Laser-induced thermal characterization of nano Ag metal dispersed ceramic alumina matrix

Sajan. D. George[1*], Aji A Anapara[2], K. G. K Warrier[2],
P.Radhakrishnan[1], C. P. G. Vallabhan[1] and V. P. N. Nampoori[1]
[1]International School of Photonics, Cochin University of Science and Technology
Kochi, India – 682 022
[2] Ceramic Technology Division, Regional Research Laboratory, CSIR, Thiruvananthapuram, India – 695 019

ABSTRACT

In this paper, we report the measurements of thermal diffusivity of nano Ag metal dispersed ceramic alumina matrix sintered at different temperatures using laser induced non-destructive photoacoustic technique. Measurements of thermal diffusivity also have been carried out on specimens with various concentration of nano metal. Analysis of the data is done on the basis of one-dimensional model of Rosencwaig and Gersho. The present measurements on the thermal diffusivity of nano metal dispersed ceramic alumina shows that porosity has a great influence on the heat transport and the thermal diffusivity value. The present analysis also shows that the inclusion of nano metal into ceramic matrix increases its interconnectivity and hence the thermal diffusivity value. The present study on the samples sintered at different temperature shows that the porosity of the ceramics varies considerably with the change in sintering temperature. The results are interpreted in terms of phonon assisted heat transfer mechanism and the exclusion of pores with the increase in sintering temperature.

Keywords: Photoacoustic, sol-gel, ceramics, thermal properties, nano composite

INTRODUCTION

Ceramic materials play a very important role in the fabrication of electronic and optoelectronic devices. Ceramic alumina is considered to be an ideal candidate for the optical, thermal and structural applications due to its special properties such as tunable electrical properties, toughness, high temperature tolerance, light weight and excellent resistance against corrosion and wear [1-2]. The thermal properties of these ceramics are basically determined by their composition and structure. It is the rate of heat diffusion that essentially determines the thermal shock resistance of brittle solids such as ceramics. In such materials, thermal accumulation causes thermal induced stresses in the sample, which in turn causes catastrophic failure and deterioration in ceramic-based devices. The thermal shock resistance of the ceramics can be improved by the incorporation of a metal with high thermal conductivity value into the ceramic matrix [3]. In the recent years, fabrication of nano metal dispersed ceramics has gained much attention due to its excellent structural and electrical properties. In addition, these materials posses excellent chemical inertness, good oxidation resistance and an enhanced toughness. It has been observed that the nano metal dispersed ceramics exhibit different thermal characteristics compared to the intrinsic bulk specimen. Thermal diffusivity value is an important thermophysical parameter in this context, as this quantity determines the heat propagation and thermal shock resistance in these materials.

During the last two decades, the non destructive and non intrusive laser induced photothermal methods have emerged as an effective research and analytical tool for characterizing the thermal, optical and transport properties of a variety of materials such as ceramics, liquid crystals, semiconductors etc [4-8]. All these photothermal methods are based on the detection, by one means or other, of a transient temperature change that characterizes the thermal waves generated in the sample due to the nonradiative deexcitation followed by an intensity modulated optical excitation. In the simple and elegant photoacoustic (PA) technique, these periodic thermal waves causes density fluctuation in the sample and in the coupling medium.

*sajan@cusat.ac.in, International School of Photonics, Cochin University of Science and Technology, Kochi, India –682 022

These density fluctuations can be detected either by a piezoelectric transducer or by a sensitive microphone. The measured PA signal depends on the interplay of three factors namely, the optical absorption coefficient of the sample at the incident wavelength, light to heat conversion efficiency and the rate of heat diffusion through the sample. The dependence of PA signal on the rate of heat diffusion allows us to evaluate the thermal parameters of the sample, especially thermal diffusivity. Like optical absorption coefficient, thermal diffusivity is an important thermophysical parameter for device modeling and system fabrication. Physically, the inverse of thermal diffusivity is a measure of the time required to establish the thermal equilibrium in the sample in which a transient temperature change has occurred. The thermal diffusivity of the sample depends strongly on the structural properties of the sample [9].

