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Synthesis of Nanocrystalline PZT by Hydrothermal Method

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ABSTRACT

Synthesis of lead zirconium titanate by a simple, low-energy consumption hydrothermal means is being reported. The precursor materials have been chosen and the method is tailored so that the process becomes economical and offers low lead loss. The synthesised powders have been analysed by FTIR, XRD, SEM, TEM, and TGA. The results show the formation of tetragonal PZT nanoparticles with an average yield of ~75 per cent. On the basis of FTIR, the product formation is understood to proceed via the formation of a three metal cation hydroxide complex, that under hydrothermal treatment undergoes conversion directly to form the tetragonal phase of lead zirconium titanate.

Keywords: Lead zirconium titanate, piezoelectric materials, electrostrictive materials, actuators, memory alloys, PZT nanoparticles, perovskite structure, perovskite, hydrothermal synthesis

1. INTRODUCTION

PZT ($Pb(Zr_xTi_{1-x})O_3$ offers excellent piezoelectric and electrostrictive properties making it a promising material for ferroelectric memory, optoelectronic, electrostrictive actuator, and electromechanical transducer applications, both for industries and defence requirements[1].

Amongst the several methods developed to synthesize PZT powders, the most commonly accepted method is the solid-state oxide route, which results in inhomogeneous and non-uniform powder composition. Further, the energy requirements of this method are high and results in the formation of lead oxide. Ananta[2], *et al.* have reported a modified two-stage mixed oxide route that requires subsequent calcinations on post-milling the precursors at temperatures > 700 °C. Hydrothermal processing is one of the most versatile and effective processing techniques to treat raw materials for technological applications[3]. Riman[4-5], *et al.* have investigated the use of an organic mineraliser and studied the effects of pressure, temperature, and time on the product formation. Recently, reports are available on sonochemical preparation for ferroelectric materials[6], high melting point ceramics, and others[7]. In the present study, a new methodology has been developed to synthesise PZT with perovskite structure having the tetragonal phase by hydrothermal technique.

2. EXPERIMENTAL DETAILS

The experiments were carried out in an indigenously fabricated teflon-lined autoclave as well as in a Parr digestion bomb. The procedure is depicted as a flow chart in Fig. 1.

3. CHARACTERISATION

The synthesised powders were characterised by FTIR, XRD, TGA, SEM, and TEM. FTIR

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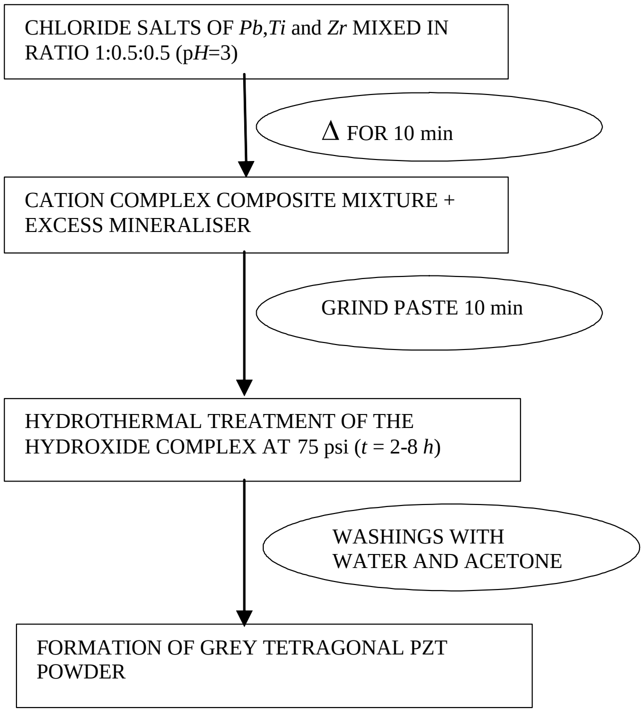


Figure 1. Schematic representation for the synthesis of PZT powder.

were recorded on a Shimadzu 8400 infrared spectrophotometer using *KBr* as a reference material. XRD characterisation of the samples was carried out on a x-ray PAN analytical XPERT-PRO diffractometer with *CuK*α radiation and Bruker-AXS D8 model. Thermograms were traced on a Perkin-Elmer TG unit (TGA 7) in nitrogen atmosphere from 50 °C to 1000 °C. SEM micrographs were recorded on JEOL, JSM 2300 Analysis Station and TEM samples were scanned on a Philips model CM-200 with an accelerating voltage of 200 kV. The powders were ultrasonically dispersed in alcohol and mounted on a carbon-coated copper grid of 400-mesh size.

