International Journal of Thermophysics, Vol. 9, No. 4, 1988

Comparison of Thermal Conductivity Data for Partially Stabilized Zirconia with Values Derived from Thermal Diffusivity Results

R. K. Williams,[1] J. B. Bates,[1] R. S. Graves,[1] D. L. McElroy,[1] and F. J. Weaver[1]

Received July 5, 1988

The thermal conductivity of partially stabilized zirconia was measured over the temperature range 320–1273 K using the radial heat flow method. The data have an absolute uncertainty of about $\pm 2\%$ and repeat measurements showed no evidence of changes in the thermal conductivity at high temperatures. This also was true for the thermal diffusivity data, which were obtained in vacuum over the temperature range 300–1473 K. Both sets of thermal conductivity data pass through minima at high temperatures. Quantitative differences were observed in the temperatures and thermal conductivities of the two minima. The results were analyzed by assuming parallel conduction by phonons and photons, and the phonon component was identified by fitting lower-temperature data. Extrapolating this curve allowed identification of the photon contribution to the thermal conductivity at high temperatures. The photon contribution approached a T^3 function and was larger in the thermal conductivity specimens. The difference in the photon contributions correlates with changes in the optical properties of the samples produced during the high temperature measurments.

KEY WORDS: thermal conductivity; thermal diffusivity; zirconia.

1. INTRODUCTION

At high temperatures, both phonons and photons make significant contributions to energy transport in translucent ceramics [1]. The contributions of the two carriers are inferred from the observed effect of temperature on the thermal conductivity: phonons yield a contribution which decreases about as T^{-1}, while in the absence of direct radiant transmission, photons produce a contribution which is roughly proportional to T^3 [2].

---

[1] Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, Tennessee 37831-6092, U.S.A.

0195-928X/88/0700-0587$06.00/0 © 1988 Plenum Publishing Corporation

At present, thermal conductivities, λ, are usually determined from thermal diffusivity, α, and specific heat data. The main purpose of this study was to make a comparison of results obtained in this way with data obtained by direct measurements of λ. This comparison was required because the data are used to design various advanced ceramic components which may be used in insulated heat engines [3], and studies of fibrous insulating materials (4) suggest that the two methods for determining λ do not always yield identical results.

2. EXPERIMENTAL METHODS

The thermal diffusivity was obtained by the laser flash method [5], and a differential scanning calorimeter was used to measure the specific heat. The thermal diffusivity apparatus had been highly developed over several years [6] and a Perkin Elmer Model DSC-2 [7] was used to make the specific heat measurements. Thermal diffusivity values were measured in vacuum over the temperature range 300–1473 K, and repeat measurements indicated that heating the samples to 1473 K did not cause significant changes in the measured α values. Specific heat data were obtained up to 873 K and linearly extrapolated to higher temperatures. Generally, λ values obtained in this way are thought to have absolute uncertainties of about $\pm 10\%$.

The thermal conductivity was directly measured by two methods. A comparative longitudinal heat flow apparatus [8] was used to make preliminary measurements over the temperature range 305–365 K. The uncertainty of these data is about $\pm 3\%$ [9] and the 2–3% corrections used for metals [10] were not applied because tests with a Pyroceram standard [9] indicated that they are not appropriate for low-λ materials.

Higher-temperature λ measurements were made by the absolute radial heat flow method [11]. The data, which span the temperature range 320–1273 K, have an absolute uncertainty of about $\pm 2\%$ [12]. These measurements were made in a helium atmosphere, which is required to produce satisfactory thermal contacts between the sample and the Pt–Pt 10% Rh thermocouples.

3. SAMPLE CHARACTERISTICS

The partially stabilized zirconia (PSZ) material was MS grade produced by Nilcra [13]. All of the stock was obtained in the form of 51-mm-diameter, 25.4-mm-tall disks; the samples were machined with diamond tools. Two 12.7-mm-diameter, 1.5-mm-thick samples were produced for the α measurements and the axes of these samples were oriented parallel and perpendicular to the axis of the starting stock. The material had a bulk density of 4.78 $Mg \cdot m^{-3}$. A quantitative electron microprobe measurement showed that $8.4 \pm 0.9\%$ of the metallic ions were Mg^{2+}.

