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A Study of Dopant Composition and Sintering Time Effect on Thermal Diffusivity of Doped and Undoped BSCCO Superconducting Ceramics

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ABSTRAK

Dalam kertas ini, sampel superkonduktor BSCCO yang didop dan yang tidak didop disediakan pada pelbagai suhu sinteran (cth. 24, 48 dan 100 jam) telah dikaji sifat resapan termanya. Nilai resapan terma telah diukur pada suhu bilik menggunakan teknik sinar kilat. Punca pengujaan dan sistem pengesanan merangkumi satu lampu kilat kamera dan termogandingan jenis K. Nilai resapan terma yang diukur didapati sangat bergantung pada kepekatan dopan, tetapi sebaliknya bebas daripada faktor masa sinteran. Dalam kajian ini, morfologi permukaan diperhati menggunakan imbasan mikroskopi elektron (SEM) adalah menyokong kuat hasil resapan terma yang diperoleh.

ABSTRACT

In this paper, the undoped and Sm doped BSCCO superconducting ceramic samples prepared at various sintering times (i.e. 24, 48 and 100 hours) were investigated for their thermal diffusivity. The thermal diffusivity value was measured at room temperature using photoflash technique. The excitation source and detection system consisted of a high intensity camera flash and K-type thermocouple. The measured thermal diffusivity value was found to be highly dependent on dopant concentration but not on sintering time. In this study, the surface morphology observed using Scanning Electron Microscopy (SEM) strongly supports the thermal diffusivity results.

Keywords: Dopant composition, thermal diffusivity, BCSSO, sintering time

INTRODUCTION

Bi(Pb)–Sr–Ca–Cu–O System has been investigated by many research groups concerning the preparation, superconducting properties, effect of doping as well as the structure of these compounds (Trong *et al.* 1999; Mulay *et al.* 1990; Halim *et al.* 1999). Studying the effect of doping on BSCCO system provides an opportunity to vary functional and mechanical properties of the material (Kazin *et al.* 1998). The dopant can influence kinetics and mechanism of HTSC phase formation, thus changing the final microstructure of the superconductor. In addition the dopant can form fine inclusions of stable phases serving as effective pinning centers. This method seems attractive for further improvement of critical current density in Bi(Pb)–2223 tapes (Ishizuka *et al.* 1995; Mao *et al.* 1997). The chemical routes such as oxalic acid coprecipitation, sol–gel (Shieh *et al.* 1991) and micro–emulsion–based techniques (Kumar *et al.* 1993) are given priority to fabricate Bi(Pb)SrCaCuO powder in order to get high compositional homogeneity in such multi-component powder.

The importance of thermal property in physics is well known because it indicates the presence of phase transitions from a thermodynamic point of view (Bougrine *et al.* 2000). Thermal diffusivity is a measure of how quickly a temperature disturbance can propagate through a material and is related to thermal conductivity through the following equation

$$\alpha = \frac{\lambda}{\rho C_p} \tag{1}$$

This relationship allows the thermal conductivity (λ) to be calculated if thermal diffusivity (α), bulk density (ρ) and specific heat (C_p) are known. Photoflash method is one of the techniques that has been used intensively in determining the thermal diffusivity of solid sample. This technique, originally described by Parker *et al.* (1961) is a transient heat flow technique primarily used to measure the thermal diffusivity of the materials. The photoflash method involves rapidly heating one face of a small disk specimen with a single optical pulse and monitoring the temperature disturbance as a function of time on the other face of the specimen (Log and Jacson 1991). Then, the thermal diffusivity is calculated from a characteristic curve (thermogram) of the temperature excursion of its rear surface as

$$\alpha = \frac{1.38L^2}{t_{1/2}} \tag{2}$$

where L is the thickness of the sample and $t_{1/2}$ is the time required for the back surface of the specimen to reach half the maximum temperature rise.

In order to improve the superconducting properties of BSCCO, serious efforts have been made by changing chemical composition, conditions of sintering and annealing atmospheres, and doping with various cations. However, to the present knowledge, there is still lack of information for the effect of Sm doping upon the superconductivity of BSCCO prepared at different sintering time. The present paper describes the effect of doping composition and sintering time on the thermal diffusivity value for doped and undoped BSCCO superconducting ceramics.

