

# Synthesis and characterization of PLZT (10/65/35)

KANHAIYA LAL YADAV, R. N. P. CHOUDHARY

*Department of Physics and Meteorology, Indian Institute of Technology, Kharagpur 721 302, India*

Lead zirconate titanate (PZT) powder of composition  $\text{Pb}(\text{Zr}_{0.65}\text{Ti}_{0.35})\text{O}_3$  was modified by incorporation of 10% lanthanum as a polyvalent cation by the process of evaporative decomposition of aqueous solutions of lead nitrate, lanthanum nitrate, zirconyl nitrate and tetra-isopropyl titanate. X-ray diffraction patterns and infrared spectra of the compound calcined at different temperatures indicate that formation of rhombohedral PLZT is possible at 550 °C for 1 h. The room-temperature dielectric constant measured at 1 kHz was found to be 991. From the study of dielectric constant as a function of temperature,  $T_c$  was found to be at 85 °C. SEM study of the compound has shown grain-size homogeneity and quality of the compound. All these results suggest that this PLZT powder may be suitable for device applications.

## 1. Introduction

Lead zirconate titanate (PZT) is a solid solution of  $\text{PbTiO}_3$  and  $\text{PbZrO}_3$  which are ferroelectric (FE) and anti-ferroelectric (AFE) materials, respectively. Since Jaffe *et al.* [1, 2] found enhanced piezoelectric (i.e. maximum electromechanical coupling coefficient and low dielectric constant) properties in  $\text{Pb}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$  near the morphotropic phase boundary (MPB), PZT ceramics have been considered to be important materials in modern piezoelectric technology. Addition of some impurities to PZT has also improved its piezoelectric constants [3–8].

Lanthanum-modified transparent lead zirconate titanate (PLZT) ceramics, prepared by the conventional hot-pressing method, have been used for electro-optic applications [9, 10]. Recent works on PLZT have demonstrated that its transparency can be greatly enhanced if it is synthesized through chemical routes [11–13]. Although some chemical methods have been used to synthesize this compound, some improvement in the process or an alternative suitable process is still required to obtain a fine and homogeneous PLZT powder for device applications. In the present study, we have synthesized the material by a nitrate method and characterized it using X-ray, infrared, scanning electron microscopy, differential scanning calorimetry, thermogravimetric analysis-differential thermogravimetry and dielectric techniques, to find the suitability of the material for such applications.

## 2. Experimental procedure

For the synthesis of PLZT, the following starting compounds were used:  $\text{Pb}(\text{NO}_3)_2$ ,  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  and  $\text{C}_{12}\text{H}_{28}\text{O}_4\text{Ti}$  of analytical

grade. The powder of composition  $(\text{Pb}_{0.90}\text{La}_{0.10})(\text{Zr}_{0.65}\text{Ti}_{0.35})\text{O}_3$  (PLZT (10/65/35)) was prepared by the following process. Lead, lanthanum and zirconyl nitrates were dissolved in doubly distilled water. Tetra-isopropyl titanate (a liquid) was then added directly to the above nitrate solution while stirring the solution. The titanium hydrolysed to an intermediate  $\text{Ti}(\text{OH})_4$  phase and slowly redissolved. The intrinsic acidity of the solution was kept at  $\text{pH} < 1$  (which is a controlling factor) 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 stuck to the glass beaker, therefore it was again heated at 230 °C to break the bond between the powder and the glass. The powder was calcined at different temperatures ranging from 230–920 °C. Alumina crucibles were used for this purpose.

The formation and quality of the desired compound were checked by X-ray diffraction (XRD) technique with  $\text{CuK}_\alpha$  radiation ( $\lambda = 0.15418 \text{ nm}$ ) and infrared spectroscopy (Perkin Elmer 843). The sample for infrared analysis was prepared by mixing KBr with PLZT powder in the ratio 7:1. For studying particle size and shape and the microstructure of the prepared materials, micrographs were taken using the scanning electron microscope (SEM).

Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), along with differential thermogravimetry (DTG) of the material were carried out using DuPont Instruments (model 9000) in the temperature ranges 40–550 °C and 40–1000 °C, respectively. For DSC analysis, about 15–20 mg powder were used together with a reference material (empty aluminium pellet). The heating rate of the furnace was  $20 \text{ }^\circ\text{C min}^{-1}$ .

The powder calcined at 920°C was cold pressed into discs (pellet) at  $6 \times 10^7 \text{ Kg m}^{-2}$  pressure using a hydraulic press. Sintering of these pellets was carried out at different temperatures (920–1200°C) and sintering times (2–2.5 hr). In order to prevent PbO vaporization, an equilibrium PbO vapour pressure was established using  $\text{PbZrO}_3$  as setter, and placing everything in the covered alumina crucible. After sintering, the samples were subjected to annealing at 970°C to provide further evidence of the effect of the dopant. The density of the sample was found to be approximately 97% theoretical. Dielectric properties of the PLZT samples were measured with a GR-1620 AP capacitance measuring assembly as a function of temperature (room temperature to 160°C) at different frequencies.

### 3. Results and discussion

Fig. 1 shows the XRD patterns of the specimen calcined at different temperatures. The onset of formation of the rhombohedral phase of PLZT is observed after the 350°C calcination. Calcination of PLZT at 550°C is sufficient to achieve the complete crystallization of PLZT. Diffraction lines of PLZT, calcined at 920°C are found to be very sharp and single which indicates the single-phase compound with better homogeneity and crystallization of the materials. The PLZT thus obtained is stoichiometric and very pure.

Figs 2–5 give the resulting infrared spectra as a function of the calcination temperature. There are many organic bonds present in the uncalcined powder, as shown in Fig. 2. Most of the organic bonds disappear after calcination at 350°C for 1 h and removal of the organic residue is completed at 550°C, as indicated in Figs 4 and 5, respectively.

DSC and TGA–DTG curves of PLZT are shown in Figs 6 and 7, respectively. Endothermic peaks observed at 100°C in the DSC experiment are due to removal of water molecules, as indicated by the corresponding weight loss in the TGA and DTG curves. The

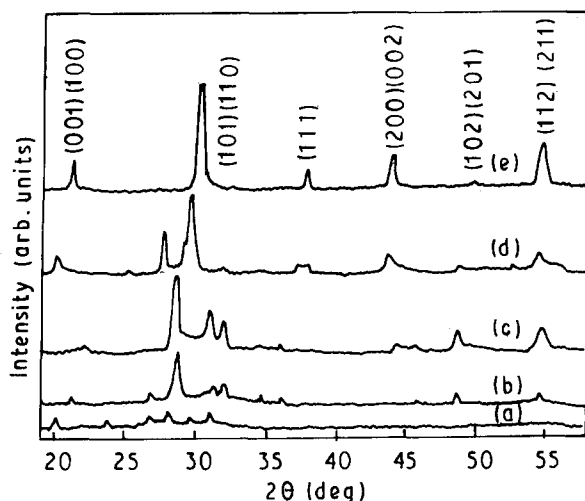


Figure 1 XRD of chemically prepared PLZT(10/65/35): (a) as-prepared powder, and powders calcined at (b) 350°C, (c) 450°C, (d) 550°C, (e) 920°C for 1 h.

