

Thermal Diffusivity Measurement of La Doped SrSnO₃ (Sr_{1-x}La_xSnO₃) Ceramics by Photoflash Method

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Received: 10 February 2003

ABSTRAK

Keresapan terma, a satu medium adalah sifat fizikal terma yang menentukan kelajuan haba merambat melalui proses kekonduksian semasa wujudnya perubahan suhu dengan masa. Pengukuran keresapan terma boleh dilakukan pada suhu bilik dengan kaedah cahaya kilat, dengan menggunakan sinar kilat kamera berkeamatan tinggi sebagai punca pengujaan. Dalam kertas ini, seramik Sr_{1-x}La_xSnO₃ didop dengan komposisi La yang berbeza (x = 0.1, 0.4, 0.6, 0.8 dan 1.0) telah dikaji sifat keresapan termannya. Nilai keresapan terma berubah daripada 0.44 x 10⁻² - 1.15 x 10⁻³ cm² /s bersepadanan dengan x = 0.1 hingga x = 1.0. Morfologi dan struktur seramik Sr_{1-x}La_xSnO₃ telah dianalisis daripada pengukuran SEM dan XRD untuk menyokong pelaksanaan keresapan termal dalam kajian ini.

ABSTRACT

Thermal diffusivity, α of a medium is the thermophysical property which determines the speed of heat propagation by conduction during changes of temperature with time. The measurement of thermal diffusivity can be carried out at room temperature by photoflash method, which employs a high intensity camera flash as the excitation source. In this paper, Sr_{1-x}La_xSnO₃ ceramics doped with different compositions of La (x = 0.1, 0.4, 0.6, 0.8, 1.0) was investigated for their thermal diffusivity. The thermal diffusivity values varied from 0.44 x 10⁻² - 1.15 x 10⁻² cm²/s corresponding to x = 0.1 to x = 1.0. The morphology and structure of Sr_{1-x}La_xSnO₃ ceramics were analysed from SEM and XRD measurements to support the thermal diffusivity behaviour.

Keywords: Ceramic, doping effect, thermal diffusivity, XRD, SEM

INTRODUCTION

Alkaline earth stannates have received more attention as a component of ceramic dielectric elements (Jaffe *et al.* 1971; Buchanan 1986). The phase equilibria in the SrO-SnO₂ system have been studied by several authors, and the existence of the two stable phases have been reported (Pfaff 2000). A number of investigations has been carried out for humidity sensors utilising porous ceramic material. For application in the fields of drying processes and

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combustion control systems, there is a need for humidity sensor, which operates above 100. From the standpoint of the temperature capability of the sensing element, ceramic materials appear to be the most suitable candidates. It has been reported that CaSnO_3 , SrSnO_3 and BaSnO_3 are sensitive to humidity and oxygen gas (Shimzu *et al.* 1985; Upadhyay *et al.* 2001).

Despite the recent interest in the use of stannates as ceramic dielectric bodies, humidity sensing, gas sensing, cell devices, and structural similarity with well understood alkaline earth titanates (Upadhyay *et al.* 2001), it is important that the effect of dopant on crystal structure, microstructure and thermal properties is studied. In this paper, we report the effect of substituting La^{3+} ions in SrSnO_3 element on the thermal diffusivity values. Characterisation of the ceramic samples have also been carried out using X-Ray Diffraction (XRD) and Scanning Electron Microscope (SEM). The purpose of the current investigation is to fill the information gap on literature about the doped- SrSnO_3 systems. Therefore, a series of solid solutions ($\text{Sr}_{1-x}\text{La}_x\text{SnO}_3$) having different compositions of La^{3+} ($x = 0.1, 0.4, 0.6, 0.8$ and 1) were investigated.