4. RESULTS AND DISCUSSION

The chloride precursor salts, on mixing with acid resulted in a frothy, wet mixture. The slurry was transferred into an elongated alumina crucible and heated directly for 20 min on an electrical heater at 220 V. Evolution of *HCl* gas was observed and the formation of a friable mound was observed that could be easily dislocated out of the crucible. It was a fine network of *Zr* and *Ti* interspersed with *Pb* ions.

The FTIR of the same [Fig. 2(a)] shows a prominent, broad band ascribable to *O-H* stretching vibration for water at ~3200 cm^{-1} and an additional band correspondingly for the bending vibrations at 1614 cm^{-1}. A broad band in the 350-750 cm^{-1} range indicates the formation of an amorphous cation complex of *Ti*, *Zr*, and *Pb* oxide(s). On addition of the excess mineraliser, *KOH* (p*H*=13.8), a highly exothermic reaction takes place with evolution of water vapour and a coloured (orange/olive green; depending on the concentration of *Ti* salt) complex paste. The FTIR of the same is seen as [Fig. 2(b)]. It shows sharp peaks at ~1360 cm^{-1}, 1445 cm^{-1} and 1585 cm^{-1}. This again accounts for the chloro complex of the cation salts and the peak at ~3200 cm^{-1} for the *O-H* stretching vibration. The paste along with 20 ml of millipore water was taken in a teflon cup which was hydrothermally treated in two types of reactors: (i) indigeneously made autoclave and (ii) Parr acid digestion vessel, Moline, Illinois.

A series of hydrothermal experiments were carried out with: (a) varying hydrothermal treatment time and (b) variation in the concentration of the B-site ion $(0 \le x \ge 0.75)$. The pressure was kept below 75 psi and temperature < 200 °C. The powders were thoroughly washed with de-ionized water followed by acetone and dried in air for 24 h [Fig. 2(c)]. The final product obtained was grey with the average yield being ~75 per cent.

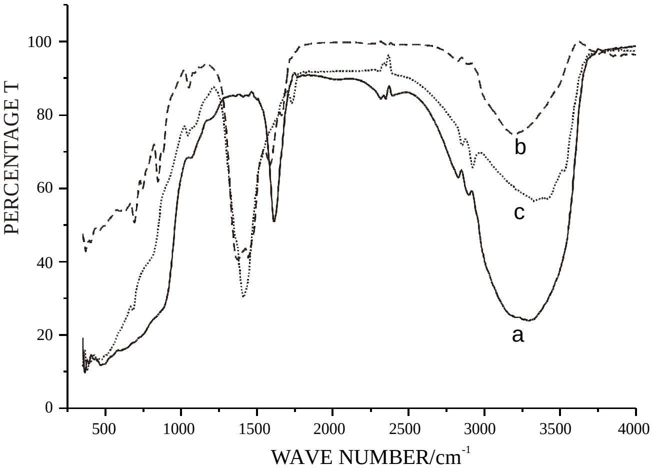
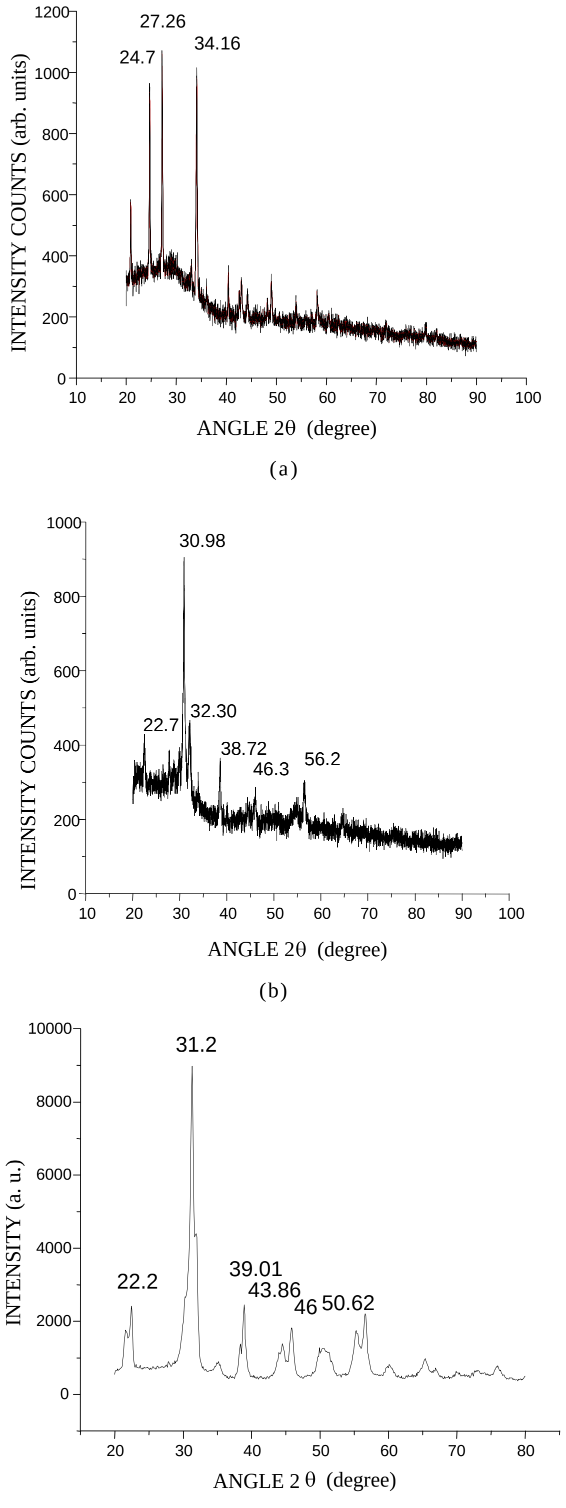