The microstructure of the material is shown in Figs. 1, 2, and 3. These three figures show that the grain-size and pore-size distributions of the samples were not altered by high-temperature anneals associated with the thermal property measurements. Also, X-ray diffraction measurements on specimens with metallographically polished surfaces showed that the ratio of monoclinic (grain boundary) to cubic plus tetragonal (matrix) zirconia remained at about 3% after all of the thermal treatments. The tetragonal phase is present as a finely dispersed precipitate in the cubic matrix of the ZrO_2 grains, and the MS grade generally contains about 35 vol% of tetragonal ZrO_2 [14].

The appearance of the samples did change during the α and λ measurements. Figure 4 shows that a darkened layer formed on the surface of the thermal conductivity samples, affecting about 10% of the sample volume. The change was more severe for the α samples, which turned from white to light brown during the measurements. This change appeared to alter the opacity of the material, since it was noted that the α sample was

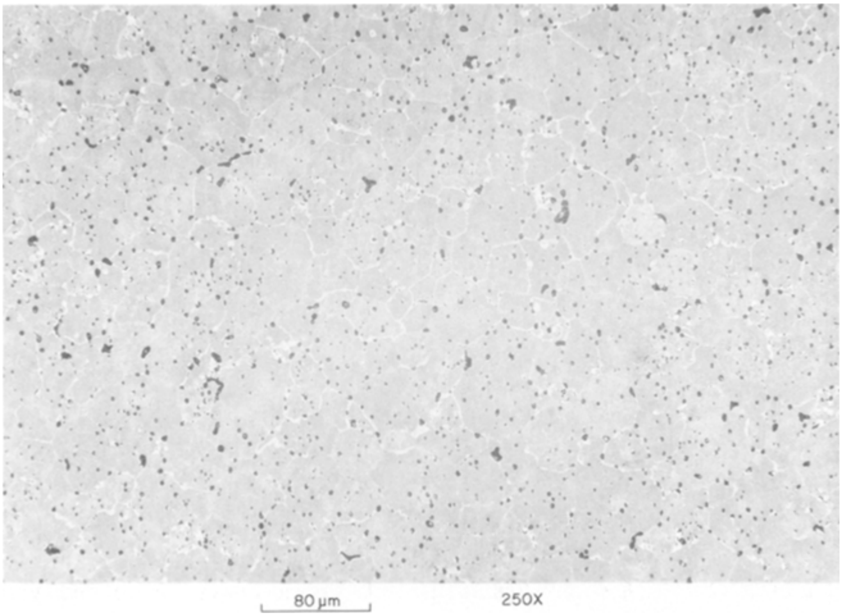

Fig. 1. As-received MS grade partially stabilized zirconia. Etched in water–10% HF.

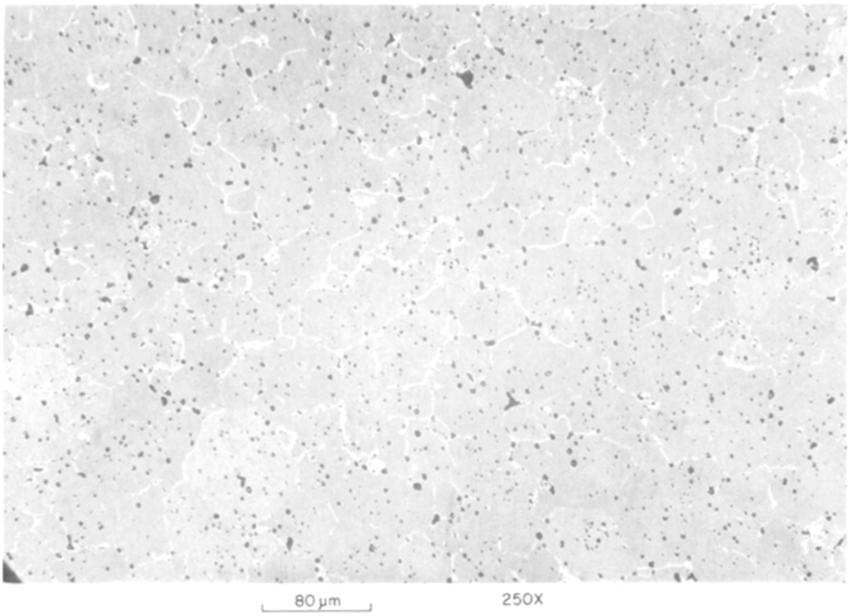

Fig. 2. MS-grade partially stabilized zirconia after the radial heat flow thermal conductivity experiments. Sample was at 1273 K for about 48 h. Etched in water 10% HF.

