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Structural, SEM and dielectric properties of PLZT

K. L. YADAV, R. N. P. CHOUDHARY, T. K. CHAKI*
*Department of Physics, and *Rubber Technology Centre, Indian Institute of Technology, Kharagpur 721 302, India*

Powder of lanthanum-modified lead zirconate titanate (PLZT) with the composition La/Zr/Ti = 8/65/35, was synthesized from aqueous nitrate solutions. A single-phase PLZT was obtained at ~550 °C. The reactivity of the powder during low-temperature heating was determined using X-ray diffraction and various thermal analysis techniques. The dielectric properties of the compound were also studied at 1 and 10 kHz frequency from room temperature to 200 °C. Diffuse phase transition (DPT) in the material was observed around 136 °C at 1 kHz. An increase in peak-permittivity temperature (i.e. the transition temperature) with increasing frequency (a characteristic of relaxor ferroelectrics) was also observed.

1. Introduction

Lead zirconate titanate (PZT) ceramics are widely used for some electronic devices because they have excellent piezo- and ferroelectric properties [1]. Generally, PZT is fabricated by the conventional high-temperature solid-state reaction technique from PbO, TiO_2 and ZrO_2. It has been found that the properties of PZT synthesized by this technique are very sensitive to compositional fluctuations near the morphotropic phase boundary [2], particle size [3], calcination temperature [4], doping [5] and sintering temperature [6]. It has also been observed that the particle distribution and size have a significant effect on the PZT properties. Chemically prepared (Pb, La) (Zr, Ti)O_3 (PLZT) powder is usually finer and less easily processed because, on a submicrometre scale, the smaller the particles the greater is their tendency to aggregate during calcination. This particle size precludes the dense packing and uniform small pore size which, in turn, permit 100% relative density at relatively low temperature. This chemical method involves the physico-chemical reaction of the precursor compounds of the required oxides, such as alkoxides, oxalates, nitrates, sulphates, etc. In this work, fine PLZT powders were prepared by a chemical method which differs slightly from previously reported techniques [7–9]. In the present paper, we report structural (X-ray), microstructure, thermal and dielectrical properties of PLZT which have provided better and improved properties of this compound in comparison with other works.

2. Experimental procedure

The starting materials were $Pb(NO_3)_2$, $La(NO_3)_3 \cdot 6H_2O$, $ZrO(NO_3)_2 \cdot 2H_2O$ and $C_{12}H_{28}O_4Ti$ of AR grade. The powder of composition $(Pb_{0.92}La_{0.08})(Zr_{0.65}Ti_{0.35})O_3$ i.e. PLZT (8/65/35), was prepared by dissolving lead, lanthanum and zirconyl nitrates in distilled water in the desired ratio. Liquid tetra isopropyl titanate was then added directly to the nitrate solution while stirring. The titanium hydrolysed to an intermediate $Ti(OH)_4$ phase and slowly redissolved. The intrinsic acidity of the solution was kept at pH < 1, which is a controlling factor of the rate at which the precipitate dissolved. Then nitric acid was added to obtain a clear solution. Later, the desired PLZT powder was obtained by heating the above nitrate solution at 130 °C until it dried up. The resulting precipitate sticks to the glass beaker, so it was again heated at 230 °C to break the bonds between the powder and the glass. The powder was calcined at 550 °C and 920 °C for 16 h in air in alumina crucibles. The phases formed were identified by X-ray diffraction (XRD) using CuK_α radiation. The size, shape and microstructure of particles were determined by scanning electron microscopy (SEM). The chemical compositions were determined using an energy dispersive X-ray detector (EDX) attached to the SEM. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) of the powders prepared were carried out using model 9000 M/S DuPont Instruments, USA. For DSC analysis, ~ 15–20 mg powder was used, together with a reference material (empty aluminium pellets). The heating rate of the furnace was 20 °C min^{-1}. In TGA, the weight loss of the PLZT powder was recorded as a function of temperature, together with the DTG curves. The powder calcined at 920 °C was cold pressed into a disc (pellet) sample under 6×10^7 kg m^{-2} pressure using a hydraulic press. Sintering of the pellets was carried out at different temperatures (920–1200 °C) and sintering times (120–150 min). In order to prevent PbO vaporization, an equilibrium PbO vapour pressure was established using $PbZrO_3$ as setter, and placing everything in an alumina crucible covered with another small crucible. After sintering, the samples were subjected to annealing at 970 °C to provide further evidence to confirm the effect of the dopant. The density of the sample

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was approximately 97% theoretical. Silver electrodes were then fired on the specimens, and the dielectric constant of the samples was measured using a GR1620 capacitance measuring assembly as a function of temperature (room temperature to 200 °C) at two frequencies, 1 and 10 kHz.