THEORY OF FLASH METHOD

Thermal diffusivity, α is of direct importance in heat-flow studies, as it determines the rate of periodic or transient heat propagation through a medium. Because of its controlling effect and common occurrence in heat flow problems, its determination is often necessary, and the knowledge of the thermal diffusivity can in turn be used to calculate the thermal conductivity (Rosencwaig 1980). Thermal diffusivity is related to thermal conductivity (k) by a simple relation,

i.e. $\alpha = \frac{k}{\rho C_p}$, where ρ is the apparent density and C_p is the heat capacity at

constant pressure. The photoflash method is one of the most common ways to measure thermal diffusivity of solid sample. It is based on depositing a very short energy pulse on the front surface of a small disc-shaped sample, and calculating its thermal diffusivity from the characteristic curve (thermogram) of the temperature excursion of its rear surface (Parker *et al.* 1961).

If the initial temperature distribution within a thermally insulated solid of uniform thickness L is $T(x,0)$, the temperature distribution at any later time t is given by Carslaw and Jaeger (1959) as

$$T(x,t) = \frac{1}{L} \int_0^L T(x,0) dx + \frac{2}{L} \sum_{n=1}^{\infty} \exp\left(\frac{-n^2 \pi^2 \alpha t}{L^2}\right) \cos \frac{n\pi x}{L} \int_0^L T(x,0) \cos \frac{n\pi x}{L} dx \quad (1)$$

where α is the thermal diffusivity in cm^2/s .

For an opaque material, the temperature at the rear surface where $x = L$ can be expressed as (Parker *et al.* 1961).

$$T(L,t) = \frac{Q}{\rho C_p L} \left[1 + 2 \sum_{n=1}^{\infty} (-1)^n \exp\left(-\frac{n^2 \pi^2 \alpha t}{L^2}\right) \right] \quad (2)$$

where Q is the energy of the light pulse, ρ is the density, C_p is the heat capacity, L is the thickness of a sample, and t is time. The term in the square bracket can be expressed as

$$V = \left[1 + 2 \sum_{n=1}^{\infty} (-1)^n \exp\left(-\frac{n^2 \pi^2 \alpha t}{L^2}\right) \right] \quad (3)$$

which represents a function of temperature rise at the rear surface and varies from 0 to 1. The maximum temperature of the rear surface can be written as

$$T(L,t)_{\max} = \frac{Q}{\rho C_p L} \quad (4)$$

Hence, two dimensionless parameters, V and ω can be defined as

$$V(L,t) = \frac{T(L,t)}{T(L,t)_{\max}} \quad (5)$$

$$\omega = \frac{\pi^2 \alpha t}{L^2} \quad (6)$$

Plotting V against ω yields a dimensionless plot of the rear face temperature history which represents the theoretical ideal response of a material.

The value of V can vary from 0 to 1 and in principle, any fractional rise on the curve may be used to calculate thermal diffusivity. But the half rise time, $t_{1/2}$ ($V=0.5$) is usually employed for convenience since this point lies within the linear region of the curve enabling the fractional rise time to be determined more easily. Therefore when $V=0.5$, $\omega=1.37$ and the thermal diffusivity, α can be calculated as

$$\alpha = \frac{1.37 L^2}{\pi^2 t_{1/2}} \quad (7)$$

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

Numerous corrections have been introduced to account for radiative heat losses during the process, the finite width of the energy pulse, and other factors interfering with the experiment. The effect of radiation heat loss at the rear surface can be calculated from the transient response curve by employing the

ratio technique. Heat loss corrections are based on Clark and Taylor rise-curve data or Cowan cooling-curve effect (Maglic and Taylor 1992).

MATERIALS AND METHOD

Thermal diffusivity analysis was carried out by a photoflash technique. The photoflash technique is a well-established method for measuring the thermal diffusivity with very simple procedures in a wide temperature range. The photoflash technique setup used in the present experiment is schematically shown in Fig 1.

