Synthesis and characterization of nanocrystalline PZT powders: From sol to dense ceramics

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Abstract

In this study ferroelectric lead zirconate titanate PZT (0.523/0.477) nanocrystalline powders have been successfully synthesized by an alkoxide based sol-gel process. Crystallinity of the prepared ceramic powders was studied using X-ray diffractometer. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) studies were performed to study morphology of the calcined powders. EDX analysis was employed to demonstrate purity of the synthesized powders. Surface nature of the powders was studied by using FTIR technique. TGA/DTA analysis was employed to study thermal behaviour of powders. Spectroscopic techniques (FTIR and XRD) results indicated that the as-dried amorphous powders can be completely crystallized at 600 °C. In order to investigate the densification behaviour of the calcined powders, the crystalline PZT powders were pelletized into discs and sintered at various temperatures from 900 °C to 1150 °C, with a heating rate of 10 °C/min and holding time of 2 h to find the optimum combination of temperature and time to produce high density ceramics. Microstructural characterization was conducted on the fractured surface of the samples using SEM. It was found that the PZT ceramics calcined at 600 °C for 4 h then sintered at 1050 °C for 2 h had maximal density (98% of the theoretically density).

Keywords: ferroelectric, PZT, sol-gel process, XRD, FTIR, sintering

I. Introduction

Lead zirconate titanate (Pb(Zr1-x,Tix)O3, PZT) having a perovskite type ABO3 structure is a solid solution of a ferroelectric phase i.e. lead titanate (PbTiO3) and an antiferroelectric phase, i.e. lead zirconate (PbZrO3) [1]. In the 1950’s, Jaffe et al. discovered that PZT ceramics with a Zr/Ti ratio approximately 52:48 have excellent properties such as, high Curie temperature, high electromechanical coupling coefficient, easy poling and doping, and high dielectric, ferroelectric and piezoelectric properties. Owing to these excellent properties, PZT ceramics have been extensively used in many applications such as nonvolatile ferroelectric random access memories (NVFRAMs), pressure and force sensors, accelerometers, computers and microphones, air and underwater transducers, FM coupled mode filters, actuators, etc. [3,4]. Traditionally PZT ceramics are prepared by solid-state reaction process because of their facile processing and economic considerations [5]. In this process mechanically mixed starting materials, which are typically oxides or carbonates, are heated at high temperatures to obtain desired product [6]. However, high calcinations temperatures employed in this method lead to aggregation of powders and loss of PbO which are responsible for degradation of electrical properties of PZT ceramics [7]. Furthermore, low homogeneity due to poor mixing and low purity due to presence of impurities in raw materials and contaminations from jar are other drawbacks of solid-state process [8,9]. Accordingly, in order to obtain PZT ceramics with good electrical properties, it is necessary to use other methods for synthesis of fine and homogeneous PZT powders with high purity. For synthesis of such powders, in recent years chemical methods such as sol-gel [10,11], citrate nitrate [12], hydrothermal [13], spray drying [14], co-precipitation [15], sol-hydrothermal [16] etc., were used. Owing to mixing of components at molecular level and purity of starting materials, all of these methods result in fine, homogeneous and pure powders. However, among these methods, sol-
gel method has been widely employed for synthesis of PZT powders. This is due to inherent advantages of this process, such as simple set up, high homogeneity, high purity and excellent control of stoichiometry [17,18]. Besides, the use of highly reactive metal alkoxides as precursors allows the synthesis of ceramic materials at lower temperatures than other common solid state reactions [19]. Finally, the rheological properties of sols or gels of this technique provide a new approach to the preparation of powders, thin films [20], fibers [21] and porous ceramics [22].

The present work concerns the synthesis of PZT nanocrystalline powders via sol-gel method with a special attention to characterization of synthesized powders from sol to dense ceramics. Also sintering behaviour of dense ceramics was studied.