Figure 2. FTIR of: (a) acid-treated complex of the three metal ions, (b) alkali-treated complex, (c) product (PZT) obtained after hydrothermal synthesis.



(a)

(b)

(c)

Figure 3. XRD of: (a) paste prior to hydrothermal synthesis (b) PZT formed after hydrothermal reaction, time: 8 h, and (c) PZT powder subsequent to annealing at 600 °C for 4 h.

Figure 3 represents the XRD patterns of (a) intermediate the as-synthesised powder (b) for 8 h and (c) the annealed sample. The pattern matches close to the JCPDS card no 50-0346, indicating the composition to be $Pb\,Zr_xTi_{1-x}O_3$ having the perovskite structure. The XRD appears to reveal fairly crystalline nature of the synthesised powders. Characteristic peak splitting of the major reflections at (101) and (110) plane was observed as also at 2θ° ~ 45° for (002) and (200) planes for the tetragonal phase. It was observed that the time of hydrothermal treatment does not affect the product formation. However, the crystallinity of the powder was enhanced with the treatment time. Also, the colour of powders obtained was darker shade of grey for longer hydrothermal synthesis. When the concentration of *Zr*/*Ti* is 3:1, the colour of the powder is light-orange. The powder obtained from the Parr bomb was also found to be more crystalline than the ones obtained in the indigenously fabricated bomb but yield was slightly higher in the case of the latter.

The powders of PZT were observed initially under a SEM. Figure 4(a) and 4(b) show the PZT powder masses which appear to be dense and homogeneous. Close inspection of the PZT powders calcinated at 600 °C by TEM showed large number of oblong shaped particles with an average size of 10-12 nm (Fig. 4(c)). Figure 4(d) depicts the SAED pattern for the nanocrystalline powders.

Further, the thermogravimetric analysis was carried out for 8 h as-synthesised powder (Fig. 5). A total weight loss of 9.0 per cent was evident. Between 50–250 °C, a loss of 4.2 per cent was indicated that could be attributed to adsorbed water loss. The loss up to 550 °C (3 %) was accounted for the hydrogen-bonded water molecules in the powder. Towards a high temperature of 1000 °C, a low weight loss of ~2 per cent was predicted towards loss of *PbO* from the sample. Thus, low weight loss indicates stability of the material at higher temperatures.

Apart from this, during experimentation, it was noted that lower concentrations of mineraliser did not promote the reaction, the desired p*H* being 12-14