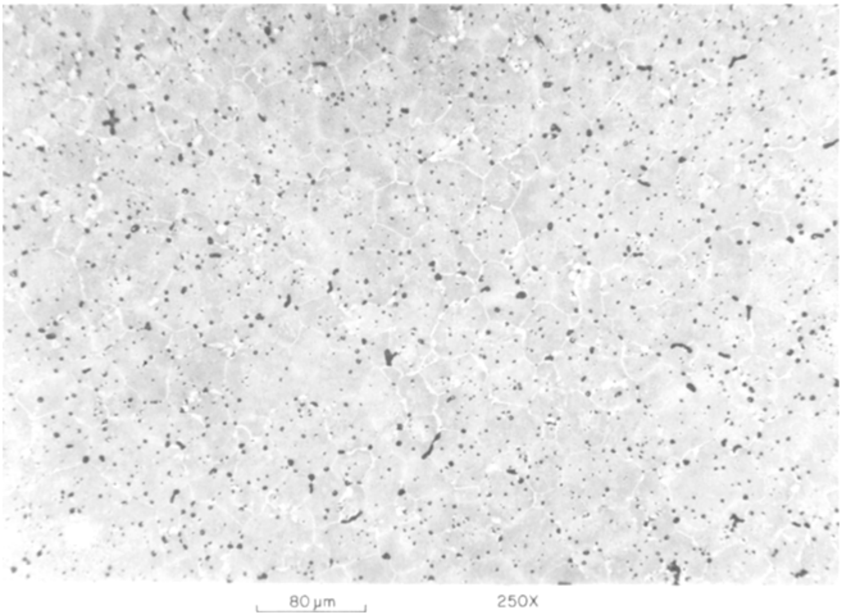

Fig. 3. MS-grade partially stabilized zirconia after thermal diffusivity measurements. Sample was at 1473 K in vacuum for about 30 min. Etched in water–10% HF.

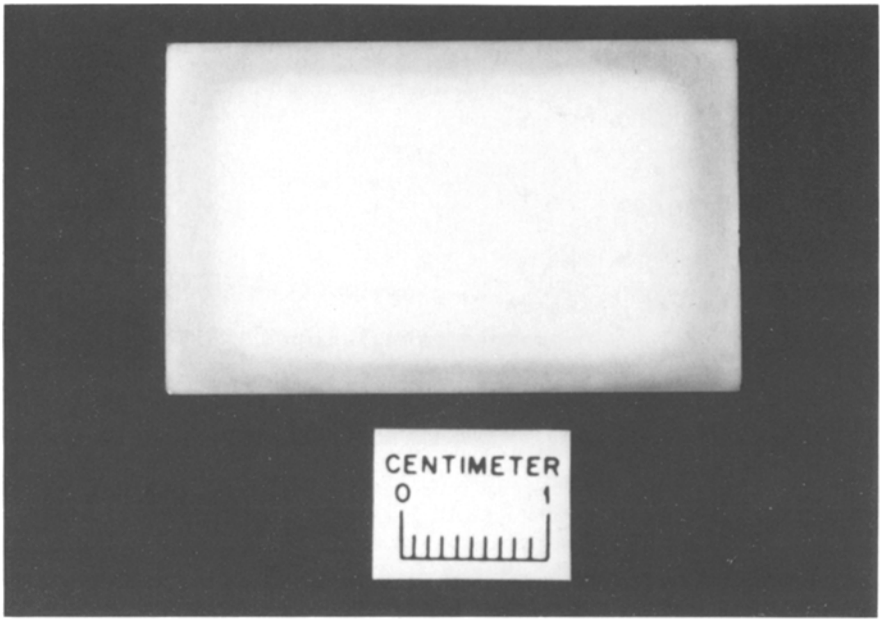

Fig. 4. Section through one of the radial heat flow samples after the measurements were completed. Darkened layer on surface affects about 10% of the sample.

much easier to examine with a light microscope. The absorption coefficients of the samples are compared in Fig. 5. These data were obtained in a Cary 17D spectrophotometer [15], and the results were experimentally corrected for reflective losses. The data show that heating PSZ increases its absorption coefficient by about a factor of two. This is presumably due to microstructural coarsening, which has no effect on the energy transport. The results also show that the darkened region in Fig. 4 transmits about as well as the α sample, and the central region of the radial heat flow samples is significantly ($\sim$25%) less opaque than either the darkened case or the α sample.

