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Anisotropic thermal conductivity of thin polycrystalline oxide samples

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This paper reports about the development of a modified laser-flash technique and relation to measure the in-plane thermal diffusivity of thin polycrystalline oxide samples. Thermal conductivity is then calculated with the product of diffusivity, specific heat and density. Design and operating features for evaluating in-plane thermal conductivities are described. The technique is advantageous as thin samples are not glued together to measure in-plane thermal conductivities like earlier methods reported in literature. The approach was employed to study anisotropic thermal conductivity in alumina sheet, textured kaolin ceramics and montmorillonite. Since it is rare to find in-plane thermal conductivity values for such anisotropic thin samples in literature, this technique offers a useful variant to existing techniques. [http://dx.doi.org/10.1063/1.4836555]

I. INTRODUCTION

Efficient and accurate measurement of thermal conductivity is critical to the continued development of materials with engineered thermal transport properties for applications such as thermal management, thermoelectric and thermal insulation. Thermal characterization techniques should be simple and reliable despite being constrained by the unpredictable nature of the materials being tested. Conventional steady-state thermal conductivity measurement techniques like the heat flow meter[1] are simple and easy to use but are limited to certain ranges of values of thermal conductivity, often require specific geometries for testing, and even minor heat losses can significantly influence accuracy. In contrast, transient techniques, such as laser-flash or transient hot-strip, are known to be reliable over the entire range but conductivity measurements typically involve relatively complicated data analysis and are contingent upon the accurate determination of specific heat capacity and density.[2,3] Additionally, most conventional techniques, namely laser-flash or three-omega, may only provide an effective thermal conductivity when used for characterizing materials with anisotropic thermal properties unless modifications are applied.[2,4] Thus, a simple and versatile characterization technique that is capable of measuring the thermal conductivity in a particular direction without requiring any knowledge or assumption about the properties in the other directions is desirable.

The importance of the thermal conductivity measurements of thin samples has recently been recognized in parallel with the progress in various functional materials such as metallic glasses, super-lattice films and highly conductive substrates.[5] Anisotropic materials like muscovite are technologically important because of their properties of easy cleavage combined with sheet strength. Muscovite finds use in electrical components as an insulator and a dielectric and as a window in r.f. and infra-red radiation applications.[6] Textured ceramics obtained by the tape casting process also show alignment of grains resulting in anisotropy of the material.[7] Türkes *et al.*[8] studied thermal

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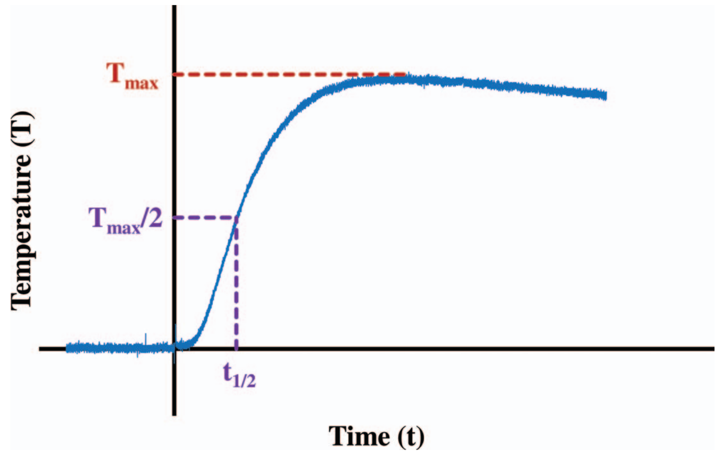

FIG. 1. Typical thermogram in laser-flash method.

conductivity of SnO_2 single crystals. They reported that phonon-phonon scattering and isotope scattering are two dominant scattering mechanisms in SnO_2 crystals and anisotropy of thermal conductivity is caused only by phonon-phonon scattering. Nishimura *et al.*[9] studied dielectric breakdown and thermal conductivity of textured alumina from platelets and reported that thermal conductivity of textured alumina was improved due to anisotropic grain growth. Effect of microstructure, grain size, pressure tuning, mineralogy and porosity and fluid control on thermal conductivity of anisotropic ceramics have been studied as relevant factors in earlier research.[10–15]

The present work sets out to study the anisotropic thermal conductivity in polycrystalline oxide materials. Standard methods to measure the thermal conductivity using a heat flow technique and laser-flash technique have been used wherever sample sizes were suitable for these methods. However, in the case of thin materials, it is difficult to measure in-plane thermal conductivity using these standard methods. So we have introduced a useful modification to the laser-flash technique and the associated relation to evaluate the in-plane thermal diffusivity. The approach has been tested on a number of anisotropic materials: alumina substrates, textured fired kaolin ceramics and textured montmorillonite.