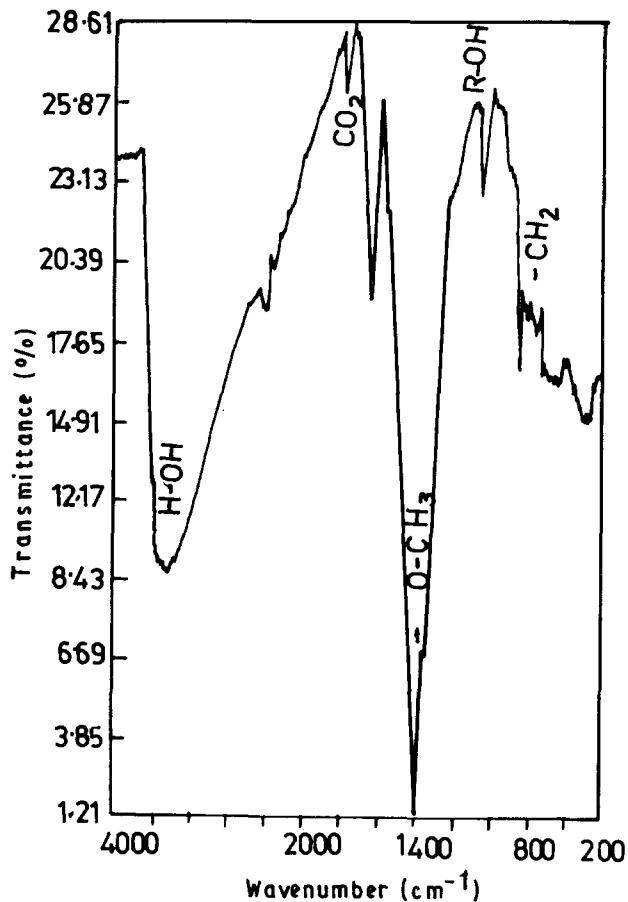


Figure 2 Infrared spectra of as-prepared PLZT powder.

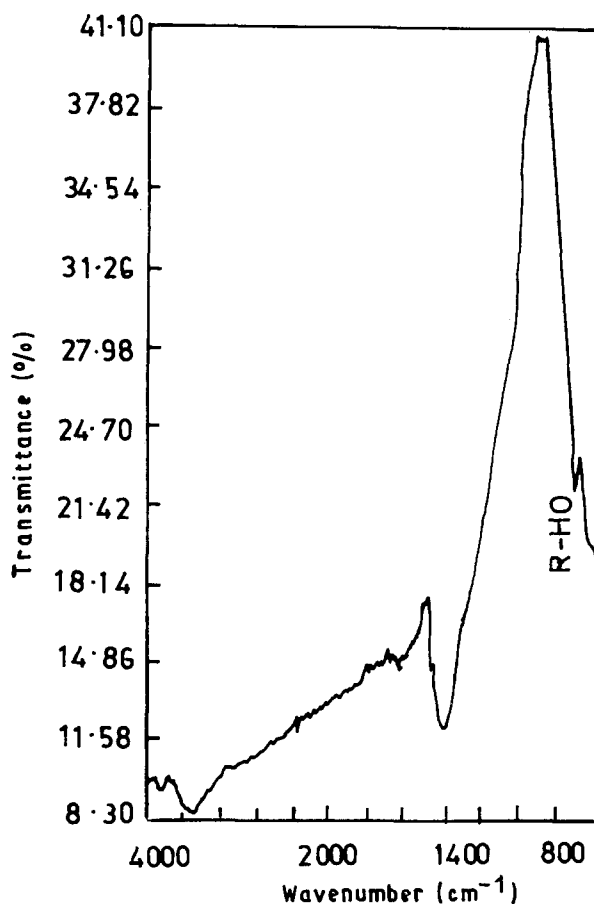


Figure 3 Infrared spectra of PLZT powder calcined at 350°C, 1 h.

