Effect of specimen thickness on the thermal diffusivity of $(Sr, K)Zr_4(PO_4)_6$ ceramic via a laser-flash technique

DEAN-MO LIU
Materials Research Laboratories, Industrial Technology Research Institute, Chutung, Hsinchu, Taiwan 31015

It has recently been found that the thermal diffusivity of materials determined by means of a pulse method is strongly dependent on the specimen size, due to factors such as a strongly negative temperature-dependent diffusivity and the non-linearity of the detector response, etc. In polycrystalline $(Sr, K)Zr_4(PO_4)_6(SrKZP)$ ceramic, which has a low and weak temperature-dependent thermal conductivity, it has been found the thermal diffusivity increases with increasing specimen thickness and decreases with increasing specimen temperature rise, ΔT. In the limiting of $\Delta T \rightarrow 0$, the SrKZP ceramic shows a thickness-dependent thermal diffusivity. The limiting diffusivity of the ceramic for different thicknesses can be corrected to a value of $7.84 \times 10^{-3} \, cm^2 \, s^{-1}$ by taking the radial heat conduction effect into account. A reliable measurement of the thermal diffusivity of the SrKZP ceramic can be obtained by using a specimen with thickness not exceeding ~ 1 mm and keeping the specimen temperature rise to less than $\sim 3\,°C$.

1. Introduction

The first measurement of thermal diffusivity using a pulse technique dates back to Parker *et al.* [1]. Because the sample size required is small and the geometry is simple, together with a rapid data acquisition, the flash-diffusivity technique has become an increasingly important and popular method for measuring the thermal diffusivity of a variety of solids. Later, Cape and Lehman [2] further modified Parker *et al.*'s model by taking the finite pulse-time effect into account to correct the diffusivity data with high accuracy.

Recently, a number of investigators [3–6] have found that the measured values of thermal diffusivity of solids decrease with increasing pulse energy. This observation was found to relate to several factors, such as uniformity of the energy pulse, specimen thickness, non-linearity of the infrared detector response, and the negative nature of the temperature-dependent thermal diffusivity of materials. Hasselman and Merkel [3] reported the effect of specimen thickness on measured values of the thermal diffusivity of aluminium nitride, a high thermal conductivity solid, with the conclusion that a small temperature rise of the specimen, not exceeding $\sim 1\,°C$, with a favourable specimen thickness of near 3 mm, is essentially required for a reliable measurement. The requisite of a smaller specimen temperature rise in their experiment is to ensure a linear response of the infrared detector which they used and to avoid a decreased diffusivity due to the strongly negative nature of the temperature-dependent diffusivity of AlN. A similar

trend was also seen in graphite materials [4]. In view of these experiments, all the diffusivities measured under a variety of test conditions for a specific material tend towards a limiting value, regardless of the thickness effect, once the specimen temperature rise approaches $0\,°C$. Because, to the best of our knowledge, most of the investigations concerning the above discussion are on high thermal conductivity materials, it is essential to consider whether a solid possesses low thermal conductivity, or even has a weaker temperature-dependent diffusivity. Therefore, in this study, a low-conductivity material [7], $(Sr, K)Zr_4(PO_4)_6$, was employed. The effect of sample thickness on the measured value of the thermal diffusivity of $(Sr, K)Zr_4(PO_4)_6(SrKZP)$ was investigated.

2. Experimental procedure

Specimens used for this study were cut ultrasonically from a single hot-pressed block of SrKZP into a disc shape with dimensions of 10 mm diameter, and thickness varying from 0.68–3 mm. These specimens were gold-sputtered to approximately 100 nm thick, followed by slightly coating with colloidal graphite in order to promote the entire absorption of incident pulse energy. The energy pulse was generated from a ruby laser having a beam diameter of 10 mm. The energy of the laser pulse was adjustable by controlling a capacitor discharge voltage, and the minimum voltage required to yield a uniform laser pulse was ~ 2.3 kV, corresponding to an energy of 2.5 J. The thermal diffusivity (Ulvac, Sinku-Riko, Inc., model

TC-3000H) of the specimens was obtained by monitoring the transient temperature of the rear face of the specimen by means of a liquid-nitrogen-cooled InSb infrared detector, which views the specimen, at a distance of 30 cm from the centre of the specimen, through a circular sapphire window of diameter 30 mm. To reduce the heat losses by any possible heat conductance, the specimen was mounted in a low-conductivity quartz glass sample protector and placed in a vacuum environment.