EXPERIMENTAL SETUP

The experimental setup of photoflash technique is shown in *Fig.* 1. A normal electronic camera flash (Maxxum, model 5400HS) as an energy pulse source was positioned 2 cm from front surface of the sample. A disk-shaped sample was placed on the sample holder and the K-type thermocouple was attached to the back surface of the sample. The front block of the sample was covered with the aluminium foil to shield the light from the photoflash reaching any part of the thermocouple.

In this setup, a fast response K-type thermocouple was attached directly to the rear surface of the sample to monitor the temperature at the rear surface of the sample. The signal from the thermocouple was then amplified by a preamplifier (SR560) and monitored by the digital oscilloscope (Tektronix TDS 220). The signal was then analyzed for thermal diffusivity value using equation (2). The photodiode (model RS 308(067) was used to trigger the oscilloscope. A period of 10 minutes was allowed in between the measurements in order to make sure the sample has reached the initial temperature (room temperature) before proceeding to a new measurement. For each sample, the measurements were repeated for more than three times.

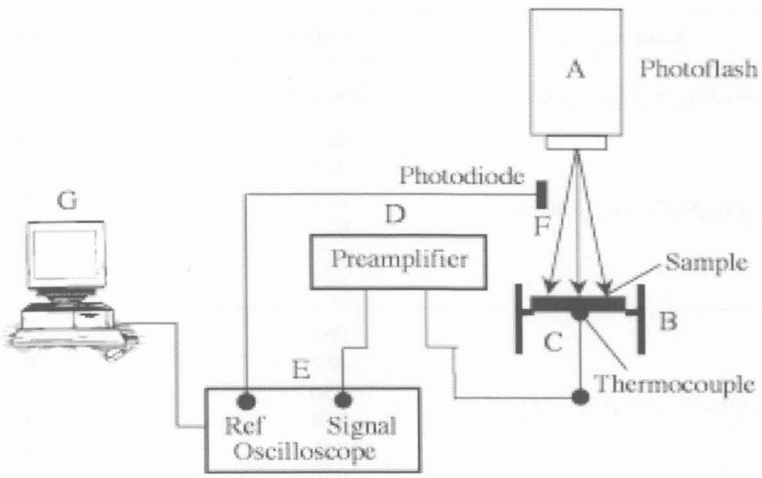


Fig. 1: Schematic experimental setup of the photoflash technique (A) light source, (B) sample holder, (C) thermocouple, (D) low noise preamplifier, (E) oscilloscope, (F) photodiode and (G) personal computer

SAMPLES PREPARATION

The general chemical stoichiometry for different substitutional doping in Bi–Pb–Sr–Ca–Cu–O system is shown in Table 1. The materials used in the preparation of $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_\delta$ were metal acetates of bismuth, strontium, lead, calcium and copper, oxalic acid, deionized water and isopropanol. A stoichiometric amount of each component was weighed and dissolved in isopropanol– water solution with ratio 1: 1.5 at 0–2°C to produce a solution with a concentration of 0.5M. The solution was added to oxalic acid solution and stirred in an ice bath to obtain a uniform, stable and blue suspension. The final pH during the co–precipitation was between 2.0–2.5. The slurry was filtered off after 5 minutes of reaction. The drying stage was carried out in the temperature range of 80–85°C for 8–12 h. The blue precipitate powder is slightly aggregated with particle size of 0.1–0.6 μm. The powder precursor was heated up to 730°C in air for 12 hours to remove the remaining volatile materials. The calcined powder was reground again and then pressed into pellets of ~ 12.5 mm diameter. The pellets were sintered at 850°C for 24, 48 and 100 hours and slow cooled to room temperature at a rate of 120°C/h. A similar procedure was repeated for $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_{3-X}Sm_XO_\delta$ (x = 0.02 – 0.4), and $Bi_{1.6}Pb_{0.4}Sr_{2-x}Sm_XCa_2Cu_3O_\delta$ (x = 0.02 – 0.4). The stoichiometric amount of each component was calculated and weighed to ensure a proper proportion of Sm^{3+} was used to dope in to the Cu or Sr site.