II. PROPOSED NEW FORMULA FOR THERMAL DIFFUSIVITY BY USING MODIFIED LASER FLASH METHOD

The flash method to determine thermal diffusivity was first introduced by Parker *et al.*[2] in 1961. Nowadays, in this method the sample whose thermal diffusivity is to be determined is exposed to a laser beam pulse and the temperature of the rear surface of the sample is recorded using oscilloscope connected via thermocouple. The thermal conductivity is calculated by product of heat capacity, thermal diffusivity and density. The thermal diffusivity in Parker's method is given by the following expression:

$$\alpha = \frac{0.139\ell^2}{t_{1/2}} \tag{1}$$

where ℓ is the thickness of the sample and $t_{1/2}$ is the time to reach half of the maximum temperature in the thermogram (Fig. 1). The Parker's model ignores the heat loss due to convection-radiation or residual thermal contact with the sample holder.

Degiovanni[15] has developed a model to take into account the heat losses on all sides of a cylindrical sample. Heat exchange coefficients are used that may be different on upper and lower side surfaces. In this model, the calculation of the diffusivity requires values at particular times of the temperature-time behaviour. In noting $t_{1/3}$, $t_{1/2}$, $t_{2/3}$ and $t_{5/6}$, the times needed for the temperature to reach the corresponding fractions to its maximum temperature, Degiovanni proposed equations to calculate thermal diffusivity. As an example, one of these is given by following expression:

$$\alpha = \frac{e^2}{t_{5/6}}\left[0.968 - 1.6382\frac{t_{1/2}}{t_{5/6}} + 0.6148\left(\frac{t_{1/2}}{t_{5/6}}\right)^2\right] \tag{2}$$

The thermal conductivity is then calculated with the relation

$$\lambda = \alpha\rho C_p \tag{3}$$

where α = thermal diffusivity, ρ = apparent density and C_p = specific heat capacity.

By considering resolution of the heat equation in the case of radial heat flow, Yang *et al.*[16] proposed a relation for determining thermal diffusivities of thin samples by a laser- flash method. When a focused laser beam irradiates a disc sized thin sample, the temperature versus time curve at a radial position ℓ is assumed to be obtained under thermally insulating conditions and the thermal diffusivity is given by:[16]

$$\alpha = 0.112\frac{\ell^2}{t_{1/2}} \tag{4}$$

Starting from equation (4) we propose a useful variation in the method for calculating the in-plane thermal conductivities of thin samples.

Rearranging equation (4)

$$\ell^2 = \frac{\alpha t_{1/2}}{0.112} \tag{5}$$

Taking the square root of equation (5)

$$\ell = \sqrt{\frac{\alpha t_{1/2}}{0.112}} \tag{6}$$

Differentiating ℓ with respect to $\sqrt{t_{1/2}}$ yields

$$\frac{d\ell}{d\sqrt{t_{1/2}}} = \sqrt{\frac{\alpha}{0.112}} \tag{7}$$

Squaring equation (7)

$$\alpha = 0.112\left(\frac{d\ell}{d\sqrt{t_{1/2}}}\right)^2 \tag{8}$$

If we vary the distance between the laser spot and the temperature measurement point, we can then plot distance versus the square root of the time to reach half the maximum temperature $t_{1/2}$ which should give linear behavior providing a constant value of α corresponding to homogeneous material can be assumed.

The slope of thus obtained graph is

$$\frac{d\ell}{d\sqrt{t_{1/2}}}$$

Using above derived equation (8), we have a measure of the in-plane thermal diffusivity for a thin sample. The conductivity is then deduced with equation (3). A useful advantage is that the systematic error in $t_{1/2}$ due to heat losses will tend to compensate in the slope evaluation for equation (8), improving the accuracy of diffusivity values.