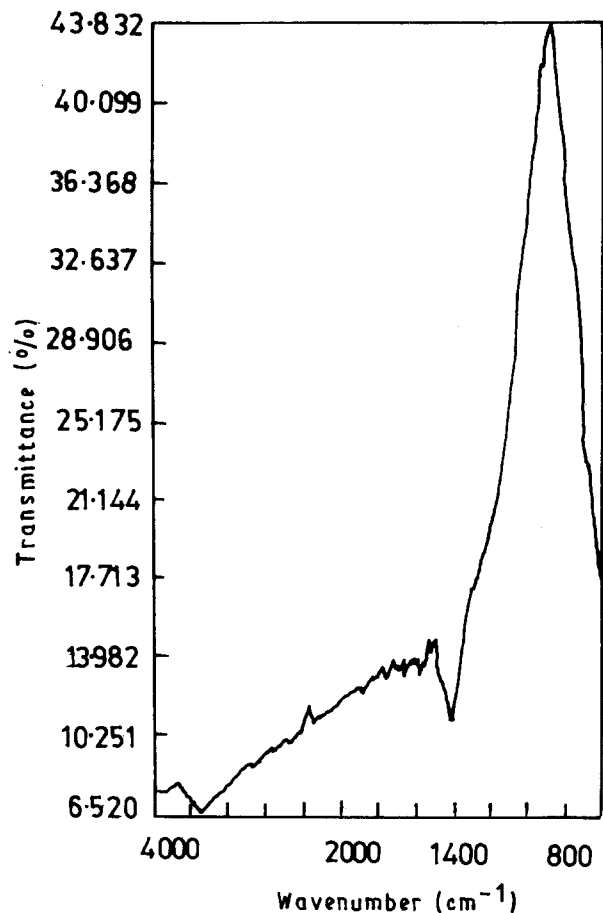


Figure 4 Infrared spectra of PLZT powder calcined at 450°C, 1 h.

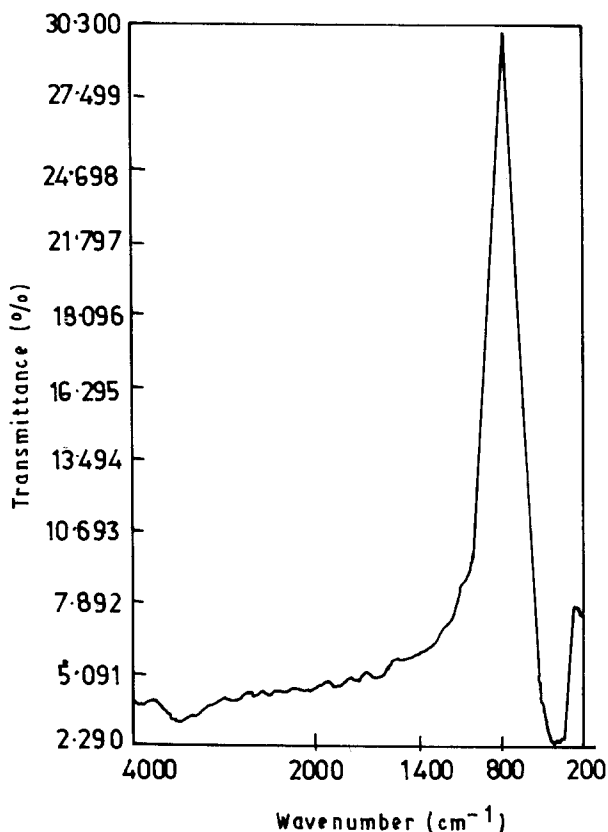


Figure 5 Infrared spectra of PLZT powder calcined at 550°C, 1 h.

appearance of two endothermic peaks at 450 and 500°C in the DSC curve, Fig. 6, indicates the decomposition of  $\text{Pb}(\text{NO}_3)_2$  into  $\text{PbO}$  is a two-step process, as reported in Dayal *et al.* [16]. It should be

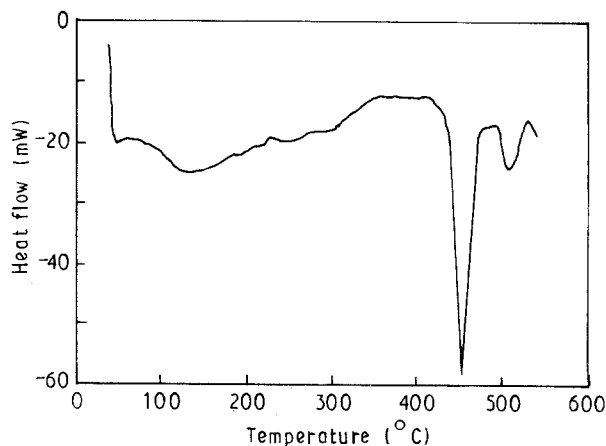


Figure 6 DSC of PLZT as-prepared powder.