TABLE 1
Specimen formulation data for different substitutional doping in Bi-Pb-Sr-Ca-Cu-O system

Sample	Symbol	Dopant Sm, x
$Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_\delta$	BSCCO	0
$Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_{3-x}Sm_XO_\delta$	BC1	0.02
	BC2	0.06
	BC3	0.1
	BC4	0.2
	BC5	0.3
	BC6	0.4
$Bi_{1.6}Pb_{0.4}Sr_{2-X}Sm_XCa_2Cu_3O_\delta$	BS1	0.02
	BS2	0.06
	BS3	0.1
	BS4	0.2
	BS5	0.3
	BS6	0.4

RESULTS AND DISCUSSION

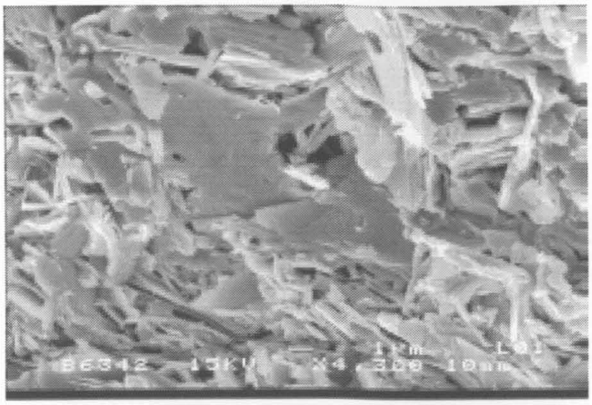
Numerous corrections have been introduced to account for radiative heat losses during the process such as the finite width of the energy pulse and other factors which are interfering factors observed during the experiment. The effects of radiation heat loss at the rear surface were calculated from the transient response curve by employing the ratio technique. From this calculation, the heat loss occurred in the experiment were corrected using Clark and Taylor rise-curve technique (Maglic and Taylor 1992). The calculated ratio τ/t_c (pulse duration, $\tau = 5$ ms for photoflash (Maxxum flash 5400HS)) from the experiment for the superconducting samples prepared at different sintering time showed that $\tau/t_c \ll 1$, therefore the finite pulse time effect in the present case is negligible (Cape and Lehman 1963).

TABLE 2
Thermal diffusivity values for pure $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_\delta$ and Sm doped $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_\delta$ superconductor ceramic sintered at 850 for various sintering time (24, 48 and 100 hours)

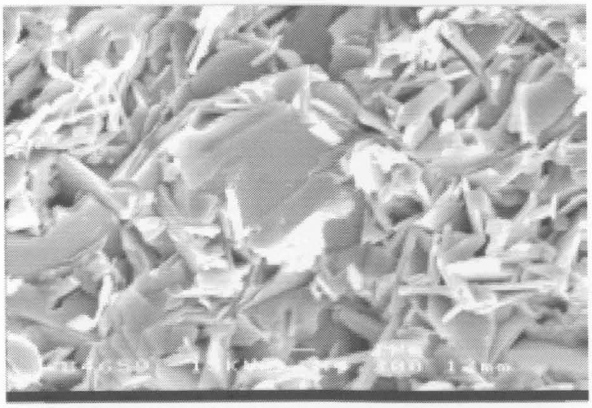
Material	$\alpha_c \times 10^{-3}$ (cm²/s) of Samples Sintered for 24 h	$\alpha_c \times 10^{-3}$ (cm²/s) of Samples Sintered for 48 h	$\alpha_c \times 10^{-3}$ (cm²/s) of Samples Sintered for 100 h
BSCCO	5.93 ± 0.07	5.93 ± 0.09	5.93 ± 0.09
BC1	7.36 ± 0.10	–	7.37 ± 0.10
BC2	8.99 ± 0.13	8.99 ± 0.12	8.98 ± 0.13
BC3	8.37 ± 0.11	8.37 ± 0.10	8.36 ± 0.12
BC4	6.51 ± 0.08	6.52 ± 0.12	–
BC5	5.56 ± 0.07	5.54 ± 0.07	5.55 ± 0.07
BC6	–	3.97 ± 0.04	–
BS1	7.76 ± 0.09	7.77 ± 0.11	7.77 ± 0.10
BS2	8.80 ± 0.14	8.81 ± 0.12	8.80 ± 0.13
BS3	8.09 ± 0.10	8.10 ± 0.11	8.08 ± 0.11
BS4	7.73 ± 0.10	7.71 ± 0.10	7.72 ± 0.10
BS5	–	7.05 ± 0.08	7.06 ± 0.09
BS6	6.76 ± 0.08	5.21 ± 0.06	5.22 ± 0.06