3. Results and discussion

Fig. 1 shows the XRD patterns of the specimen calcined at two different temperatures. The major phase formed was PLZT. The diffraction peaks in the powder pattern of the samples calcined at 550 °C are not sharp. This suggests that the powders are not well crystallized. The diffraction lines of PLZT calcined at 920 °C, were found to be very sharp and single indicating the better homogeneity and crystallization of the materials.

Fig. 2 shows scanning electron micrographs of PLZT powders prepared by the chemical method and sintered at different temperature and times. The average grain size of the powders was uniform and the size distribution was quite narrow. The grains were spherical in shape, with a grain-size range of PLZT powder, as measured by SEM, of 0.5–3.8 μm on average.

DSC, TGA and DTG curves of PLZT are shown in Figs 3 and 4, respectively. Endothermic peaks observed at 100 °C in the DSC experiment were due to the removal of water molecules, as indicated by a corresponding weight loss in the TGA and DTG curves. The appearance of two endothermic peaks at 450 and 500 °C in the DSC curve (Fig. 3) indicates that the decomposition of $Pb(NO_3)_2$ into PbO and it is a two-step process, as reported in Dayal *et al.* [9]. It should be pointed out that we found no exothermic peak in the DSC or TGA plot around 230 °C, as reported by these authors. This is because titanium, hydrolysed to an intermediate $Ti(OH)_4$ phase, slowly redissolves.

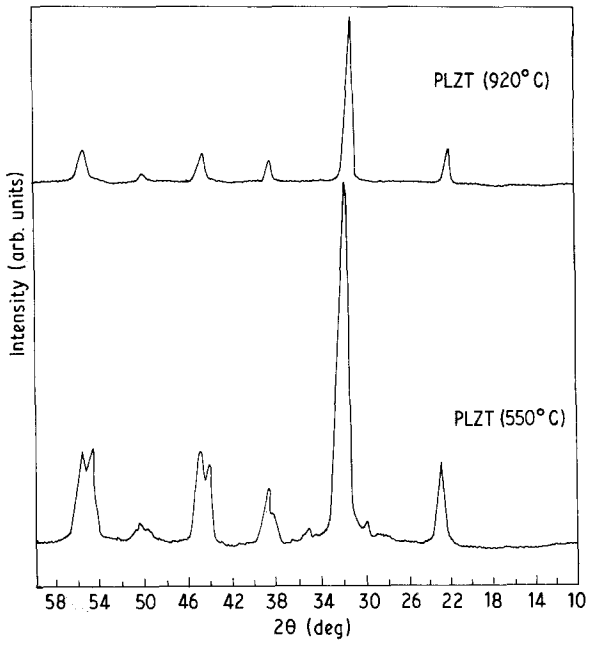

Figure 1 XRD of chemically prepared PLZT.

The variation of dielectric constants of PLZT at 1 and 10 kHz is shown in Fig. 5. It was found that there is no sharp dielectric peak. The dielectric loss (not shown here) has the same trend. Broadening of the