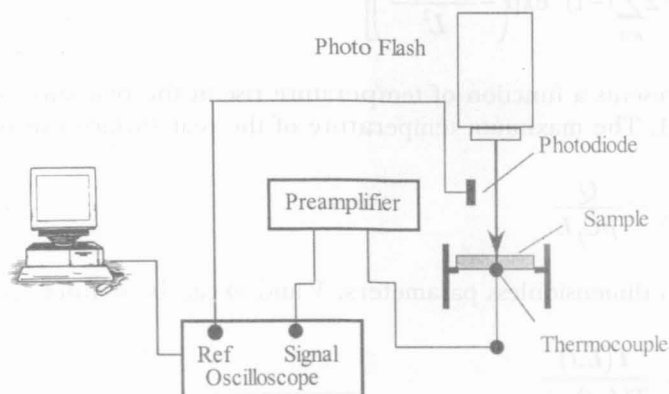


Fig. 1: Schematic experiment setup of the photoflash technique

A camera flash (Maxxum flash 5400HS) was used as an energy pulse source. It was located 2 cm in front of the sample as shown in Fig. 1. A photodiode was used to detect the pulse from the camera flash and subsequently trigger the oscilloscope. In this setup, a K-type thermocouple was used to monitor the temperature at the rear surface of the sample. The signal was then amplified by a preamplifier (SR560) and was transferred to a digital oscilloscope (Tektronix TDS 220). The signal was then analysed for the thermal diffusivity calculation using a personal computer. Every measurement was made at an interval of 10 minutes to allow the sample to be thermally equilibrated with room temperature. All measurements were carried out at room temperature.

Samples based on the formula (where $x = 0.1, 0.4, 0.6, 0.8$ and 1) were synthesised via conventional solid-state reaction. The starting compounds for preparation were LaO_3 (99.5%), from Sterm Chemicals, SrCO_3 and SnO_2 (purity 99.99 %) were from Aldrich Chemical. Stoichiometric amounts of respective compounds were weighed and milled in a ball mill for 24 hours with zirconia balls. Acetone was used as a mixing medium. The mixtures were dried and calcined at 1100°C for 24 hours in the air. The calcined powders were ground and mixed with 2-wt. % of water solution of polyvinyl alcohol (PVA) aqueous solution as a binder. The mixtures were dried overnight in the oven at 110°C , and was ground again, then finally pressed into pellets of 12 mm diameter, under a pressure of 5 tons. These pellets were kept in an alumina

crucible and sintered at 1400°C for 12 hours. Initially, the pellets were heated slowly at a rate of 1.5°C/min to 500 to burn off the binder; then the temperature was increased to 1400°C for 12 hours at a heating and cooling rate of 3°C/min. The dimension (thickness and diameter) of each sample was measured to be 0.1770-0.1902 cm for thickness and 0.12 cm for diameter. For the thermal diffusivity measurement, the Sr_{1-x}La_xSnO₃ samples were coated with a layer of carbon soot to enhance the absorption of flash energy.

RESULTS AND DISCUSSION

Fig. 2 (a), (b) and (c) show the thermogram for sample Sr_{1-x}La_xSnO₃ at x = 0.1, 0.4 and 1.0 respectively. From the curve, we could easily determine the $t_{1/2}$ for each of the samples. Here, we notice that the response time for Sr_{1-x}La_xSnO₃ at x = 1.0 is the fastest. It is known that the faster the propagation of heat into the medium, the higher the thermal diffusivity value. Fig. 2 also shows that heat loss occurred and it was corrected using Clark and Taylor rise-curve (Maglic and Taylor 1992). Therefore, the ratio $t_{3/4}/t_{1/4}$ is determined from the experimental data where $t_{3/4}$ and $t_{1/4}$ are the times to reach 75% and 25% of the maximum respectively. The correction factor, K_R will be calculated using:

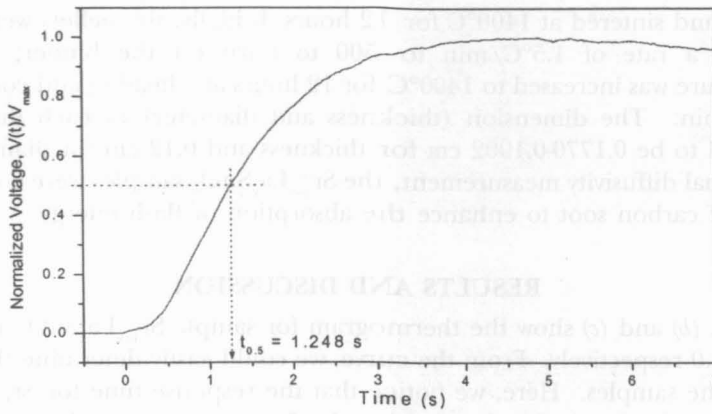
$$K_R = -0.3461467 + 0.361578 \left(\frac{t_{3/4}}{t_{1/2}} \right) - 0.06520543 \left(\frac{t_{3/4}}{t_{1/2}} \right)^2 \quad (8)$$

