

Photoacoustic investigation of the effect of excess lead oxide on thermal diffusivity of PLZT ceramic

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The versatility as well as the potential of the photoacoustic (PA) technique as a material characterization method has been established by several workers [1–6]. Apart from providing direct optical absorption spectra, the PA technique can also be used to perform depth profile analysis, thermal characterization as well as investigation of nonradiative relaxation processes [7–10]. In a typical PA experimental arrangement the sample enclosed in an airtight cavity is exposed to an intensity modulated light beam. The resulting periodic heating of the sample is strongly dependent on the interplay of three factors, namely, the optical absorption coefficient at the incident radiation wavelength, light-into-heat conversion efficiency and the heat diffusion through the sample. The light-into-heat conversion efficiency of each material depends on the nonradiative de-excitation processes taking place within the sample. The dependence of the PA signal on the rate of heat diffused through the sample allows us to perform thermal characterization, especially the determination of thermal diffusivity.

Ceramics are considered as the optimum materials to solve a number of scientific and technological problems due to the availability of raw material as well as their resistance to corrosion and irradiation. The unique electro-optic and photo-electric properties of transparent ferroelectric ceramics (TFC) have helped them to acquire a significant fraction of the solid state optoelectronic device market, particularly in high speed light modulators and shutters, thermal and light filters, electrically controlled color filters, alphanumeric displays, block data composers, video projectors and optoelectronic voltmeters [11–16]. The majority of the TFC compositions include materials prepared on the basis of the well-known PZT system with the ABO_3 perovskite structure. One such material is lanthanum doped lead zirconate-titanate (PLZT), in which some Pb^{2+} ions in the A sites are replaced by the higher valence La^{3+} ions. As a result of the difference in the valency between Pb^{2+} and La^{3+} , some of the A sites and B sites will be vacant in order to maintain electrical neutrality in the structure. Earlier studies show that the nonstoichiometry of lead oxide as well as the doping of lanthanum introduces a large number of vacancies in PLZT [17, 18].

This letter deals with a study of the effect of excess lead oxide on the thermal diffusivity of PLZT ce-

ramic carried out using the laser induced photoacoustic technique. Since the material preparation was done at $1200\text{ }^\circ\text{C}$, some fraction of the lead may escape during the preparation, so the actual lead content may be slightly less than the initial concentration. Samples were prepared with excess lead oxide in different weight percentages and the thermal diffusivity was determined for each sample with different amounts of excess lead oxide.

The experimental set up used for the present investigation is similar to the one used by George *et al.* [19] as shown in Fig. 1. The 488 nm line of an argon ion laser (Liconix 5000 series) was used as the pump beam. The laser beam at a power level of 70 mW was intensity modulated using an electromechanical chopper (Ithaco HMS 230) before it was made to fall on the sample. The sample compartment of the non-resonant PA cell made of stainless steel has a diameter of 8 mm and a depth of 5 mm. The PA signal produced in the cavity was detected using a miniature electret microphone kept in a side chamber coupled to the sample compartment. The output of the microphone was processed using a lock-in-amplifier (Stanford Research Systems SR 510).

We measured the PA signal amplitude as a function of chopping frequency. Charpentier *et al.* have presented a frequency analysis of the PA signal for the determination of thermal diffusivity based on the Rosencwaiger-Gersho theory for the PA effect [20, 21]. According to this model, knowing the actual thickness (l_s) of the sample and the characteristic frequency (f_c) at which the sample becomes thermally thick, the thermal

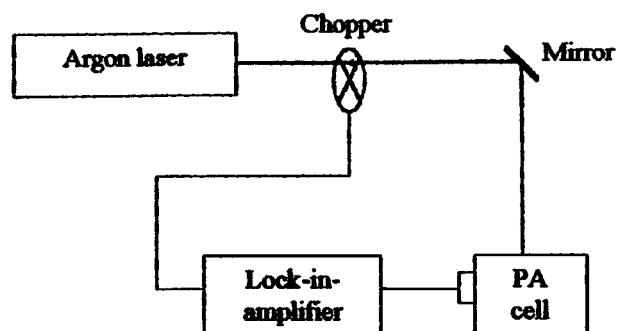


Figure 1 Block diagram of the experimental set up.

diffusivity (α) can be calculated using the relation $\alpha = f_c l_s^2$ [21].