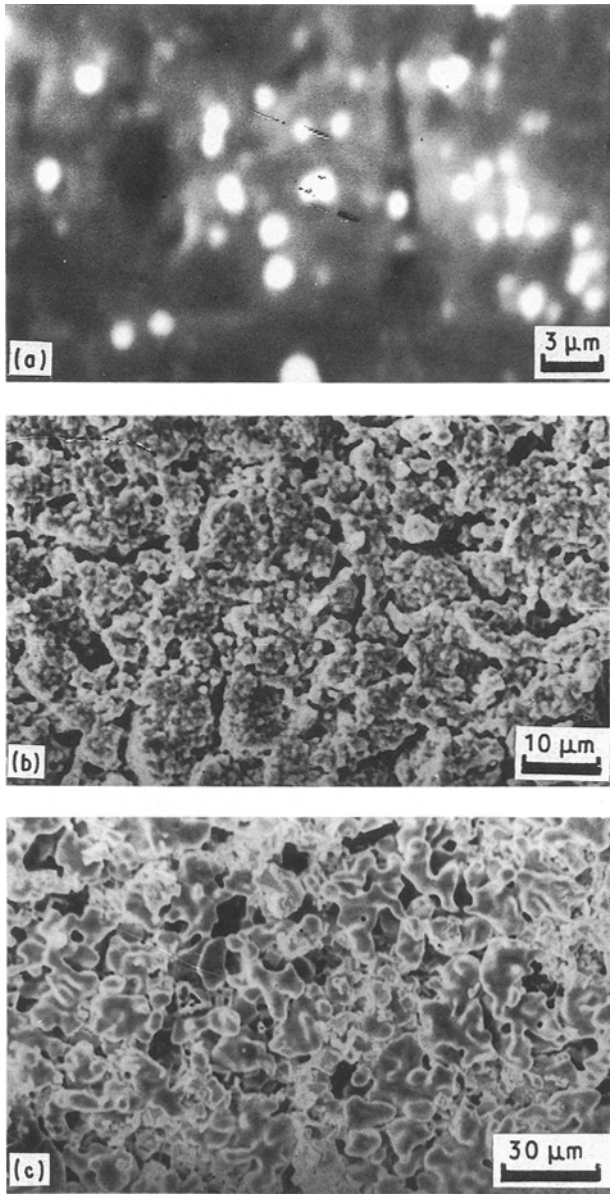

Figure 2 Scanning electron micrographs of PLZT: (a) powder calcined at 920 °C, 16 h; (b) pellet sintered at 1125 °C, 2 h; (c) pellet sintered at 1225 °C, 2 h.

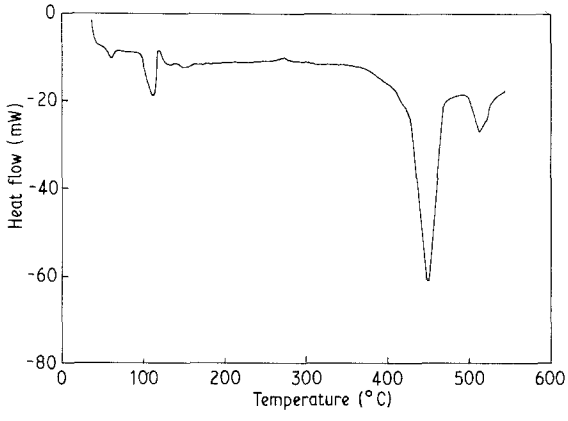

Figure 3 DSC of PLZT (as-dried powder).

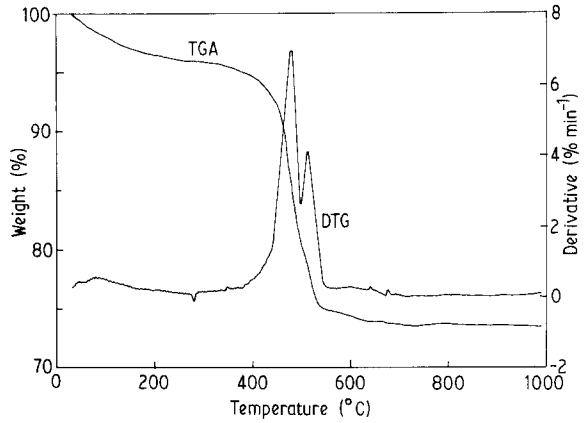

Figure 4 TGA and DTG of PLZT (as-dried powder).

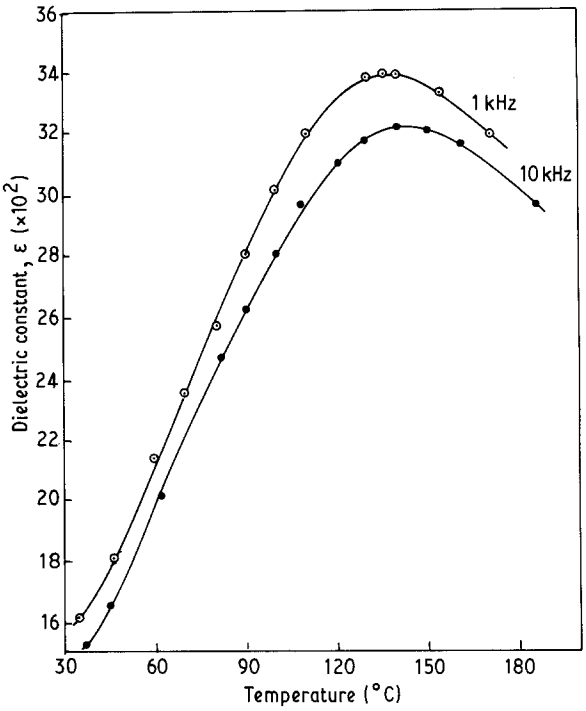

Figure 5 Variation of dielectric constant as a function of temperature in annealed PLZT (8/65/35).

peak may be concluded to be due to the compositional fluctuations and structural disorder of the compound. The transition temperature was found at around 136 °C at 1 kHz and at 145 °C at 10 kHz, which indicates relaxor behavior of the compounds as reported [7]. Further studies of relaxor behaviour of PLZT are in progress.

4. Conclusions

It is possible to produce single phase high-purity ultrafine (2000 nm) powders of PLZT by calcining a complex PLZT produced by precipitation from an aqueous nitrate solution with improved reactivity, even at low temperature (550 °C). Diffuse phase transition and relaxor properties in PLZT have been observed.

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