To facilitate the measurement, each specimen was attached on the rear face to a 0.1 mm diameter Pt–Rh thermocouple with the aid of silver paste, to allow simultaneous measurement of the specimen temperature rise, ΔT, during the measurement of thermal diffusivity.

Prior to conducting the experiment, it was necessary to examine the relation between specimen temperature rise and infrared detector output. A graphite disc, 3 mm thick, was employed with a thermocouple inserted into a hole of depth approaching the tip size of the thermocouple, and bonded with a silver paste. Fig. 1 shows the resulting non-linearity of the temperature rise–detector output relationship, which can be described by a third-power polynomial equation,

$$\text{Output (mV)} = 0.004\,(\Delta T)^3 + 0.104\,(\Delta T)^2$$
$$+ \ 4.128(\Delta T) + 0.256 \qquad (1)$$

Equation 1 is substantially different from that obtained in the system used by Hasselman and Merkel [3]. This finding implies that the ΔT–IR response correlation varies system by system and thus Equation 1 cannot be strictly applicable to other infrared detectors.

3. Results and discussion

Because the detector output varies with specimen temperature rise, ΔT, in a non-linear manner, Fig. 1 suggests that a temperature rise of no more than $\sim 3\,^{\circ}\text{C}$ is an essential requirement for a reasonable linear detector response. Nevertheless, sufficient deviation may arise between the detector and the real specimen temperature rise, ΔT, if ΔT is greater than $3\,^{\circ}\text{C}$, and which can cause significant error in quantitative estimation [4, 5].

The effect of specimen thickness on the thermal diffusivity of the SrKZP ceramic is illustrated in Fig. 2 with different pulse energies. The values of thermal diffusivity increase with specimen thickness, which resembles the trends for AlN [3] and graphite [4], up to a thickness of 2.5 mm. The diffusivity decreases with further increase of the specimen thickness. This decrease in diffusivity for a 3 mm thick specimen is probably due to an unfavourable specimen diameter to thickness ratio. The thermal diffusivity of the specimen in turn, decreases with increasing energy of the laser pulse for a given specimen thickness. The degree of the difference in diffusivity becomes more pronounced for the thinnest specimen than for the thicker one, e.g. 2.5 mm. This may be caused by a non-linearity response of the infrared detector output
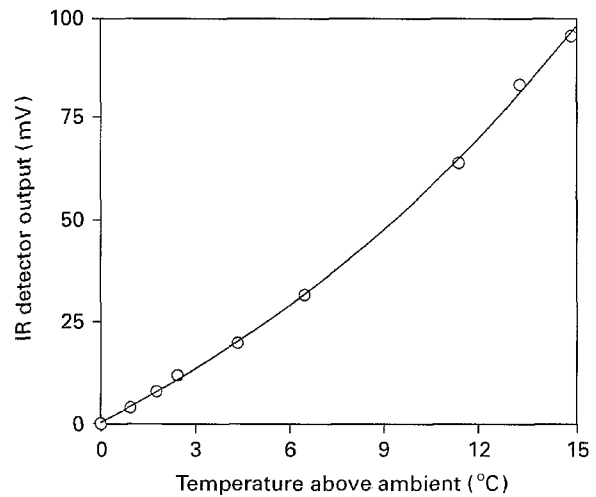