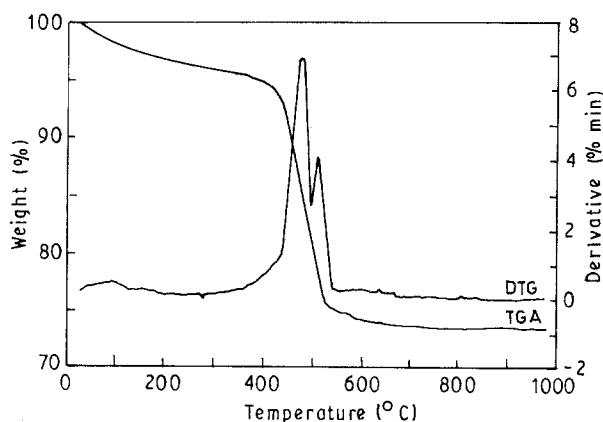


Figure 7 TGA and DTG of as-prepared powder.

pointed out here that no exothermic peak was found in the DSC or TGA plot around 230°C, as reported earlier [16]. This is because titanium hydrolysed to an intermediate  $\text{Ti}(\text{OH})_4$  phase and slowly redissolved.

Fig. 8 shows scanning electron micrographs of PLZT powder and pellet sintered at 1225°C. These microstructures suggest that the sintered pellet was not fully dense and some porosity still remains, Fig. 8b.

The room temperature dielectric constant of the silver-electroded sample was 991. The temperature dependence of the dielectric constant, Fig. 9, showed the highest dielectric constant (1108) at 85°C. The nature of the dielectric constant,  $K$ , versus temperature curve was found to be diffuse, because the lanthanum concentration used (i.e. 10%) was relatively high, which indicates the presence of mixed  $\text{FE}_{\text{Rh}}$ /cubic phase on a microscopic or macroscopic scale [14, 15].

#### 4. Conclusions

PLZT ceramic with the composition 10/65/35 synthesized from nitrate solutions was found to be very fine (17  $\mu\text{m}$ ) and homogeneous. X-ray diffraction patterns and infrared spectra indicate that calcination at 600°C for 1 h is sufficient for the formation of PLZT. A study of the dielectric constant suggests the diffuse type of phase transition and relaxation behaviour in the material.

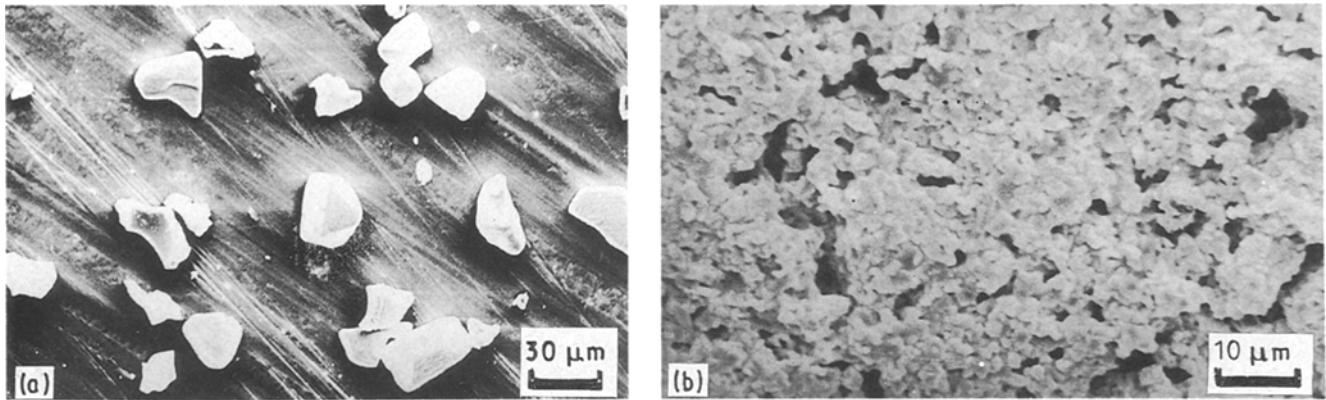


Figure 8 Scanning electron micrographs of PLZT (a) as-prepared powder, and (b) pellet sintered at 1225°C, 2 h.