Then the corrected value of thermal diffusivity at half rise time will be

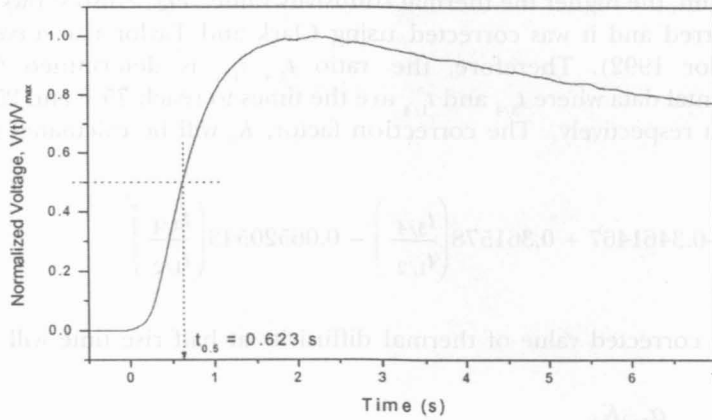
$$\alpha_{corrected} = \frac{\alpha_{t/2} K_R}{0.13885} \quad (9)$$

The calculated ratios τ/t_c (pulse duration, $\tau = 5$ ms in our case) in the present experiment are much smaller than 1 ($\tau/t_c \ll 1$), therefore the finite pulse time in the present case is negligible (Cape and Lehman 1963). This characteristic rise time and the corrected value of thermal diffusivity of Sr_{1-x}La_xSnO₃ at different composition parameter x is tabulated in Table 1.

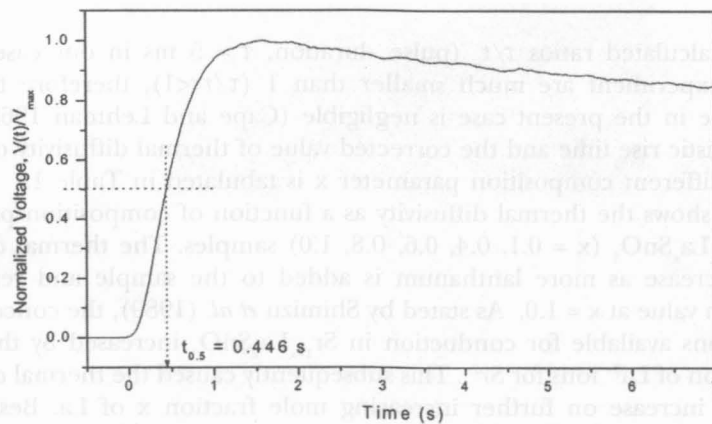
Fig. 3 shows the thermal diffusivity as a function of composition parameter x for Sr_{1-x}La_xSnO₃ (x = 0.1, 0.4, 0.6, 0.8, 1.0) samples. The thermal diffusivity values increase as more lanthanum is added to the sample and reaching a maximum value at x = 1.0. As stated by Shimizu *et al.* (1989), the concentration of electrons available for conduction in Sr_{1-x}La_xSnO₃ increased by the partial substitution of La³⁺ ions for Sr²⁺. This subsequently caused the thermal diffusivity values to increase on further increasing mole fraction x of La. Besides, the increase in thermal diffusivity should be caused by the changes in its interfacial structure, such as ordering of atomic arrangements and annihilation of interfacial defects (Qin *et al.* 1996). This is due to the thermal wave propagation in the solid materials being influenced by microstructure characteristics, size and



(a)



(b)



(c)

Fig. 2: (a) Thermogram for sample $Sr_{1-x}La_xSnO_3$ at $x = 0.1$; (b) Thermogram for sample $Sr_{1-x}La_xSnO_3$ at $X = 0.4$; (c) Thermogram for sample $Sr_{1-x}La_xSnO_3$ at $x = 1.0$