Figure 1 Response of the infrared detector as a non-linear function of specimen temperature rise, measured at 25 °C.
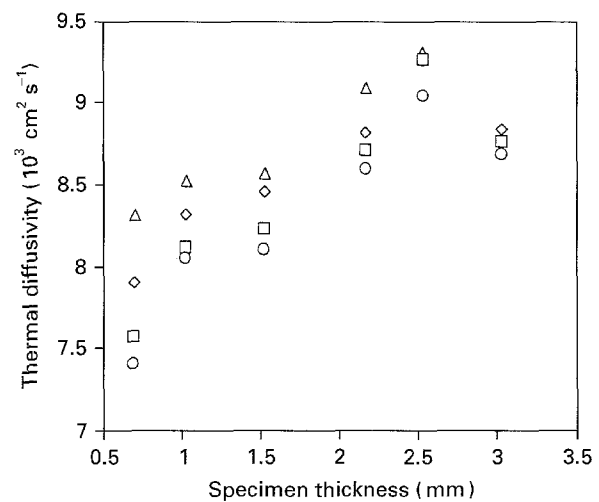

Figure 2 Thermal diffusivity of the SrKZP ceramic changes with specimen thickness for different pulse energies: (O) 10 J, (□) 8 J, (◇) 5 J, (△) 2.5 J.

mentioned above (Fig. 1 and Equation 1), because the temperature rise in the thinner specimen is higher than that in the thicker one for a given pulse energy. This non-linearity in detector output causes excessive temperature rise and leads to a lower value of diffusivity. Factors such as the negative temperature-dependent diffusivity of the SrKZP ceramic, even a weak dependence, may also have a certain contribution to reducing the thermal diffusivity, particularly for the thinner specimens.

Fig. 3 shows a summary of the experimental data for the thermal diffusivity measured for various specimen thicknesses and pulse energies with respect to specimen temperature rise. It is interesting that the thermal diffusivity of the ceramic approaches a limiting value depending on the specimen thickness as $\Delta T \to 0$. That is, specimens of different thicknesses exhibit different values of thermal diffusivity even when other effects, such as specimen temperature rise, non-linear response of the infrared detector, are neglected. This finding is significantly different from that observed in AlN, graphite, and metals such as copper,
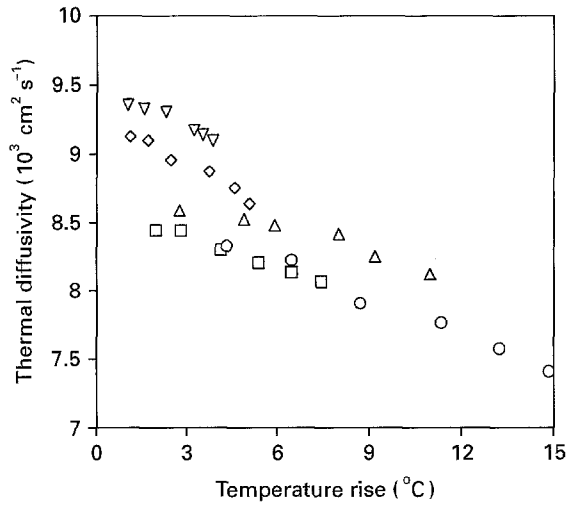
Figure 3 Thermal diffusivity of the SrKZP ceramic with respect to temperature rise at 25°C for various specimen thicknesses: (O) 0.68 mm, (□) 1.00 mm, (△) 1.50 mm, (◇) 2.14 mm, (▲) 2.50 mm.
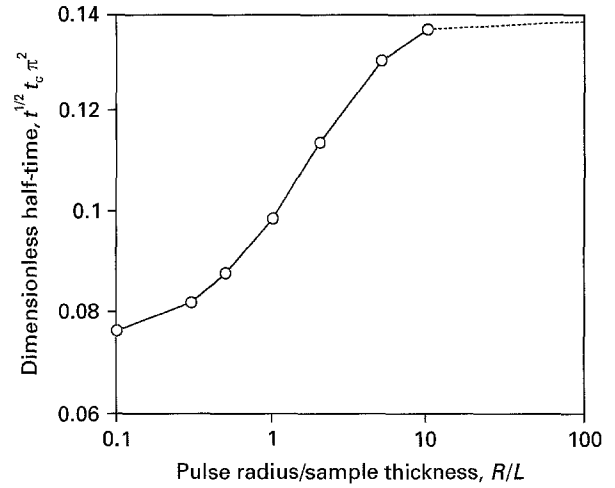

