁴J. E. Garay, U. Anselmi-Tamburini, and Z. A. Munir, *Acta Mater.* **51**, 4487 (2003).
- ¹⁵U. Anselmi-Tamburini, J. E. Garay, Z. A. Munir, A. Tacca, F. Maglia, and G. Spinolo, *J. Mater. Res.* **19**, 3255 (2004); **19**, 3263 (2004).
- ¹⁶J. Cai, C. Raptis, Y. S. Raptis, and E. Anastassakis, *Phys. Rev. B* **51**, 201 (1995).
- ¹⁷V. Lughi and D. R. Clarke, *J. Appl. Phys.* **101**, 053524 (2007).
- ¹⁸A. V. Sukhadolau, E. V. Ivakin, V. G. Ralchenko, A. V. Khomich, A. V. Vlasov, and A. F. Popovich, *Diamond Relat. Mater.* **14**, 589 (2005).
- ¹⁹J. Callaway, *Phys. Rev.* **113**, 1046 (1959); P. G. Klemens, in *Chemistry and Physics of Nanostructures and Related Non-Equilibrium Materials*, edited by E. Ma, B. Fultz, R. Shull, J. Morral, and P. Nash (The Minerals, Metals and Materials Society, Warrendale, PA, 1997), pp. 97–104.
- ²⁰A. Khitun, A. A. Balandin, J. L. Liu, and K. L. Wang, *J. Appl. Phys.* **88**, 696 (2000); A. Khitun, A. Balandin, J. L. Liu, and K. L. Wang, *Superlattices Microstruct.* **30**, 1 (2001).
- ²¹D. G. Cahill and R. O. Pohl, *Solid State Commun.* **70**, 927 (1989).
- ²²L. Braginsky, N. Lukzen, V. Shklover, and H. Hofmann, *Phys. Rev. B* **66**, 134203 (2002).
- ²³H. Hayashi, T. Saitou, N. Maruyama, H. Inaba, K. Kawamura, and M. Mori, *Solid State Ionics* **176**, 613 (2005).
- ²⁴T. Shirakami, T. Tojo, T. Atake, T. Mori, and H. Yamamura, *Thermochim. Acta* **267**, 415 (1995); E. Kisi and M. Yuxiang, *J. Phys.: Condens. Matter* **10**, 3823 (1998).
- ²⁵K. W. Schlichting, N. P. Padture, and P. G. Klemens, *J. Mater. Sci.* **36**, 3003 (2001).
- ²⁶J. F. Bisson, D. Fournier, M. Poulain, O. Lavigne, and R. M evrel, *J. Am. Ceram. Soc.* **83**, 1993 (2000).
- ²⁷M. Shamsa, W. L. Liu, A. A. Balandin, and J. L. Liu, *Appl. Phys. Lett.* **87**, 202105 (2005); Y. Bao, W. L. Liu, M. Shamsa, K. Alim, A. A. Balandin, and J. L. Liu, *J. Electrochem. Soc.* **152**, G432 (2005); Y. Bao, A. A. Balandin, J. L. Liu, and Y. H. Xie, *Appl. Phys. Lett.* **84**, 3355 (2004).