II. Experimental procedure

2.1. Nanocrystalline PZT powder preparation

The starting chemical materials were lead (II) acetate trihydrate, (Pb(CH$_3$COO)$_3$·3H$_2$O), (99.5%, Merck), zirconium (IV) n-propoxide, (Zr(OCH(CH$_3$)$_3$)$_4$), (70% w/w in n-propanol, Fluka) and titanium (IV) isopropoxide, (Ti(OCH(CH$_3$)$_3$)$_4$), (99%, Merck). 2-methoxy ethanol (CH$_3$OCH(CH$_3$)$_3$OH) (99.5%, Merck), 2-methoxy ethanol (CH$_3$OCH(CH$_3$)$_3$OH) (99.5%, Merck), 2-methoxy ethanol (CH$_3$OCH(CH$_3$)$_3$OH) (99.5%, Merck), 2-methoxy ethanol (CH$_3$OCH(CH$_3$)$_3$OH) (99.5%, Merck) was used as solvent and acetylacetone (C$_5$H$_4$O$_2$, AcAc), (99.9%, Merck) was used as a stabilizer for alkoxides. To produce 200 ml, 0.5 M PZT (52/48) sol, 41.73 g (slightly higher than stoichiometry amount, to compensate the loss of lead in the subsequent thermal treatment) lead acetate trihydrate was dissolved in 80 ml, 2-methoxyethanol while stirred at 120°C for 2 hours and then refluxed at the same temperature for another 2 hours in order to obtain a homogeneous solution. The by-products of this solution were vacuum distilled in 80°C until a white paste (i.e. the Pb precursor paste) was formed. In a separate flux set stoichiometric amounts of titanium (IV) isopropoxide (13.344 g) and zirconium (IV) n-propoxide (23.308 g) were dissolved in 40 ml 2-methoxyethanol in presence of 10.012 g acetylacetone (the molar ratio was [Zr+Ti]/[AcAc]=1/1) at ambient temperature. Then the solution was refluxed at 120°C for 2 hours forming a clear yellow solution (i.e. the Ti/Zr precursor solution). The next step was mixing of the Pb paste and Ti/Zr solution and formation of a new solution, which was refluxed at 120°C for 3 hours. Then hydrolyzing agent (distilled water in molar ratio [Ti]/[H$_2$O] = 1/2) was added to the solution and refluxed at 120°C for another 1 hour. The final product was a viscous golden solution so called “PZT sol” (Fig. 1a). The PZT concentration on the final sol was 0.5 M with pH ~ 7. The PZT sol was converted to a gel at 80°C for 4 h and after drying at 120°C for 24 h the gel was transformed to amorphous powder. The obtained amorphous powders were heat treated at 600–700°C for different times to obtain crystalline PZT powders.

2.2. Preparation of PZT ceramics

The crystalline PZT powders were used for preparation of PZT discs. The PZT powders were mixed with 5 wt.% of a water solution containing 10% polyvinyl alcohol (PVA). The powders were pressed into 10 mm in diameter by 1.5 mm thick discs in stainless steel dies under uniaxial pressure at 150 MPa. Then the samples were placed in a covered alumina crucible and atmosphere was controlled by the addition of pure PZT (52/48) + 10% ZnO powders in the crucible without contact with the samples (Fig. 1b). The discs were sintered at various temperatures from 900–1150°C for 2 h, with 4 h holding at 550°C for binder burn-out of organic species. Heating rate was 5°C/min up to burn-out temperature (550°C) and then a heating rate of 10°C/min was employed up to final sintering temperature. Figure 2 shows the detailed scheme of the experimental procedure.

2.3. Characterization

The phase composition of the powders and sintered bodies was examined by X-ray diffractometer (Brucker-Germany) using CuKα radiation (λ = 1.5418 Å). The XRD patterns were recorded at room temperature at a scan rate 0.05°/s and 2θ from 20° to 70°. Microstructural characterization was conducted by fractured surface of sintered samples using scanning electron microscopy (SEM- Cambridge). The density of sintered samples was determined by the Archimedes method. Particle size analysis of synthesized powders was per-

![Figure 1](image.png)
Figure 2. Preparation of PZT nanocrystalline powders and bulk PZT ceramics

Figure 3. Particle size distribution of 0.5 M PZT powder (results of three consequentive measurements)

Figure 3 shows particle size distribution of ultrafine particles in the PZT sol. As it can be seen, nanoparticles have a diameter below 10 nm and average particle size is 5.5 nm. Figure 4 shows FTIR spectra of the PZT sols. Figure 4a shows spectrum of the PZT sol with distillation process in the final step, whereas Fig. 4b shows...
FTIR spectrum for the sol without distillation process in the final step. As it is clearly observed, the only difference between these two sols is presence of a peak located at 1739.5 cm⁻¹ in the sol without distillation process in the final step. This peak is due to presence of ester with general formula of R'COOR, where R and R' are organic groups. During preparation of Pb solution, ester can be formed according to these reactions:

\[
Pb(OAc)_2 + ROH \rightleftharpoons Pb(OAc)(OR) + HCOOH \quad (1)
\]

\[
HCOOH + ROH \rightleftharpoons H_2O + AcOR \quad (2)
\]

where R is \(-CH_2OCH_2CH_3\) and Ac is \(CH_3CO\).

Ester can also be produced as a result of reaction between titanium isopropoxide or zirconium n-propoxide with lead acetate [24]:

\[
M(OR)_4 + Pb(OAc)_2 \rightleftharpoons (RO)\_3M-O-Pb(OAc) + R'COOR \quad (3)
\]

where M is Ti or Zr, R is \(CH_3O\) and R' is \(CH_3\).