PLZT samples were prepared using the conventional solid state reaction method [22]. Samples were prepared according to the general formula $Pb_{1-x}La_x-(Zr_yTi_{1-y})_{1-x/4}O_3$, where “□” represents the lattice vacancies created to maintain the charge balance between Pb^{2+} and La^{3+} . Although the above formula presumes that all the vacancies are in the B sites, the actual location of these vacancies in either the A^{2+} or B^{4+} sites of the unit cell has not yet been completely resolved. But the co-existence of A-site and B-site vacancies is a clearly established one [23, 24]. In the present case, we prepared three different sets of samples with 5%, 10% and 15% of excess lead oxide with respect to the stoichiometric ratio. However, in all cases the amount of lanthanum was kept constant at 9 atom percent, which is reported to be the optimum concentration of lanthanum for getting good quality PLZT. Thin disc like samples sintered at 1500 °C were used for the PA studies. Then keeping the samples in the PA cell, the frequency dependence of the acoustic signal amplitude was studied. The log-log plot of the variation of the signal amplitude versus the chopping frequency for the PLZT samples with three different excess lead oxide concentrations are shown in Fig. 2. The transition of the sample from the thermally thin to the thermally thick regime is clearly indicated in the plot by a change in the slope from -1 to $-3/2$. Measuring the characteristic frequency f_c at which the slope change occurs and the thickness l_s of the sample, the thermal diffusivity was calculated using the equation $\alpha = f_c l_s^2$. The calculated thermal diffusivity of the PLZT discs with three different excess lead oxide concentrations are given in Table I. The values are found to be same up to the third digit on repetition of the experiment. This is mainly because the accuracy of the measurements depends only on the determination of sample thickness and the characteristic frequency.

From the photoacoustic measurements it is seen that the thermal diffusivity of PLZT increases with an increase in lead content. Most probably, this may be due to the fact that a pronounced nonstoichiometry of lead

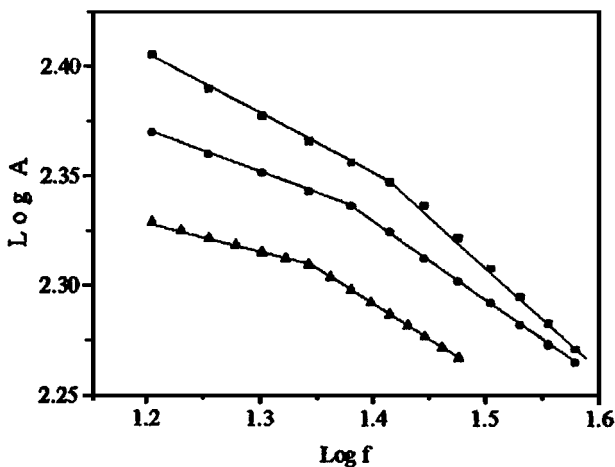


Figure 2 Log-log plot connecting PA signal amplitude to the chopping frequency. \blacktriangle -5%, \blacksquare -10% and \bullet -15% excess lead oxide than the stoichiometric ratio.

TABLE I Thermal diffusivity values of PLZT with excess lead oxide

Excess lead oxide (weight %)	Sample thickness l_s (cm)	Characteristic frequency f_c (Hz)	Thermal diffusivity α ($cm^2 s^{-1}$) $\pm 10\%$
5	0.061	22.00	0.0819
10	0.056	28.00	0.0878
15	0.062	24.00	0.0923

oxide causes a large concentration of lattice defects in PZT based compositions [17, 18]. The nonstoichiometry of lead oxide as well as the doping of lanthanum may make PLZT a material with a large concentration of defects. In the present case, deviation from the stoichiometry of lead oxide may cause formation extended defects apart from point defects and this may affect the thermal diffusivity values. Also, the thermal diffusivity of lead ($0.245 cm^2/s$) itself is higher than that of pure ceramic. Therefore, the presence of excess lead may also have some direct contribution to the increase in the thermal diffusivity value. Detailed work in this direction is in progress.

In conclusion, the effect of excess lead oxide on the thermal diffusivity of PLZT ceramic has been studied using the PA technique. The observed increase in thermal diffusivity of PLZT with an increase in lead oxide content is supposed to be due to the appearance of additional defects other than the point defects introduced in the material due to the nonstoichiometry of lead oxide.

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