We first considered the effect of the sintering time of the doped and undoped BSCCO superconducting ceramic on thermal diffusivity. The doped and undoped BSCCO superconductors were sintered at 850°C with different sintering time (24, 48 and 100 hours). Table 2 shows the summary of thermal diffusivity values for doped and undoped BSCCO superconductor ceramics sintered at 850°C for 24, 48 and 100 hours. It was noted that the thermal diffusivity values remain unchanged, as the sintering time is increased. The independence of thermal diffusivity value with the sintering time for doped and undoped BSCCO system is clearly related to its microstructural characteristics. *Figs. 2-4* show the SEM micrographs of $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_\delta$, $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_{3-X}Sm_XO_\delta$ and $Bi_{1.6}Pb_{0.4}Sr_{2-X}Sm_XCa_2Cu_3O_\delta$ prepared at various sintering time at magnification of 2300 times respectively. As the sintering time increased from 24 hours to 100 hours, the grain size for the sample remains the same. However, a change in the grain size was observed when the composition of dopant atom was changed.

The thermal diffusivity as a function of stoichiometric ratio of Sm, x for $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_{3-X}Sm_xO_\delta$ and $Bi_{1.6}Pb_{0.4}Sr_{2-X}Ca_2Cu_{3-X}Sm_xO_\delta$ sintered at 24, 48 and 100 hours is shown in *Fig. 5 (a)* and *(b)* respectively. It was noted that the thermal diffusivity for $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_{3-X}Sm_xO_\delta$ and $Bi_{1.6}Pb_{0.4}Sr_{2-X}Sm_XCa_2Cu_3O_\delta$ increased with the increase in dopant concentration to a maximum value at x = 0.06. Further increase in x resulted a decrease in the thermal diffusivity of $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_{3-X}Sm_xO_\delta$ and $Bi_{1.6}Pb_{0.4}Sr_{2-X}Sm_xCa_2Cu_3O_\delta$. These results indicate that the measured thermal diffusivity value of the BSCCO show strong



(a)



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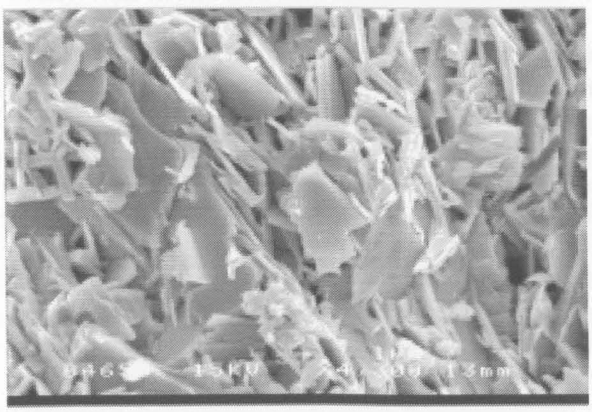
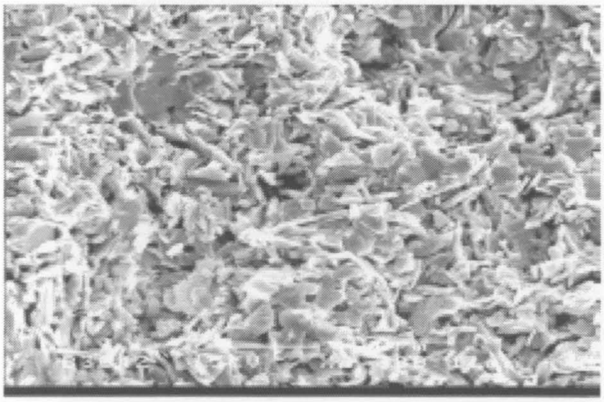
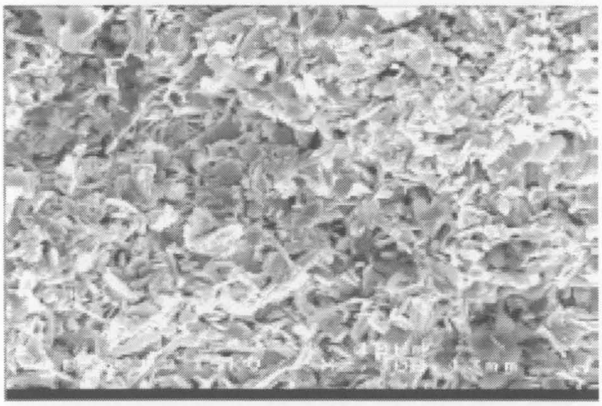