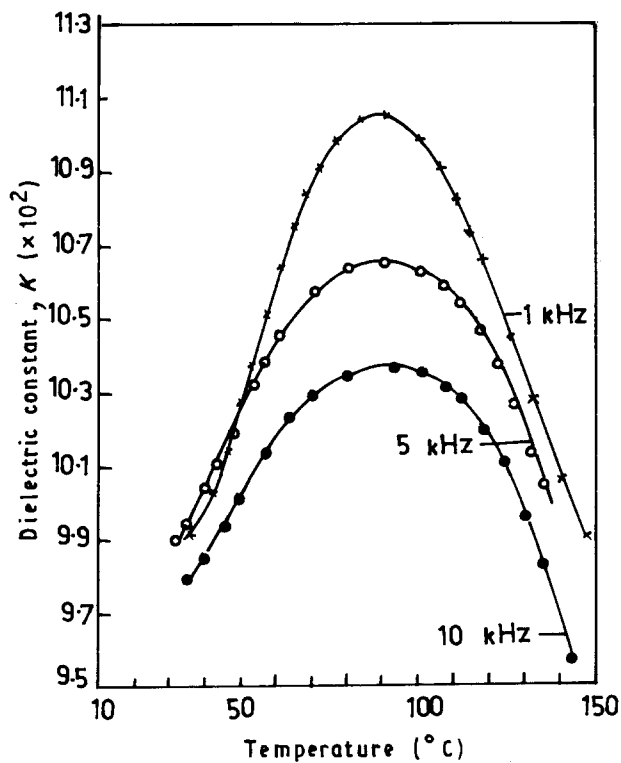


Figure 9 Temperature dependence of the dielectric constant.

### Acknowledgements

The authors wish to thank Professor S. Bhattacharjee, Mr R. P. Mukherjee and Mr Sanjoy Roy for their help in X-ray and infrared work. One of us (KLY) thanks CSIR, New Delhi, for a research fellowship. We thank

Professor B. Chakravarty, head of the Department of Physics and Meteorology, for his help and encouragement.

### References

1. B. JAFFE, R. S. ROTH and S. MARZULLO, *J. Appl. Phys.* **25** (1954) 809.
2. B. JAFFE, R. S. ROTH and S. MARZULLO *J. Res. Nat. Bur. Stand.* **55** (1955) 239.
3. F. KULCSAR, *J. Amer. Ceram. Soc.* **42** (1959) 343.
4. *Idem.*, *ibid.* **48** (1965) 54.
5. P. ROYCHOWDHURY and S. B. DESHPANDE, *Ind. J. Pure. Appl. Phys.* **15** (1977) 395.
6. T. B. WESTON, A. H. WEBSTER and V. M. McNAMARA, *J. Amer. Ceram. Soc.* **52** (1969) 253.
7. P. ROYCHOWDHURY and S. B. DESHPANDE, *Ind. J. Pure. Appl. Phys.* **17** (1979) 571.
8. *Idem.*, *J. Mater. Sci.* **22** (1967) 2209.
9. G. H. HAERTLING and C. E. LAND, *J. Am. Ceram. Soc.* **54** (1971) 1.
10. G. H. HAERTLING, *ibid.* **54** (1971) 303.
11. M. MURATA, K. WAKINO, K. TANAKA and Y. HAMA-KAWA, *Mat. Res. B* **11** (1976) 323.
12. J. THOMSON Jr, *Amer. Ceram. Soc. Bull.* **53** (1974) 421.
13. L. M. BROWN and K. S. MAZDIYASNI, *J. Amer. Ceram. Soc.* **55** (1972) 541.
14. M. WOLTERS and A. J. BURGGRAAF, *Phys. Status. Solidi(a)* **24** (1974) 341.
15. G. BURCHHART, J. VON CIEMINSKI and G. SCHIMDT, *ibid.* **59** (1980) 748.
16. RAJIV DAYAL, CH. DURGA PRASAD and RAMJI LAL. *Mater. Res. Bull.* **25** (1990) 1339.

Received 21 October 1991  
and accepted 18 March 1992