TABLE 1
Characteristic rise time and the corrected value of thermal diffusivity
for Sr_{1-x}La_xSnO₃ at composition ranging from x = 0.1 to x = 1.0

Composition x in Sr _{1-x} La _x SnO ₃ sample	Thickness, l (cm)	Characteristic rise time, $t_c = l^2 / \alpha\pi^2$	τ / t_c	Corrected thermal diffusivity, $\alpha_{corrected}$ (cm ² /s) × 10 ⁻³
x = 0.1	0.1902	0.84	0.011	4.37 ± 0.01
x = 0.4	0.1841	0.48	0.019	7.15 ± 0.02
x = 0.6	0.1780	0.41	0.022	7.86 ± 0.04
x = 0.8	0.1770	0.37	0.024	8.65 ± 0.05
x = 1.0	0.1873	0.31	0.029	11.53 ± 0.06

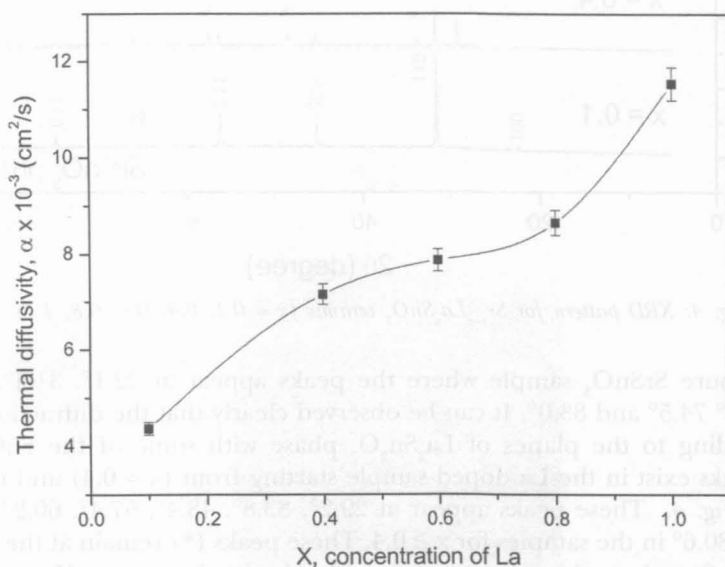


Fig. 3: Thermal diffusivity of Sr_{1-x}La_xSnO₃ at different compositions of x (sintered at 1400°C for 12 hours)

grain boundary, impurities and imperfection, where all of them contribute to the energy dispersion of the carriers like phonons and electrons inside the material (Lan *et al.* 1997).

The Sr_{1-x}La_xSnO₃ (x = 0.1, 0.4, 0.6, 0.8, 1.0) samples are characterised by a computer controlled x-ray diffractometer, XRD (Philips model 7602 EA Almelo) using Cu K α ($\lambda = 1.5418 \text{ \AA}$) irradiate with a scanning speed of 2°min⁻¹. The diffraction patterns of Sr_{1-x}La_xSnO₃ (x = 0.1, 0.4, 0.6, 0.8, 1.0) samples were obtained by scanning the samples with an interval of scanning angle (2 θ) from 5° to 85°. The XRD spectra of the Sr_{1-x}La_xSnO₃ (x = 0.1, 0.4, 0.6, 0.8, 1.0) are shown in Fig. 4. The peaks (2 θ = 22.3°, 31.6°, 45.2°, 56.1°, 65.8°, 74.7° and 83.3°) appearing in the (x = 0.1) sample remain unchanged if compared to the