(c)

Fig. 2: SEM micrograph for $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_\delta$ samples sintered at 850°C for (a) 24 hours (b) 48 hours (c) 100 hours



(a)



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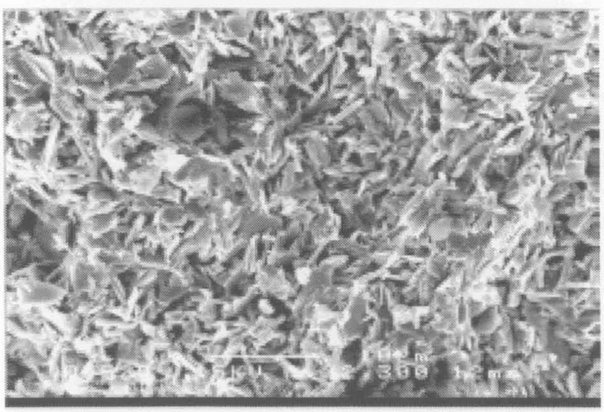
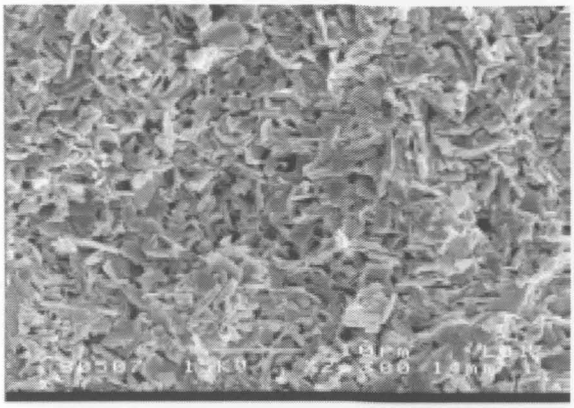
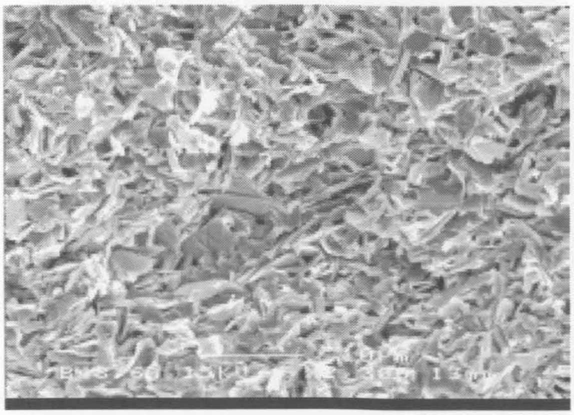


(c)

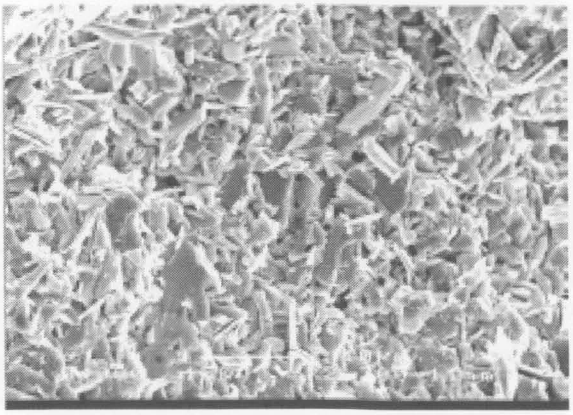
Fig. 3: SEM micrograph for $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_{3-x}O_\delta$ samples with $x = 0.06$ sintered at 850°C for (a) 24 hours (b) 48 hours (c)100 hours



(a)