4. EXPERIMENTAL DATA

The λ data are shown in Fig. 6. The two sets of λ data derived from α values for samples with different orientations differed by only 1–2%, and the results shown in Fig. 6 are their average. At ambient temperatures, the two directly measured λ values differ by only about 0.9%, while the value derived from the α measurements [16] is about 7% lower. The difference

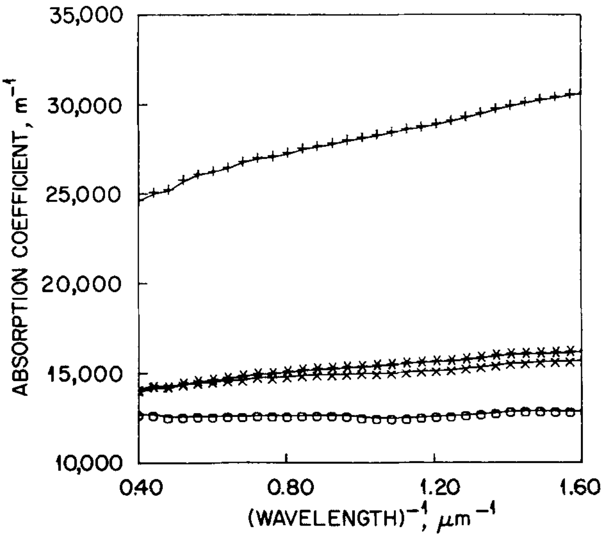

Fig. 5. Optical absorption coefficient data for the PSZ samples. (+) As received; (*) dark, core region shown in Fig. 4; (○) central, clear region shown in Fig. 4; and (X) thermal diffusivity sample.

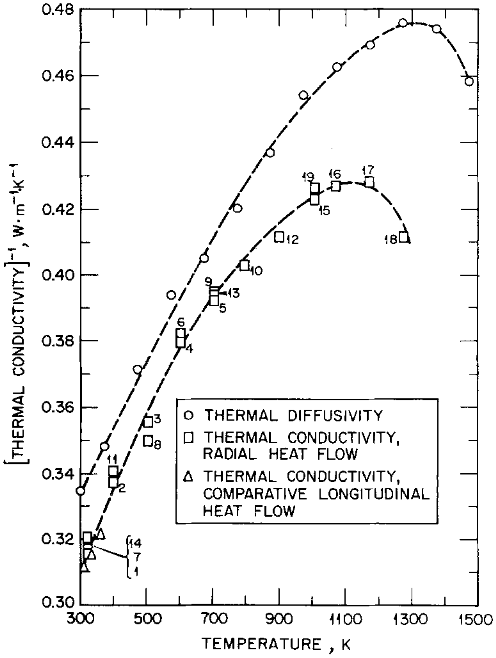

Fig. 6. Experimental thermal conductivity values for partially stabilized zirconia. The radial heat flow data points are numbered in the order they were obtained.

between the two λ determinations reaches a minimum of about 4% at ~650 K, and the two curves diverge at higher temperatures. At 1273 K, the difference amounts to about 14% and exceeds the combined experimental uncertainties. The checkpoint (No. 19) shows that this difference cannot be attributed to shifts in sample characteristics during the radial heat flow measurements of λ, which require about 48 h for each determination.

The two sets of thermal conductivity values are adequately described by the empirical equations: from steady-state measurements

$$\lambda = 3.818 - 0.00278T + 25.5/T + 0.130 \times 10^{-5}T^2 \tag{1}$$

from thermal diffusivity measurements

$$\lambda = 3.586 - 0.00228T + 0.232/T + 0.883 \times 10^{-6}T^2 \tag{2}$$

where T is in K and λ is in $\mathrm{W \cdot m^{-1} \cdot K^{-1}}$. The average deviations for Eqs. (1) and (2) are 0.82 and 0.67%.