In this paper we report the measurement of thermal diffusivity of nano sized Ag dispersed ceramic alumina matrix prepared by sol-gel method with varying concentration of Ag and sintered at different sintering temperature.

PREPARATION OF NANOCOMPOSITE

The composite precursor was prepared from a mixture of boehmite (Al-O-OH) and silver nitrate. In a typical experiment, 1000 ml of boehmite (Al-O-OH) sol was prepared by hydrolyzing 250 gm of $Al(NO_3)_3.9H_2O$ [S. D. Fine Chemicals, India] dissolved in 500ml of double distilled water followed by peptisation using nitric acid. Silver nitrate [Glaxo Laboratories, India, Purity – 99%] in aqueous solution (5gm in 100ml) is added in different weight proportions (0%, 1% and 5 % with respect to aluminium oxide), to the boehmite sol in separate batches and subjected to a mechanical stirring for a period of 4hours. The sol was first evaporated on a water bath and finally was dried at 90^0C. The precursor gel was further calcined at 450^0C for a period of 3hours. The nanocomposite samples were prepared by uniaxial consolidation to disc pellets of size 10mm diameter and 1mm thickness using a force of 4 tons for two minutes using hydraulic press. Care was taken to pelletise all the samples at identical experimental conditions. The pelletised samples are sintered at 700^0C and 800^0C with a soaking period of 3hours, to study the influence of sintering temperature on thermal diffusivity. The sintering temperature was limited due to the fact that the melting point of Ag is ~960^0C.

The Thermo Gravimetric (TG) studies undertaken by TGA-50H thermal analyzer (Shimadzu-50H, Japan) and the Differential Thermal Analysis (DTA) pattern taken by Shimadzu-50H, Japan confirm the Ag^+ ion formation. The XRDs of the specimens show that the samples are semicrystalline in nature. The microstructure of the sample is analyzed using Transmission Electron Microscopy (JEOL 3000 EX; JAPAN with an acceleration voltage 300KV and a resolution of less than 0.2 nm) and it is seen that Ag particles are almost uniformly dispersed and the particle size in the dispersed phase ranges between 5 and 20nm.

The density of the composite is determined by a water displacement method. The measured density is divided by a corresponding theoretical density, which gives the volume fraction or relative density (x) of the specimen. Then the porosity of the material is given by $p = 1 - x$ [10]. The values of porosities of specimen under study are incorporated into table I

EXPERIMENTAL SETUP

Optical radiation from an Argon ion laser at 488nm (Liconix 5300) is used as the source of excitation, and it is intensity modulated using a mechanical chopper (Stanford Research Systems SR 540) before it strikes the sample surface. Detection of pressure fluctuation (photoacoustic signal) in the cell cavity is done using a sensitive microphone (Knowles BT 1754). The amplitude of the photoacoustic signal is measured using a dual phase lock-in amplifier (Stanford Research Systems SR 830). The laser power used for the present studies is 50 mW with a stability of ± 0.5%. The experimental set up used for the present investigation is explained elsewhere [6].

THEORETICAL BACKGROUND

According to one dimensional model of Rosencwaig and Gersho [7], the pressure variation δP at the front surface of an optically thick ($l >> 1/\beta$, where β is the optical absorption length) sample irradiated with a chopped beam of monochromatic radiation depends on the thermal diffusivity α_s of the sample. The theoretical expression for δP may be written as

$$\delta P = X.Y \qquad (1)$$

In the above relation

$$X = \left[1 + g\,\frac{h^+ + h^-}{h^+ - h^-}\right]^{-1}\left[g + \frac{h^+ + h^-}{h^+ - h^-}\right]\frac{1}{\alpha_s^2 l_s^2} \tag{2}$$

where

$$h^+ = \exp.(\sigma_s l_s)$$

$$h^- = \exp.-(\sigma_s l_s)$$

$$\sigma_s = (1+j)\left[\frac{\pi f}{\alpha_s}\right]^{1/2} \tag{3}$$

$$g = \frac{e_b}{e_s} = \left[\frac{K_b}{K_s}\right]\left[\frac{\alpha_s}{\alpha_b}\right]^{1/2} \tag{4}$$

the ratio between the effusivities of the backing material (e_b) and the sample (e_s) and

$$Y = \frac{P_0 \gamma W_a I_s^2}{2 l_g T_0 K_s}\left[\frac{\alpha_g}{\alpha_s}\right]^{1/2} \tag{5}$$