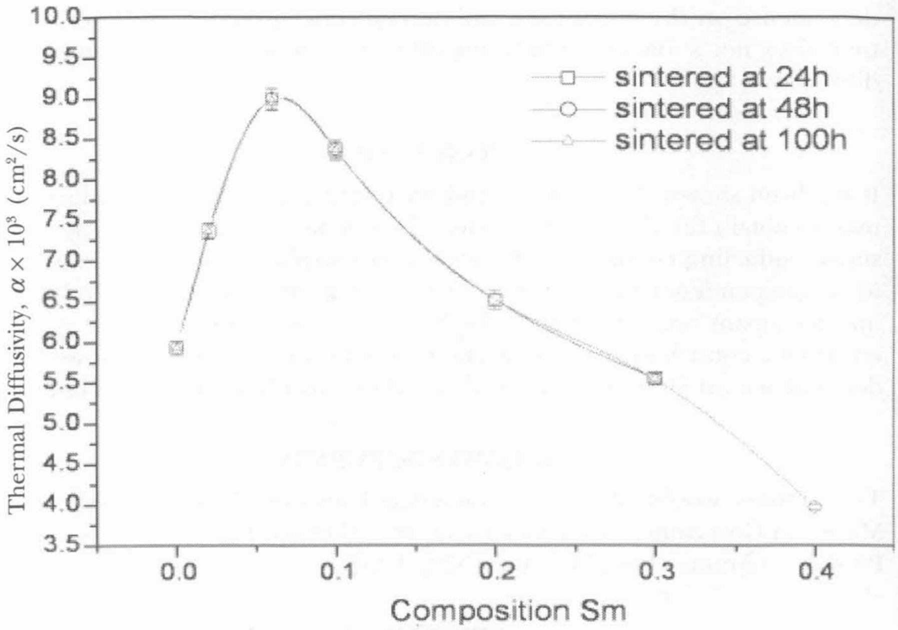


(b)



(c)

Fig. 4: SEM micrograph for $Bi_{1.6}Pb_{0.4}Sr_{2-x}Sm_xCa_2Cu_3O_\delta$ *samples with* $x = 0.06$ *sintered at 850 for (a) 24 hours (b) 48 hours (c) 100 hours*



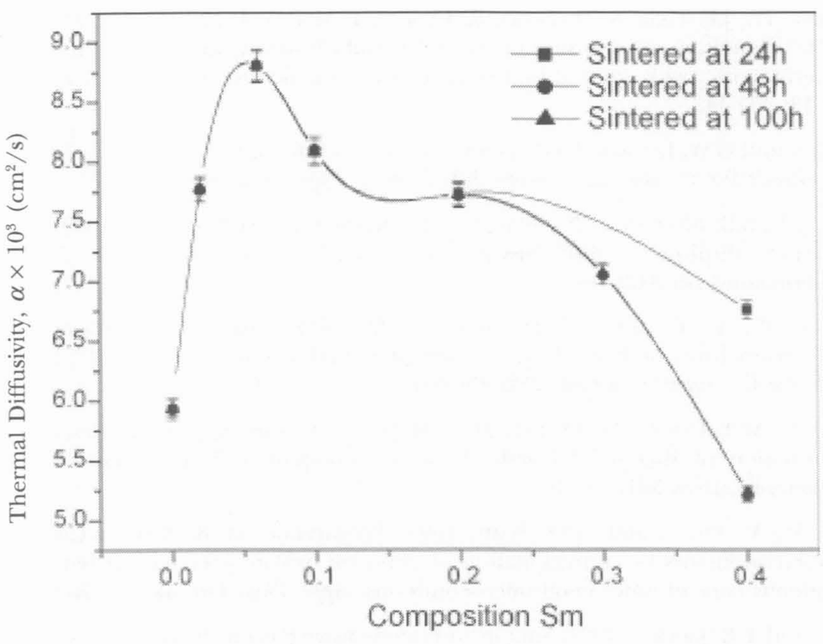


Fig. 5: Thermal diffusivity values versus composition of Sm for (a) $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_{3-X}Sm_xO_\delta$(b) $Bi_{1.6}Pb_{0.4}Sr_{2-X}Sm_XCa_2Cu_3O_\delta$ sintered at 850°C for various sintering time (24, 48 and 100 hours)

dependence on the dopant site and dopant concentration. However, sintering time does not show any significant effect on the room temperature thermal diffusivity.

CONCLUSION

It has been shown that a simple and inexpensive photoflash technique can be used to obtain the thermal diffusivity values of Sm doped and undoped BSCCO superconducting ceramics. The measured thermal diffusivity value was found to be independent of the sintering time of the sample but is strongly dependent on the dopant concentration. The SEM results indicated that the grain sizes could be a contributing factor to the thermal diffusivity as they showed similar dependence on sintering time and dopant concentration of the sample.

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