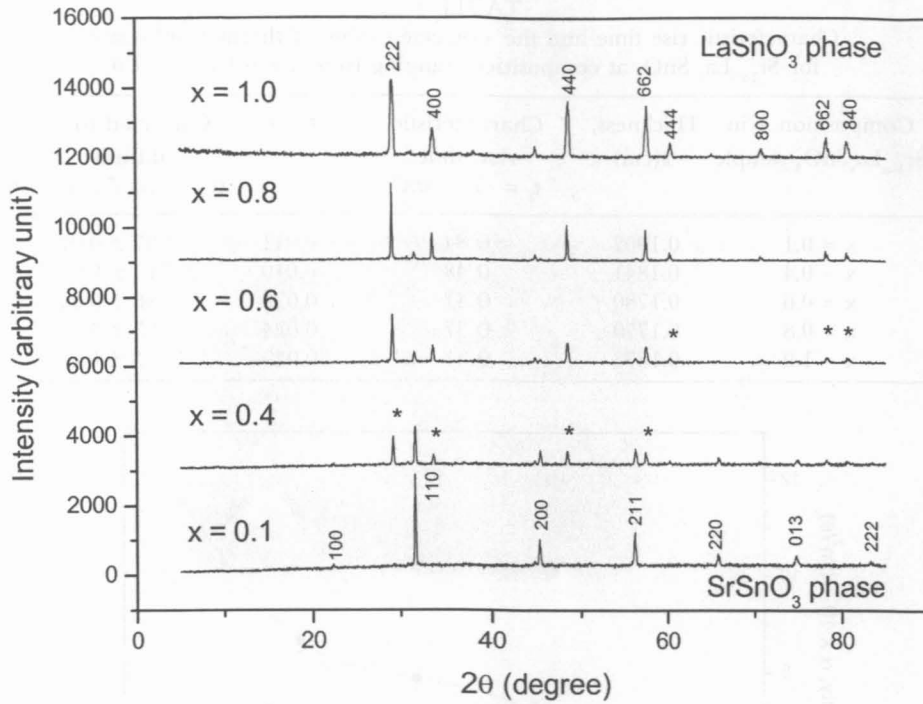


Fig. 4: XRD pattern for $Sr_{1-x}La_xSnO_3$ ceramic ($x = 0.1, 0.4, 0.6, 0.8, 1.0$)

standard pure $SrSnO_3$ sample where the peaks appear at $22.1^\circ, 31.4^\circ, 45.0^\circ, 55.9^\circ, 65.5^\circ, 74.5^\circ$ and 83.0° . It can be observed clearly that the diffraction lines corresponding to the planes of $La_2Sn_2O_7$ phase with some of the SnO_2 and La_2O_3 peaks exist in the La doped sample starting from ($x = 0.4$) and marked as (*) in Fig. 4. These peaks appear at $29.2^\circ, 33.8^\circ, 48.4^\circ, 57.4^\circ, 60.2^\circ, 70.8^\circ, 78.2^\circ$ and 80.6° in the samples for $x \geq 0.4$. These peaks (*) remain at the similar values of 2θ angle as the concentration of La doping increases. However, the intensity of the $La_2Sn_2O_7$ phase was found to increase as the lanthanum (La) concentration increased. It is also observed that the peak belonging to the $SrSnO_3$ diminishes as the La concentration increases. This changes of phase in $Sr_{1-x}La_xSnO_3$ ceramic samples affect the thermal diffusivity of a sample, where the sample with higher doping of La gives higher thermal diffusivity value.

Surface morphology of the $Sr_{1-x}La_xSnO_3$ ($x = 0.1, 0.4$ and 1.0) was investigated using a scanning electron microscope, SEM (JEOL model 6400). A uniform thin film of gold was evaporated on the exposed surfaces by a polaron coating machine to avoid electrostatic charging during microscopic viewing. The morphologies of the sample surface at magnification of 4,000X are shown in Fig. 5(a), (b) and (c). It indicates that the morphology of the $Sr_{1-x}La_xSnO_3$ at $x = 0.1$ and $x = 0.4$ is somehow different with the $Sr_{1-x}La_xSnO_3$ at $x = 1$. This SEM micrograph revealed that the materials were uniform, with spherical grains and have a small (sub- μm) grain size for $x = 0.1$ and 0.4 . The microstructure of the