III. MODIFIED LASER FLASH METHOD FOR MEASURING IN-PLANE THERMAL CONDUCTIVITY

We thus propose a modified laser-flash method to measure the in-plane thermal conductivity of thin samples which can avoid difficulties of the standard procedure due to the limited dimension perpendicular to the thin film plane. The experimental set-up consists of a neodymium glass laser (Quantel brand) operating at 1.06 μm with a pulse duration of 450 μs. The output beam has a

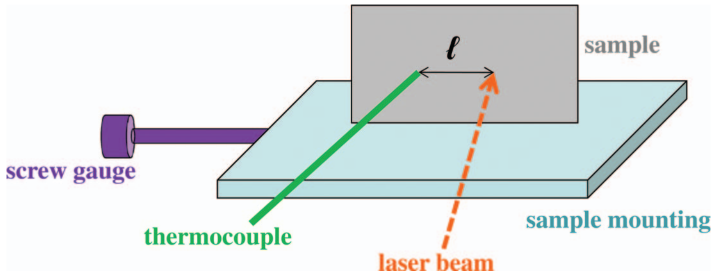

FIG. 2. Schematic diagram of modified laser flash method set-up.

TABLE I. Material selection.

Sample	Thickness (mm)	Density(kg/m^3)	Cp (JKg^{-1}K^{-1})
Alumina sheet	0.62	3900	775
Textured kaolin bip sintered at 1050 °C	0.35	2040	750
Montmorillonite	0.66	1952	753

diameter of 16 mm and its divergence is 4 milli radians. The energy sent by the laser can be adjusted between 28 J and 128 J.

To measure in-plane thermal conductivity, the infrared detector used in the standard laser flash method was replaced with a thermocouple situated on the receiving surface of the planar sample at a 10–20 mm from the centre of the laser beam spot. Similar to Parker's original work, the Chromel-Alumel thermocouple wires were separated by 1–2 mm on the sample surface, with the electrical contact made through silver paste. The thermocouple was connected to the oscilloscope via an amplifier. If the electrical resistance measured across the thermocouple wires was found to be a few ohms, then the signal to noise ratio was sufficient. We try to make the laser beam spot as small as possible to approach a point source. The sample set-up including the thermocouple was then mounted which is movable on a screw gauge translation table to vary the distance between heat source and measurement point. It is important that the laser beam spot and thermocouple contact point are at the same horizontal level as shown in Fig. 2.

It is difficult to precisely measure the distance between the laser spot and the thermocouple contact point but equation (8) only requires the relative distances between measurement points for the evaluation of the slope in the plot of distance versus square root of $t_{1/2}$. In this work, the observation points have been separated by 1.27 mm which is the displacement corresponding to two turns of screw gauge.

IV. MATERIAL SELECTION

The various materials tested in this study were alumina sheet, textured kaolin bip and textured montmorillonite. The thickness, heat capacity and density values for these materials are listed in Table I.

The alumina sheet was microelectronic grade (supplied by SYSTREL, France).

Texured kaolin bip were made with tape casting process. To prepare the tape casting slurry, a kaolin based powder (BIP Kaolin from Denain-Anzin-Minéraux) was first dispersed in water with an addition of 0.3 wt% of a huminate silicate (Dolaflux B, Ceradel). An amount of 5.5 wt% of both binder (PolyVinyl Alcohol 22000, VWR) and plasticizer (PolyEthylene Glycol 300, Merck eurolab) was used to avoid cracking of the green tape after drying. Moreover, 0.1 wt% of defoamer (Contraspum, Zschimmer & Schwarz) was required to limit the formation of air bubbles in the suspension. Batches of 100 g kaolin powder were dispersed in water with defoamer by ball milling for 1 hour and 20 minutes at 180 revolutions per minute (rpm). The second step consists of adding