5. DISCUSSION

The two sets of results shown in Fig. 6 are similar in that λ^{-1}, the thermal resistivity, initially increases approximately linearly with temperature and then passes through a maximum at a higher temperature. The differences are in the positions of the two maxima and a vertical offset between the two curves. At lower temperatures, the vertical offset is within the combined experimental uncertainties. Since the direct λ measurements are more accurate, the vertical offset between the two curves was eliminated by simply shifting the upper curve downward by $0.0185\ \mathrm{m \cdot K \cdot W^{-1}}$.

The maxima are generally thought to arise from the different temperature variations of the contributions of two types of energy carriers:

$$\lambda = \lambda_g + \lambda_p \tag{3}$$

In this equation, λ_g is the contribution from phonons or lattice vibrations and λ_p is a photon contribution. This can be expected if the sample is optically thick [2]. In the following, λ_p is experimentally estimated and compared with calculated [2] values. The experimental estimate is based on identifying λ_g from lower-temperature data and extrapolating to higher temperatures to yield values for $(\lambda - \lambda_g)$.

This material contains all three polymorphs of ZrO_2, and the net temperature variation of λ_g must depend on the λ variations of the three phases. A semicontinuous grain boundary network of monoclinic ZrO_2 and MgO [14] is present, and the grains consist of a cubic matrix containing about 35 vol% of very finely divided, rod-shaped tetragonal precipitates.

Presumably, both the monoclinic and the tetragonal phases are highly depleted in Mg.

The most direct method to estimate the behavior would be to use measured λ values for each phase in an appropriate mixing formula. However, no data are available for the monoclinic polymorph [17] and only one study [18] of tetragonal ZrO_2 is available. In this study [18], it was shown that very fine-grained ZrO_2–2.4 wt% Y_2O_3 exhibits glass-like behavior at low temperatures and that λ reaches a roughly constant value at about 40 K. This λ value ($\sim 2\ W \cdot m^{-1} \cdot K^{-1}$) is similar to values reported for the cubic phase [17], but both the fine grain size and the presence of oxygen vacancies would probably greatly reduce λ relative to values for a defect-free tetragonal single crystal.

Some λ values have been inferred from α data [19, 20]. Swain et al. [19] state that the λ values for monoclinic, tetragonal, and cubic ZrO_2 are 5.2, 4.8, and 1.8 $W \cdot m^{-1} \cdot K^{-1}$ but do not specify the temperature. Buykx and Swain [20] derived room-temperature values for α of monoclinic and tetragonal ZrO_2 from data on PSZ. With literature data for the cubic form [21], their results indicate that the λ values for the monoclinic, tetragonal, and cubic polymorphs should fall in the order 1:1.35:0.5. The difference between these two [19, 20] results shows that the experimental situation is not clear enough to provide useful guidance for an extrapolation of the data (Fig. 6) for MS-PSZ.

Figure 7 shows a theoretical calculation. Callaway's model [22] was used in the calculation and the U-process scattering strength was estimated by following the procedure given by Slack [23]. The Debye temperature, 322 K, was based on reducing the elastic constant value [24] to account for dispersion. The Grüneisen constant, 1.75, was obtained from elastic constant [24] and high-temperature expansion [25] data. The phonon-point defect scattering, which is due almost entirely to the effect of oxygen vacancies, was calculated from the prediction of Ratsifaritana and Klemens [26] and N processes were estimated to occur twice as frequently as U processes.

These estimates show that the λ values for the three polymorphs should tend to merge at higher temperatures, and this is a favorable situation because microstructural effects should be least important at high temperatures, where identification of the photon component is required. For the three phases, estimates are in better agreement with the suggestion of Swain et al. [19] than with the values from Buykx and Swain [20]. The calculated curve for the cubic phase is too low [17] and approaches the amorphous limit [1] at high temperatures. For this material, λ is almost entirely fixed by point-defect scattering, so the result suggests that the theoretical calculation of the scattering rate [26] is too large.