Figure 4 Dimensionless half-time as a function of the ratio of pulse radius, $R = 5$ mm, to specimen thickness, L.

iron [5, 6, 8]. Therefore, explanations appearing in the literature for the influence of specimen size, ΔT, and laser-beam uniformity, etc., are not satisfactory in accounting for this behaviour. Furthermore, the thermal diffusivity of the SrKZP ceramic is low and the laser pulse can be regarded as an instantaneous heat source, the finite pulse-time effects proposed by Cape and Lehman are negligible [2].

The thermal diffusivity, α, can be evaluated by the relation [9]

$$\alpha = (t_{1/2}/t_c) \, L^2/t_{1/2}\pi^2 \qquad (2)$$

where $t_{1/2}$ is the time required for the rear face of the specimen to reach half-maximum in its temperature rise and $t_c (= L^2/\pi^2\alpha)$ is defined as the characteristic time for a heat pulse to propagate the specimen of uniform thickness, L. For an adiabatic condition, $t_{1/2}/t_c = 1.37$ and Equation 2 can be rewritten [9]

$$\alpha = 1.37 L^2/t_{1/2} \, \pi^2 \qquad (3a)$$

or

$$\alpha = 0.1388 \, L^2/t_{1/2} \qquad (3b)$$

The numerical value 0.1388 is defined as a dimensionless half-time, τ, (i.e. $t_{1/2}/t_c\pi^2$) for the adiabatic case and which can be altered due to heat losses [2, 9, 10]. However, the thermal diffusivity determined from Equation 2 or 3 is strictly confined to one-dimensional (axial) heat conduction. For such a low thermal conductivity SrKZP ceramic, a longer t_c is a reasonable estimation and the consideration of a two-dimensional conduction analysis (axial and radial) is essentially required. Donaldson [11] considered a radial conduction effect in a specimen following an instantaneous disc source of energy and found that the dimensionless half-time ($\tau = t_{1/2}/t_c\pi^2$) can be modified according to the amount of heat loss (Y, usually from radiation), and ϕ, the ratio of pulse radius to sample thickness (R/L). By applying the dimensionless radial temperature distribution, T_r, appearing in Germand's

text [12], an integral function gives

$$T_r = \int_0^\phi \left(\frac{\delta'}{2\tau}\right) \exp\left(-\frac{\delta^2 + \delta'^2}{4\tau}\right) I_0\left(\frac{\delta \, \delta'}{2\tau}\right) d\phi \qquad (4)$$

where δ is referred to as the ratio of the radial position to the sample thickness, and ϕ is the ratio of the pulse radius ($R = 5$ mm in this study) to the sample thickness. For a specimen of thickness approaching 0, Equation 4 approaches unity, indicating a negligible radial conduction effect. The dimensionless axial temperature distribution, T_x, has the form