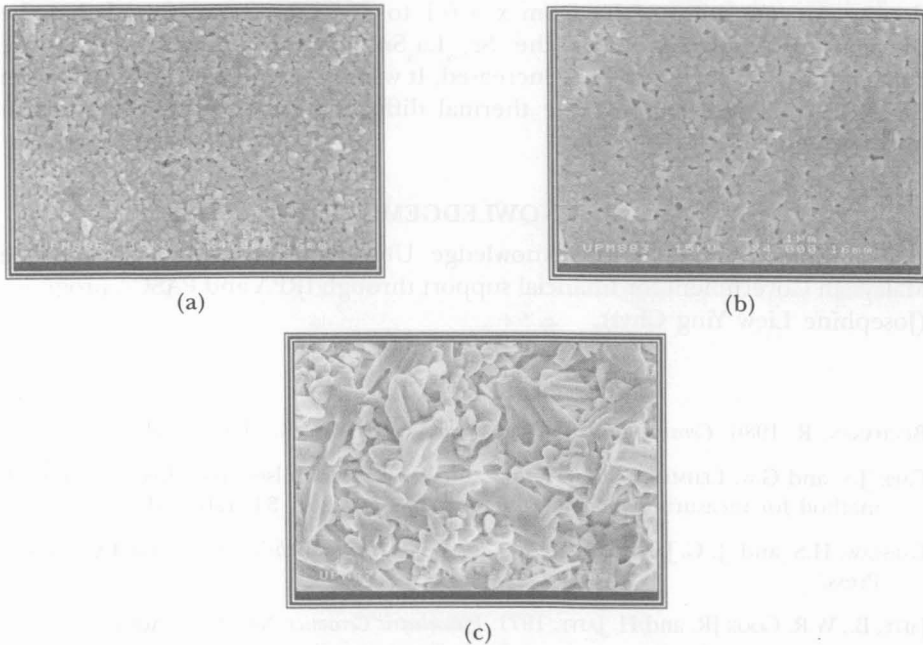


Fig. 5: (a) Microstructure of Sr_{1-x}La_xSnO₃ sample at x = 0 (b) Microstructure of Sr_{1-x}La_xSnO₃ sample at x = 0.4 (c) Microstructure of Sr_{1-x}La_xSnO₃ sample at x = 1 at magnification factor of 4,000X

Sr_{1-x}La_xSnO₃ system shows the grain size increases with increasing x and subsequently increases the thermal diffusivity of the Sr_{1-x}La_xSnO₃ sample. When the concentration of La increases until x = 1, the material underwent a drastic change in its microstructural constitution where the doped Sr_{1-x}La_xSnO₃ reveals a small number of grains in the population growing rapidly to a very large size relative to the average size of the population. This is called an abnormal grain growth (AGG) or secondary crystallisation. This is due to atomic diffusion across the grain boundaries and high curvature at the boundaries between the grains of different size. Finally, the individual grains occasionally take on highly unusual shapes (Loehman 1993; Kingery *et al.* 1976). This appearance shows a morphological change from the normal globular behavior of Sr_{1-x}La_xSnO₃ which explains why the thermal diffusivity value of Sr_{1-x}La_xSnO₃ at x = 1 increases drastically from x = 0.8.

CONCLUSION

The thermal diffusivity value of Sr_{1-x}La_xSnO₃ ceramic samples prepared at different doping concentrations of La (x = 0.1, 0.4, 0.6, 0.8 and 1.0) were investigated using a simple and inexpensive photoflash method at room temperature. The thermal diffusivity value of samples Sr_{1-x}La_xSnO₃ were determined to be $0.44 \times 10^{-2} \text{cm}^2/\text{s}$ to $1.15 \times 10^{-2} \text{cm}^2/\text{s}$ which correspond to the

doping concentration of La from $x = 0.1$ to $x = 1.0$. It was found that the thermal diffusivity value of the $\text{Sr}_{1-x}\text{La}_x\text{SnO}_3$ samples increased as the concentration of the La doping increased. It was also observed that results from the XRD and SEM support the thermal diffusivity behaviour in the present measurements.

ACKNOWLEDGEMENTS

The authors would like to acknowledge Universiti Putra Malaysia and the Malaysian Government for financial support through IRPA and PASCA programs (Josephine Liew Ying Chyi).

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