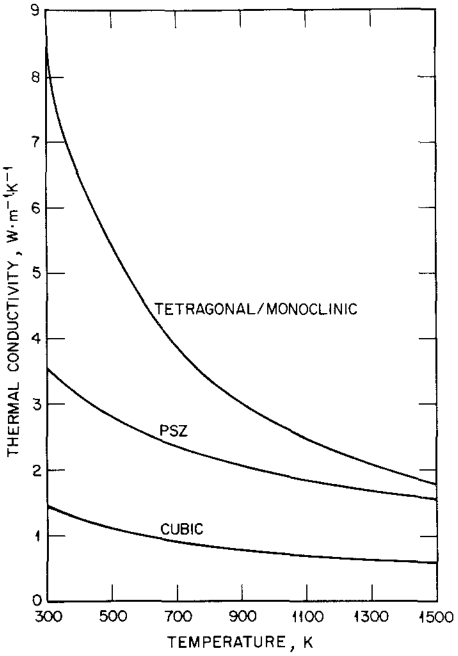

Fig. 7. Estimated thermal conductivity curves for monoclinic, tetragonal, and cubic zirconia. The model does not distinguish between monoclinic and tetragonal, and the curve for the cubic form includes point-defect scattering from oxygen vacancies. The curve labeled PSZ is described in the text.

Since neither experimental data for the three polymorphs nor theory can give a satisfactory extrapolation, a more empirical approach was adopted. For an insulator, thermal resistivity can often be approximated by

$$\lambda_g^{-1} = A + BT \tag{4}$$

This equation usually describes data when the scattering is dominated by U processes. However, when point-defect scattering is very strong, the linear term in [4] should be replaced by a slower variation [27]. Estimates of the U-process and point-defect relaxation times show that this is the case for PSZ, even at high temperatures. Also, at the highest temperatures, λ is only about a factor of 4 greater than typical, temperature-independent, values for amorphous solids. The approach adopted was to use Callaway's equation to fit the lower-temperature data. This was accomplished by reducing the point-defect scattering rate until a reasonable description of

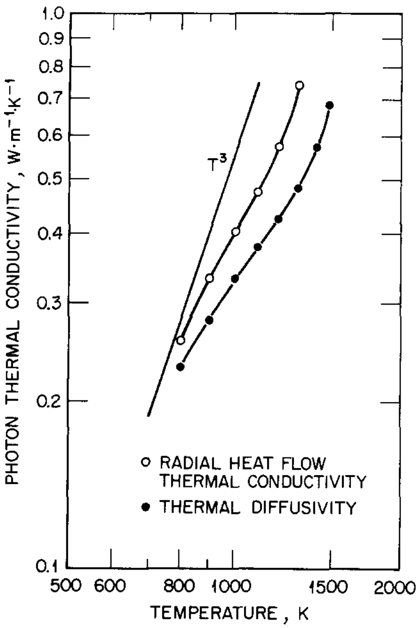

Fig. 8. Photon thermal conductivity curves derived for the PSZ samples used for the thermal conductivity and diffusivity measurements.

the lower-temperature ($\leqslant 700$ K) data was obtained. This result, labeled PSZ, is also shown in Fig. 7, and the point-defect scattering was reduced to about 50% of the theoretical value [26].

The derived $(\lambda - \lambda_g)$ photon contributions are shown in Fig. 8. At the highest temperatures, the contribution varies about as T^3 and this is as expected theoretically [2]. This is also the regime of minimum uncertainly since the component makes a larger percentage contribution and the calculation of the photon part is least sensitive to microstructural effects. The difference between the two λ_p curves is also about what would be expected from the optical characteristics shown in Fig. 5. The λ_p curve derived from the direct λ measurements exceeds the other curve by an average of about 30%, while the ratio of the two absorption coefficients averages about 1.25. The magnitude of λ_p can also also be calculated from the theory [2]. Using literature data [28] for the index of refraction of cubic zirconia with the relevant absorption coefficients shown in Fig. 5 yields λ_p values which average about one-third of the values shown in Fig. 8. The agreement improves as the temperature increases.

This analysis of phonon and photon transport shows that photon transport is probably responsible for the upturn in the thermal conductivity at high temperatures. There is no evidence that thermal diffusivity and steady-state measurements yield different results [4], but the data do show that environmentally produced changes in optical properties can alter the photon energy transport characteristics of translucent materials at high temperatures.

ACKNOWLEDGMENTS

The experimental assistance of O. B. Cavin, T. J. Henson, R. R. Leedy, and C. A. Walls is gratefully acknowledged. The authors benefited from several conversations with P. F. Becher, and G. L. Coleman prepared the manuscript. This research was sponsored by the U.S. Department of Energy, Assistant Secretary for Conservation and Renewable Energy, Office of Transportation Systems, as part of the Ceramic Technology for Advanced Heat Engines Project of the Advanced Materials Development Program, under Contract DE-AC05-840R21400 with Martin Marietta Energy Systems, Inc.