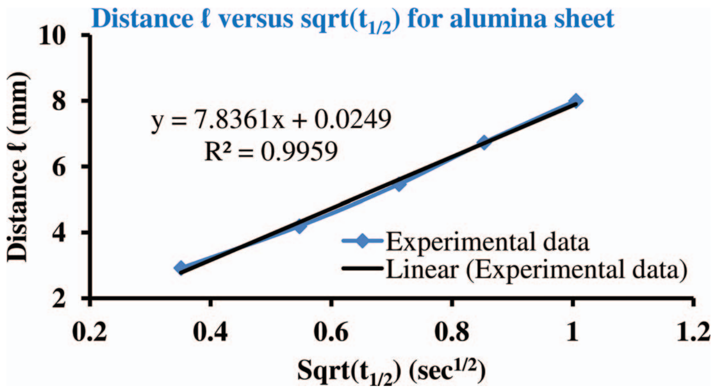

FIG. 3. Distance versus sqrt($t_{1/2}$) for alumina sheet.

PVA binder and PEG plasticizer and all the mixture is homogenized for approximately 16 hours at 100 rpm. Before tape casting, the overall mixture is sieved (63 μm) to remove possible agglomerates of kaolin/fibers and coarse air bubbles. To reduce significantly the number of smaller air bubbles, the suspension is submitted to a roller shaker for 5 hours at 60 rpm. The tape caster operating with a doctor blade was adjusted to a speed of 1 cm s^{-1} in order for the laminates to exhibit a thickness close to 700 μm. Mylar (HiFi Industrial film) with a thickness of 36 μm has been used as carrier film. At room temperature, the green tapes were very slowly dried for 24 hours in an enclosed space swept slowly with humid-air to avoid the risk of skin formation and cracking. After drying, disks of 30 mm in diameter were cut from the initial green tape. In the lamination step, 12 individual disks have been randomly stacked taking into account of the casting orientation. These stacks were then thermo-pressed at 60 °C in two steps: (i) 15 min at a pressure of 1 MPa in order for the stack to reach the pressing temperature without significant volume change and (ii) 5 min at a pressure of 5 MPa to ensure a good adhesion at the interfaces (due to the plasticizer now above its glass transition). Before sintering at 1050 °C for 2 hours and a heating rate of 5 °C/min, binder removal of green samples has been made at a constant heating rate of 0.2 °C/min upto1050 °C in air which had been layered. Montmorillonite samples prepared according to the protocol described by Bennadji-Gridi *et al.*[17] were also tested.

V. RESULTS AND DISCUSSION

Cross-plane and in-plane thermal conductivity measurements were performed for alumina sheet, textured kaolin bip sintered at 1050 °C and montmorillonite. The cross plane thermal conductivities were measured using standard laser flash method and heat flow meter while in-plane thermal conductivities were measured by newly developed modified laser flash method as described in section III and using formula derived in section II. The modified laser flash technique was studied for materials over a wide range of thermal conductivities. The newly developed modified laser-flash technique was verified for kaolin bip samples by comparing the in-plane thermal conductivity values measured by standard and modified laser-flash technique.

A. Thermal conductivity of alumina sheet

The cross plane thermal conductivity of the alumina sheet was measured using laser-flash method and is found to be 16.77 $Wm^{-1}K^{-1}$. The in-plane thermal conductivity was measured using modified laser-flash method. Fig. 3 represents the plot between the distance versus square root of the time corresponding to half of the maximum temperature obtained in the oscilloscope.

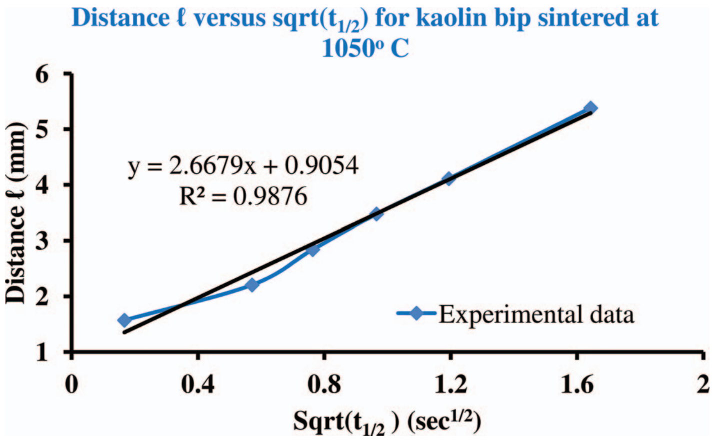

FIG. 4. Distance versus sqrt($t_{1/2}$) for kaolin bip.