Here l, K, ρ and C are the length, thermal conductivity, mass density and specific heat capacity and subscripts g, s and b refer to the gas (air), sample and backing material respectively. P_0 (T_0) is the ambient pressure (temperature), γ is the specific heat ratio for the air. W_a is the absorbed power of light. The effusivity of the gas in the cell has been neglected compared to the effusivity of the sample, since their ratio is always less than 1%. The term X depends on the modulation frequency f_c through the product $\sigma_s l_s$, which can be written as

$$\sigma_s l_s = (1+j)\left[\frac{\pi f}{f_c}\right]^{1/2} \tag{6}$$

where characteristic frequency f_c is given by

$$f_c = \frac{\alpha_s}{l_s^2} \tag{7}$$

When the thermal diffusion length $\left[\mu = \left(\alpha/\pi f\right)^{1/2}\right]$ is greater than sample thickness, the thermal properties of backing material modify the PA signal. But in the thermally thick regime the PA signal is independent of thermal properties of the backing material. For a given sample thickness, one can have transition from thermally thin regime to thermally thick regime by increasing the chopping frequency. Hence in the log (amplitude) versus log (frequency) plot a slope change occurs at the characteristic frequency (f_c) which indicates this transition. Knowing the characteristic frequency and sample thickness we can calculate thermal diffusivity as $\alpha_s = l_s^2 f_c$ (8)

RESULTS AND DISCUSSIONS

Initially, the experimental set up was standardized with the evaluation of thermal diffusivity values of pure copper and aluminium, thermal diffusivity values of which are well established. The thermal diffusivity values evaluated for copper and aluminium are 1.18 ± 0.003 cm^2s^{-1} and 0.970 ± 0.004 cm^2s^{-1} respectively, which agrees well with earlier reported values [4]. Figure 1 shows the log f versus log PA amplitude plot for the pure alumina sintered at 700^0C. By knowing the transition frequency, the thermal diffusivity value is evaluated as 0.210 ± 0.002 cm^2s^{-1}. Similar graphs are obtained for all the other samples under investigation (not shown here).

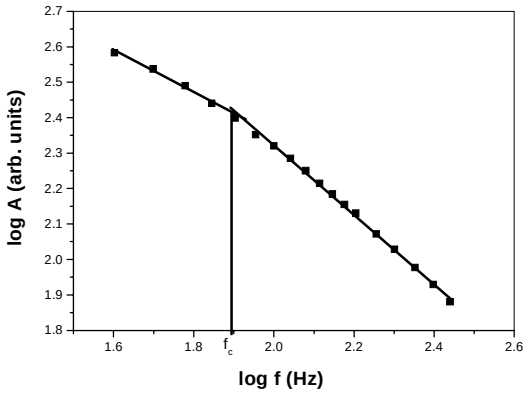

Figure 1: Log-log plot of PA amplitude against frequency for pure alumina sintered at 700^0C

The evaluated thermal diffusivity values of pure and nano Ag (1% and 5 %) dispersed ceramic alumina matrix are given in the table. The corresponding values for the samples sintered at 800^0C are also given in table I.

Table I
Thermal diffusivity of Alumina with varying concentration of Ag sintered at different temperature

Amount of Ag (in %)	Porosity (1-x)	Thermal diffusivity (cm^2s^{-1})	Evaluated value of thermal diffusivity from equation (9)
Specimen sintered at 700^0C			
0	0.488	0.210 ± 0.002	0.210
1	0.450	0.220 ± 0.003	0.220
5	0.349	0.242 ± 0.003	0.240
Specimen sintered at 800^0C			
0	0.481	0.240 ± 0.003	0.240
1	0.418	0.280 ± 0.004	0.280
5	0.234	0.360 ± 0.004	0.362