The presence of ester in the sols modified their properties. Thus, in order to eliminate this product (ester), distillation process must be done in the final step (Fig. 4b).

### 3.2. PZT powders

**X-ray diffraction studies**

During gel to ceramic conversion in the sol-gel derived PZT powders two crystalline phases were observed. The first one is a stable and desired phase with excellent electrical properties, i.e. pervoskite phase with general formula \(\text{ABO}_3\) (\(\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3\)). The second one is a metastable and undesired phase, i.e. pyrochlore phase with poor electrical properties due to large defect density as a result of oxygen or lead deficiency [6], with general formula \(\text{A}_2\text{B}_2\text{O}_{7-x}\) (\(\text{Pb}_2(\text{Zr}_{1-x}\text{Ti}_x)_2\text{O}_{7-x}\)) [25]. Therefore it is essential to avoid formation of pyrochlore phase during crystallization process. X-ray diffraction patterns of the PZT powders calcined at different temperatures with a heating rate of 5 °C/min are shown in Fig. 5. The as-dried PZT powders have an amorphous structure so XRD pattern of this powders are not shown here.

A comparison between the powders calcined at different holding time but same crystallization temperature, i.e. 600 °C for 2 and 4 h, shows that prolonged heating increases amount of pervoskite phase. It can be explained by the fact that pyrochlore phase is transformed to pervoskite phase in a slow kinetic process [25]. The observed pyrochlore peak in XRD pattern of the powders crystallized at 650 °C for 1 h, is due to insufficient holding time for complete transformation of pyrochlore to pervoskite phase. So it is necessary to prolong heating for obtaining of a pure pervoskite phase. Another comparison between the powders calcined at different temperatures but same holding time, i.e. 600 °C and 700 °C

### Table 1. Relative amount of perovskite phase (\(P_{\text{per}}\)) and crystalline size of calcined PZT powders

<table>
<thead>
<tr>
<th>Sintering conditions</th>
<th>600 °C/2 h</th>
<th>600 °C/4 h</th>
<th>650 °C/1 h</th>
<th>650 °C/4 h</th>
<th>700 °C/2 h</th>
</tr>
</thead>
<tbody>
<tr>
<td>(P_{\text{per}}) [%]</td>
<td>95</td>
<td>~100</td>
<td>93</td>
<td>100</td>
<td>97</td>
</tr>
<tr>
<td>Crystallite size [nm]</td>
<td>63</td>
<td>67</td>
<td>64</td>
<td>70</td>
<td>68</td>
</tr>
</tbody>
</table>
Average of crystalline size and amount of pervoskite phase of the calcined PZT powders are shown in Table 1. Average of crystalline size was calculated using Scherrer-Warren equation:

\[ x = \frac{C \cdot \lambda}{\beta \cdot \cos \theta} \] (4)

where \( x \) is crystal size in angstrom, \( C \) is a numerical constant (\( \sim 0.9 \)), \( \lambda \) is the wavelength (1.5418 Å), \( \beta \) is full width at half maximum (FWHM) of the XRD (110) peak in radians and \( \theta \) is Bragg angle for the peak in degrees. Fraction of pervoskite phase \( (P_{\text{per}}) \) was calculated approximately, for comparative purposes, from the XRD intensity peaks using the following expression [31]:

\[ P_{\text{per}} = \frac{I_{110(\text{perovskite})}}{I_{110(\text{perovskite})} + I_{110(\text{pyrochlore})}} \cdot 100 \] (5)

Based on the results presented in Table 1, the powders calcined at 600 °C for 4 h were selected for further sintering studies.

**Particle size studies**

Figure 6 shows particle size distribution of the PZT calcined at 600 °C for 4 h. A salient feature of these powders is that they have a narrow distribution and mean particle size were approximately 100 nm, indicating of formation of nanosized powders.

**Fourier transformed infrared studies**

Figure 7 shows the FTIR spectrum of the as-dried and calcined powders. The as-dried powders have several peaks that are disappearing after heat treatment at higher temperatures. Also at higher temperatures a new peak is observed. The absorption band at 3444.6 cm\(^{-1}\) may be assigned to the stretching of –OH groups present in 2-methoxyethanol, acetylacetone or chemically combined water in Pb(C\(_2\)O\(_2\)H\(_7\))\(_2\) × 3 H\(_2\)O [32]. The bands between 1439.9 cm\(^{-1}\) and 1623.9 cm\(^{-1}\) correspond to the symmetric and antisymmetric –COO– stretching modes of the acetate groups [26]. These peaks are very weak at high temperatures and finally completely disappear. The peaks between 600 to 1338.5 cm\(^{-1}\) may be assigned to the carbonate presents in the as-dried powders that corresponds to the stretching mode of C–C bands and vibration modes of CH\(_3\) groups (basic intermediate acetate salts) [26,27]. The presence of carbonaceous species in the as-dried particles is also confirmed by black colour of the powders. A sharp band at 582.5 cm\(^{-1}\) was formed in the powders calcined at 600 °C and 650 °C, that were attributed to the M–O bonding (M = Ti, Zr and Pb).