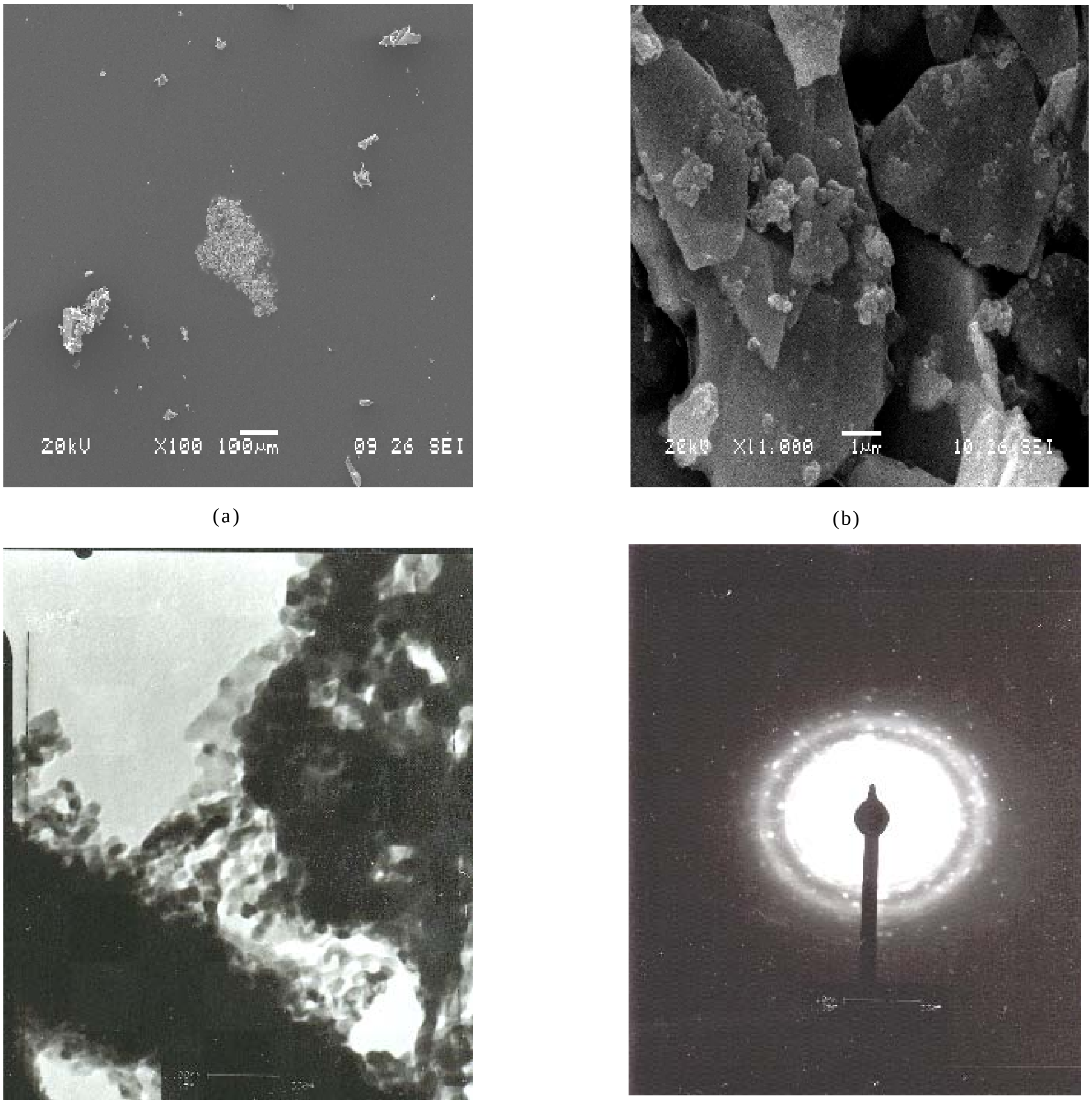


Figure 4. (a) and (b) SEM of PZT powder masses after washing, (c) TEM of the calcined PZT particles, and (d) SAED of the 8 h hydrothermally synthesised PZT powder.

for the reaction to proceed. The effect of hydrothermal treatment time resulted in increased crystallinity of the product. The general mechanism for the formation of PZT is under study. It is understood that the hydroxide cation complex of *Pb*, *Zr*, and *Ti* in aqueous medium under basic p*H* on hydrothermal treatment undergoes conversion to PZT.

5. CONCLUSION

A simple, hydrothermal treatment route towards the synthesis of PZT using inexpensive laboratory chemicals and conditions is reported. Preliminary investigations relating to the formation of PZT, reproducibility of the method, and the ability to use laboratory-grade chemicals have been studied.

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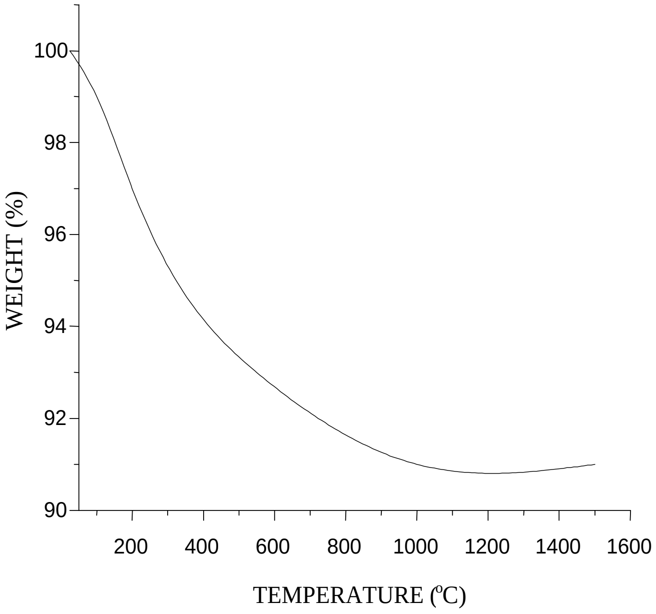

Figure 5. TGA of the hydrothermally synthesised (8 h) PZT sample.

nanopiezoelectrics were carried out. Malini Bapat is grateful to ISRO for the Senior Research Fellowship.

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