It is clear from the table that for the specimens sintered at a particular temperature, the value of thermal diffusivity increases with Ag content. This can be understood in terms of variation in porosity with the inclusion of nano metal and carrier assisted heat transfer mechanism in the samples. From the tables, it is also obvious that the porosity of the samples decreases with inclusion of nano metal. This is because the inclusion of metal increases the relative density of the composite and results in a higher mechanical strength. This fact has wide applicability in device fabrication. In order to explain the variation in thermal diffusivity with porosity, we considered the specimen as a two-phase mixture of regular shaped particles embedded in a continuous matrix. The corresponding thermal conductivity of the specimen is given by the Leob equation $K_c(p) = K_0(1-p)$ where K_0 is the thermal conductivity of the specimen having zero porosity (p). Correspondingly, the thermal diffusivity value of the specimen having porosity ' p ' is given by the expression $k_c(p) = k_0 \frac{(1-p)}{(1-p)}$ resulting in thermal diffusivity values, which are independent of porosity. But the experiments show that there is a strong dependence of porosity on thermal diffusivity value.

In order to incorporate the influence of pores into the propagation of thermal waves and hence the thermal diffusivity value A. Sanchez etal. [10] modified the Leob equation for the evaluation of thermal diffusivity value as

$$k_c(p) = k_0 \frac{(1-\gamma p)}{(1-p)} \qquad (9)$$

where γ is an empirical constant which essentially determines the significance of pores of thermal diffusion processes. The evaluated values of γ are 1.264 and 1.472 for the specimens sintered at 700^0C and 800^0C respectively. The value of γ >1 also implies the fact that the effect of porosity on heat conduction processes is not a mere density effect (air holes in the bulk volume) but it is also related to the structure of the material. Thus enhancement in relative density with the inclusion of metal into the ceramic matrix and consequent lowering of porosity of the specimen result in the efficient heat transfer in the metal dispersed ceramics which in turn causes higher value for thermal diffusivity. Besides that, in the case of metal dispersed ceramics, the interconnected metal network provides an efficient way to heat transport processes across the composite by electron and therefore enhances the thermal diffusivity value. Thus in the case of metal dispersed ceramic matrix heat is essentially carried by both phonons and electrons. Such an increase in thermal diffusivity with the inclusion of Ag doped Zirconia composites have already been reported [11]. An increased thermal diffusivity (thermal conductivity) reduces thermal accumulation in the specimen and a consequent increase in the resistance against thermally induced fracture and enhances its applicability in the industry.

It is also seen from the tables that the sintering temperature also influences the thermal diffusivity value. Calcination of the specimen during its preparation results in the expulsion of organic material, volatile impurities and moisture content in the sample. The treatment of gel at higher temperature (sintering) substantially reduces the number of pores in the lattice and enhances the connectivity. This fact is obvious from the relative density measurements, that the relative density increases with sintering temperature, which in turn results in the lowering of porosity with sintering temperature. The reduction in pores in the lattice reduces scattering centers for heat carriers and increases its mean free path. This increase in the mean free path of heat carriers results in an increased value of thermal diffusivity [12] of the specimens sintered at higher temperature. It is worthwhile to point out that the calculated values of thermal diffusivity using equation (9) for the specimens having zero porosity are 0.281 cm^2s^{-1} and 0.4256 cm^2 s^{-1} respectively which in turn suggests that the connectivity and heat transport by carriers are increases with sintering temperature and it is not mere the porosity that determines the thermal diffusivity value. Thus from the analysis it is obvious that the porosity decreases with sintering temperature which results in a higher value for thermal diffusivity with sintering temperature

CONCLUSION

In the present study, we have measured the important thermophysical parameter namely thermal diffusivity of pure alumina and nano Ag metal dispersed alumina ceramic matrix prepared by gel route. The present investigation throws light into the dynamics of heat diffusion process in the two-phase network. The present study also shows the heat diffusion processes, which is essentially characterized by the thermal diffusivity value, is sensitive to porosity of the specimen as well as to the inclusion of foreign atom into the host lattice. Present investigation shows that thermal diffusivity value increases with decrease in porosity as well as with increase in metal content in a ceramic host. The sintering temperature also has a great influence on the structural properties and hence on the thermal diffusivity value of the ceramics.

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