**TGA/DTA studies**

The TGA curve (Fig. 8) shows a weight loss of about 27 wt.% in the temperature range of 25–600 °C where mass loss occurs in three steps. The decomposition of
Table 2. A comparison between calcination temperature and time in this study with other papers

<table>
<thead>
<tr>
<th>Crystallization temperature [°C]</th>
<th>Crystallization time [h]</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>600</td>
<td>4</td>
<td>Present work</td>
</tr>
<tr>
<td>900</td>
<td>4</td>
<td>[29]</td>
</tr>
<tr>
<td>700</td>
<td>12</td>
<td>[30]</td>
</tr>
<tr>
<td>700</td>
<td>4</td>
<td>[31]</td>
</tr>
<tr>
<td>650</td>
<td>2</td>
<td>[9]</td>
</tr>
</tbody>
</table>

the PZT gel is characterized by one endothermic peak at 100 °C due to the evaporation of physically absorbed water, solvent and volatile esters and two main exothermic peaks. Two exothermic peaks in the range of 200–300 °C are attributed to the decomposition of organic species accompanied by a large weight loss. The last two exothermic peaks are assigned to the formation of pyrochlore and of perovskite phases. There is a small weight loss along with these peaks indicating that both phenomena were accompanied by the residual combustion of the organic species. TGA/DTA and FTIR results in conjunction with XRD results show that the complete formation temperature of the perovskite PZT is 600 °C. Table 2 presents a comparison between calcination temperature and time in this study with some other researchers.

SEM/TEM and EDX analysis

The PZT powders calcined at 600 °C for 4 h were further analysed by SEM/TEM and EDX analysis. Figure 9 shows SEM micrograph of the PZT powders indicating presence of some agglomeration. Figure 10 shows TEM micrograph of these powders confirming presence of particles with irregular shape and particle sizes smaller than 100 nm.

Figure 11 presents EDX result of the PZT powder prepared by sol-gel process showing relative quantity of principal elements of PZT, i.e. Pb, Zr and Ti. It can be observed that there is no impurity in synthesized powders demonstrating high purity of starting materials and reliability of sol-gel process. Furthermore, calculated Zr/Ti ratio was 0.523/0.477 which is very close to MPB (52.3/47.7). This shows another advantage of sol-gel process, i.e. possibility exact control of stoichiometry.

3.3. PZT ceramics

Figure 12 shows effect of sintering temperature on density of the PZT ceramics. It can be observed that density increases from 6.9 g/cm³ up to 7.8 g/cm³ with increase of sintering temperature form 900 to 1050 °C. A further increase of temperature over 1050 °C caused the drop of density to 7.2 g/cm³ at 1150 °C. This variation of density with temperatures can be explained by the fact that at low temperatures, such as 900 and 950 °C, sintering is incomplete since diffusion is a thermally activated process, so density is low. Decrease of density at high temperatures is probably due to volatilization of lead and grain growth caused by high temperatures [28]. Figure 13 shows the SEM micrographs of fractured surfaces of the PZT ceramics sintered at various temperatures. It can be seen from Fig. 13a that the PZT powders sintered at 950 °C have porous structure because of incomplete sintering. At 1000 °C grain size was approximately 2 μm and sintering was not fully completed (Fig. 13b). Density of 7.8 g/cm³, very close to the theoretical density of 7.9 g/cm³, with similar grain size was achieved at 1050 °C (Fig. 13c).
At higher temperature lead volatilization caused appearance of porosities and hence a drop in density (Fig. 13d). From the density results and SEM micrographs, it can be deducted that optimum sintering condition for the PZT discs is 1050 °C for 2 h. With sintering at such condition the pure PZT ceramics without presence of any impurity or pyrochlore phase and relative density of 98% can be obtained (Fig. 14).

IV. Conclusions

In this study nanocrystalline PZT powders (0.523/0.477) were successfully synthesized by sol-gel process. The PZT powders were completely crystallized at relatively low temperature, i.e. 600 °C. The calcined powders were sintered at various temperatures for 2 h, and the optimum sintering condition was found to be 1050 °C for 2 h. The sintered PZT ceramics have single phase perovskite structure and relative density of approximately 7.8 g/cm³, which is about 98% of their theoretical density.

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References

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