REFERENCES

1. R. Berman, *Thermal Conduction in Solids* (Clarendon Press, Oxford, 1976), p. 106.
2. L. Genzel, *Z. Phys.* **135**:177 (1953).
3. S. Wahiduzzaman and T. Morel, *Proceedings of the 25th Automotive Technology Development Contractors Coordination Meeting* (Society of Automotive Engineers, Inc., Warrendale, Pa.) (in press). [Also available as ORNL/Sub/86-22042/1 (Oct. 1987).]
4. D. L. McElroy, R. S. Graves, D. W. Yarbrough, and T. W. Tong, *High Temp. High Press.* **17**:395 (1985).
5. W. J. Parker, R. J. Jenkins, C. P. Butler, and G. L. Abbott, *J. Appl. Phys.* **32**:1679 (1961).
6. R. E. Taylor, *High Temp. High Press.* **11**:43 (1979).
7. The Perkin Elmer Corp., 761 Main Avenue, Norwalk, Conn. 06859.
8. R. K. Williams, R. K. Nanstad, R. S. Graves, and R. G. Berggren, *J. Nucl. Mater.* **115**:211 (1983).
9. R. K. Williams, R. S. Graves, and J. P. Moore, Oak Ridge National Laboratory, Report No. ORNL-5313 (1978).
10. R. K. Williams, R. S. Graves, F. J. Weaver, and D. W. Yarbrough, *J. Appl. Phys.* **62**:2778 (1987).
11. J. P. Moore, in *Compendium of Thermophysical Property Measurement Methods, Vol. 1. Survey of Measurement Techniques*, K. D. Maglic, A. Cezairliyan, and V. E. Peletsky, eds. (Plenum Press, New York, 1984), p. 61.
12. W. Fulkerson, J. P. Moore, R. K. Williams, R. S. Graves, and D. L. McElroy, *Phys. Rev.* **167**:765 (1968).
13. Nilcra Ceramics Pty. Ltd., 239 Separation St., Northcote, Vict. 3070 Australia.
14. P. F. Becher, M. V. Swain, and M. K. Ferber, *J. Mater. Sci.* **22**:76 (1987).
15. Varian Instruments Div./Cary Products, Palo Alto, Calif. 94303.

16. R. E. Taylor, H. Groot, and J. Larimore, Private Communication, Purdue University, West Lafayette, Ind. (1987).
17. Y. S. Touloukian, R. W. Powell, C. Y. Ho, and P. G. Klemens, *Thermal Conductivity, Nonmetallic Solids* (IFI/Plenum, New York, 1970), pp. 246, 442.
18. W. N. Lawless and T. K. Gupta, *Phys. Rev. B* **28**:5507 (1983).
19. M. V. Swain, L. F. Johnson, R. Syed, and D. P. H. Hasselman, *J. Mater. Sci. Lett. (GB)* **5**:799 (1986).
20. W. J. Buykx and M. V. Swain, in *Advances in Ceramics, Vol. 12*, N. Claussen, M. Ruhle, and A. Heuer, eds. (American Ceramic Society, Columbus, Ohio, 1984), p. 518.
21. Y. S. Touloukian, R. W. Powell, C. Y. Ho, and M. C. Nicolau, *Thermal Diffusivity* (IFI/Plenum, New York, 1970), p. 409.
22. J. Callaway, *Phys. Rev.* **113**:1046 (1959).
23. G. A. Slack, in *Solid State Physics*, F. Seitz and D. Turnbull, eds. (Academic, New York), (1979), Vol. 34, p. 1.
24. H. M. Kandil, J. D. Greiner, and J. F. Smith, *J. Am. Ceram. Soc.* **67**:341 (1984).
25. Y. S. Touloukian, R. K. Kirby, R. E. Taylor, and T. Y. R. Lee, *Thermal Expansion, Nonmetallic Solids* (IFI/Plenum, New York, 1977), p. 603.
26. C. A. Ratsifaritana and P. G. Klemens, *Int. J. Thermophys.* **8**:737 (1987).
27. B. Abeles, *Phys. Rev.* **131**:1906 (1963).
28. D. L. Wood and K. Nassau, *Appl. Optics* **21**:2978 (1982).