According to this graph, it has been concluded that the slope of the graph between distance versus square root of the time to reach half the maximum temperature $t_{1/2}$ for alumina sheet is 7.836 mm.second$^{-1/2}$.

Hence the in-plane thermal diffusivities and in-plane thermal conductivities are:

$\alpha_{alumina\ sheet} = 0.112\left(7.836 \times 10^{-3}\right)^2 = 6.877 \times 10^{-6}$ m^2/s (using equation (8))

$\lambda_{alumina\ sheet} = \alpha\rho C_p = \left(6.877 \times 10^{-6}\right)(3900)(775) = 20.78$ Wm^{-1}K^{-1}

This gives the in-plane thermal conductivity of alumina sheet to be 20.78 Wm^{-1}K^{-1}.

The anisotropy ratio (in plane thermal conductivity to cross plane thermal conductivity ratio) is 1.24. The alumina samples are generally homogeneous and the anisotropy ratio should be equal to 1. However in this case since the thickness of the alumina sample is 0.62 mm, there is certainty that the grains are textured. So the anisotropy ratio here is justified.

B. Thermal conductivity of kaolin bip

The kaolin bip samples sintered at 1050 °C were cut to appropriate size to measure cross plane and in-plane thermal conductivity of the sample. The cross plane thermal conductivity of the kaolin bip sintered at 1050 °C is found to be 0.51 Wm^{-1}K^{-1} using laser-flash method. The in-plane thermal conductivity was measured using modified laser-flash method.

The Fig. 4 shows the plot between the distance versus square root of the time corresponding to half of the maximum temperature obtained in the oscilloscope. According to this figure, the slope of the graph between distance versus square root of the time to reach half the maximum temperature $t_{1/2}$ for kaolin bip is 2.668 mm.second$^{-1/2}$.

Hence the in-plane thermal diffusivities and in-plane thermal conductivities are:

$\alpha_{kaolinbip} = 0.112\left(2.668 \times 10^{-3}\right)^2 = 7.97 \times 10^{-7}$ m^2/s (using equation (8))

$\lambda_{kaolinbip} = \alpha\rho C_p = \left(7.97 \times 10^{-7}\right)(2040)(750) = 1.22$ Wm^{-1}K^{-1}.

Therefore, the in-plane thermal conductivity of the kaolin bip sintered at 1050 °C is 1.22 Wm^{-1}K^{-1}.

The ratio of in-plane thermal conductivity to cross plane thermal conductivity for kaolin bip sintered at 1050 °C is 2.39. The anisotropy of kaolin bip is justified on the basis of microstructure as we can clearly see the aligned grains i.e. textured structure (see Fig. 5).

C. Thermal Conductivity of Montmorillonite

The cross plane thermal conductivity of montmorillonite was measured using laser-flash method and is found to be 0.20 Wm^{-1}K^{-1}.