$$T_x = 1 + 2 \sum \cos(n \, \pi \, \xi) \exp(-n^2\pi^2\tau) \qquad (5)$$

where ξ is the ratio of axial position to the sample thickness. Equation 5 is valid only for a slight or negligible heat loss Y ($\simeq 4\varepsilon\sigma T^3/K$, where ε is the hemispherical total emissivity of the sample, σ is the Stephan–Boltzmann constant, and K the thermal conductivity of the material). The half-time, τ, due to radial conduction effect, can be deduced inversely from Equation 4 with respect to the specimen thickness and a resulting curve (for the case of $Y = 0$) is obtained as shown in Fig. 4. τ is close to 0.1388 (Equation 3) when the specimen thickness is below approximately 0.5 mm, in which case the radial conduction effect is negligibly small. Increase of the specimen thickness causes a decrease in τ, indicating an increasing degree of radial conduction effect for thicker specimens. On modification of the dimensionless half-time (in Equation 3) to the corresponding limiting thermal diffusivity for each specimen thickness, Table I gives the corrected thermal diffusivities for different thicknesses, which are closely consistent, regardless of the effect of specimen thickness. An average thermal diffusivity (7.84×10^{-3} cm^2 s^{-1}) is then obtained and is considered to be the true thermal diffusivity of the SrKZP ceramic. Accordingly, the optimum specimen thickness for an accurate measurement of the thermal diffusivity of the SrKZP ceramic should not be greater than 1 mm and to be more precise, 0.5–0.6 mm is favourable.

TABLE I The thermal diffusivity, (α) of the SrKZP ceramic of different thicknesses before (read from Fig. 3 as $\Delta T \rightarrow 0$) and after correction (taking the radial conduction effect into account, Fig. 4), for the case of negligible heat losses

Thickness (mm)	Limiting α (10^{-3} cm^2 s^{-1})	α after correction (10^{-3} cm^2 s^{-1})
0.68	8.35	7.98
1.00	8.49	7.93
1.50	8.60	7.70
2.14	9.25	7.85
2.50	9.37	7.75

Average thermal diffusivity = 7.84×10^{-3} cm^2 s^{-1}

4. Conclusion and implications

The effect of specimen thickness on the thermal diffusivity of a low thermal conductivity $(Sr, K) Zr_4(PO_4)_6$ ceramic was investigated by using a laser-pulse technique with various pulse energies. The increased thermal diffusivity due to increase of specimen thickness and decrease with increasing pulse energy was primarily a result of the non-linear response of the infrared detector coupled with an excessive specimen temperature rise (for $\Delta T > \sim 3\,°C$). Taking the radial conduction effect into account, a more reliable measurement of thermal diffusivity using a specimen of thickness not exceeding 1 mm (especially 0.5–0.6 mm), and a temperature rise less than $\sim 3\,°C$, can be achieved for the SrKZP ceramic.

In view of the present study, together with related reports in the literature, it is seen to be critically important to establish experimentally a thermal diffusivity–thickness correlation with more refinement for pulse methods for a wide variety of materials.

References

1. W. J. PARKER, R. J. JENKINS, C. P. BUTLER and G. L. ABBOT, *J. Appl. Phys.* **32** (1961) 1679.
2. J. A. CAPE and G. W. LEHMAN, *ibid.* **34** (1963) 1909.
3. D. P. H. HASSELMAN and G. A. MERKEL, *J. Am. Ceram. Soc.* **72** (1989) 967.
4. D. P. H. HASSELMAN and K. Y. DONALDSON, in "Thermal Conductivity 21", edited by C. J. Cremers and H. A. Tine (Plenum Press, New York, 1990) p. 123–32.
5. H. GROOT, in "Thermal Conductivity 20", edited by D. P. H. Hasselman and J. R. Thomas (Plenum Press, New York, 1989) pp. 357–66.
6. R. E. TAYLOR, in "Thermal Conductivity 19", edited by D. W. Yarbrough (Plenum Press, New York, 1988) pp. 403–12.
7. D. M. LIU, C. J. CHEN, and L. J. LIN, *J. Appl. Phys.* **75** (1994) 3765.
8. N. KURAMOTO, H. TANIGUCHI, and I. ASA, in "International Symposium on Ceramic Substrates and Packages", Denver, CO, 19–21 October 1988.
9. L. E. CLARK III and R. E. TAYLOR, *J. Appl. Phys.* **46** (1975) 714.
10. D. A. WATT, *Br. J. Appl. Phys.* **34** (1966) 926.
11. A. B. DONALDSON, *ibid.* **43** (1972) 4226.
12. H. H. GERMAND, "The Circular Coverage Function" (The Rand Corporation, Santa Monica, CA, 1950).