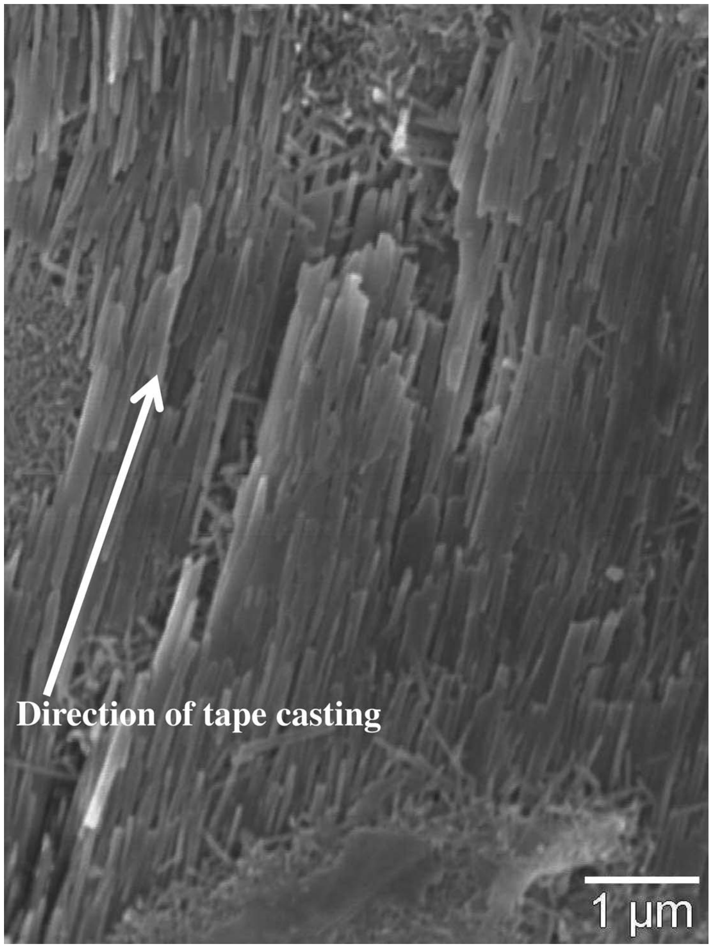

FIG. 5. Textured kaolin bip ($\lambda_{ab} = 1.22\ Wm^{-1}K^{-1}$, $\lambda_c = 0.51\ Wm^{-1}K^{-1}$).

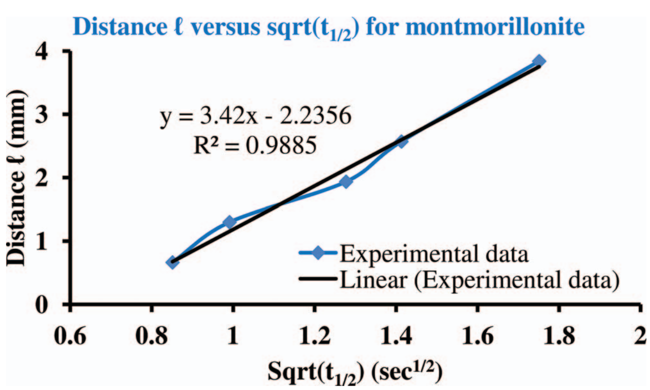

FIG. 6. Distance versus sqrt($t_{1/2}$) for montmorillonite.

The in-plane thermal conductivity of montmorillonite was measured using our new modified laser-flash method and the formula used for calculating the in-plane thermal conductivity is explained in experimental procedure.

Fig. 6 shows the plot between the distance versus square root of the time corresponding to half of the maximum temperature obtained in the oscilloscope.

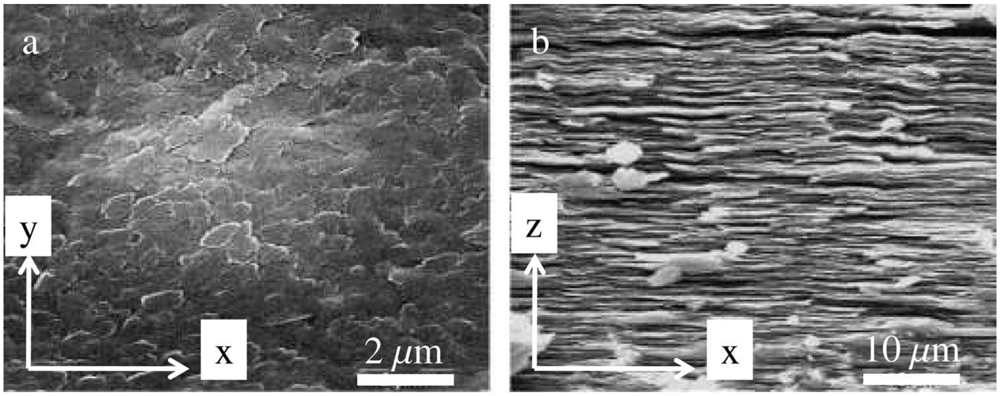

FIG. 7. (a) upper surface of montmorillonite (textured like nacre) (b) fractured surface of textured montmorillonite[17] ($\lambda_{ab} = 1.92$ Wm^{-1}K^{-1}, $\lambda_c = 0.20$ Wm^{-1}K^{-1}). Reprinted with permission from F. Bennadji-Gridi, A. Smith, and J.-P. Bonnet, Materials Science and Engineering: B **130**, 132 (2006). Copyright 2006 Elsevier.

TABLE II. Thermal diffusivities of various samples.

Sample	Cross-plane thermal diffusivity (experimental value) m^2/s	In-plane thermal diffusivity (experimental value) m^2/s
Alumina sheet	5.55×10^{-6}	6.877×10^{-6}
Textured kaolin bip sintered at 1050 °C	3.33×10^{-7}	7.97×10^{-7}
Montmorillonite	1.36×10^{-7}	1.310×10^{-6}

TABLE III. Thermal conductivities of various samples.

Sample	Cross-plane thermal conductivity (experimental value) Wm^{-1}K^{-1}	In-plane thermal conductivity (experimental value) Wm^{-1}K^{-1}	Anisotropy ratio
Alumina sheet	16.77	20.78	1.24
Textured kaolin bip sintered at 1050 °C	0.51	1.22	2.39
Montmorillonite	0.20	1.92	9.60

According to this figure, the slope of the graph between distance versus square root of the time to reach half the maximum temperature $t_{1/2}$ for montmorillonite is 3.42 mm.second$^{-1/2}$.

Hence the in-plane thermal diffusivities and in-plane thermal conductivities are:

$\alpha_{montmorillonite} = 0.112\left(3.42 \times 10^{-3}\right)^2 = 1.310 \times 10^{-6}$ m^2/s (using equation (8))

$\lambda_{montmorillonite} = \alpha\rho C_p = \left(1.310 \times 10^{-6}\right)(1952)(753) = 1.92$ Wm^{-1}K^{-1}.

This gives the in-plane thermal conductivity of montmorillonite to be 1.92 Wm^{-1}K^{-1}.

The ratio of in-plane thermal conductivity to cross-plane thermal conductivity is 9.60.

The high anisotropic thermal conductivity ratio is justified by the textured structure of montmorillonite shown in Fig. 7.

Table II lists the experimental values of cross-plane and in-plane thermal diffusivities of various materials. Table III lists the experimental values of cross-plane and in-plane thermal conductivities of various materials. According to literature survey, no data appears to be available relating to cross-plane and in-plane thermal diffusivities/ thermal conductivities for such anisotropic materials. For validation of this technique, we cut the kaolin bip sample in perpendicular direction and put the sample in such a way that cross-plane thermal conductivity measured by standard laser flash technique should be equal to in-plane thermal conductivity measured by modified flash laser method developed in this study. We found these values to be same which validates the accuracy of this technique.

VI. CONCLUSIONS

The results show that the cross-plane thermal conductivity of alumina sheet, kaolin bip and montmorillonite found using laser-flash method were 16.77, 0.51, 0.20 $Wm^{-1}K^{-1}$ respectively. A new modified laser-flash method has been developed for measuring in-plane thermal conductivity of thin polycrystalline oxide samples. In-plane thermal conductivities of alumina sheet, kaolin bip, and montmorillonite were measured using new modified laser-flash method and a formula was derived to calculate the thermal conductivity which is useful when it is difficult to measure the precise distance between laser spot and thermocouple contact. The new formula uses just the lateral displacement of laser spot which can be measured accurately using screw gauge attached to the mounting.

The in-plane thermal conductivity of alumina sheet, kaolin bip and montmorillonite found using new modified laser-flash method were 20.78, 1.22, 1.92 $Wm^{-1}K^{-1}$ respectively.

In the cases of kaolin and montmorillonite the anisotropic ratios are justified on the basis of textured morphology related to the processing method.

The modified laser flash method was successfully tested for various thicknesses listed in Table I. Therefore, this method is proved to be promising for measuring in-plane thermal conductivities of thin polycrystalline oxide samples.

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Abhishek Tiwari designed and performed the experiments and wrote the paper. Kévin Boussois and Philippe Blanchart helped with a few samples. David Stanley Smith and Benoît Nait-Ali directed the research.

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