Piezoelectric and Structural Study of Zr–rich PZT Nanopowders Prepared by Sol-Gel Method

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ABSTRACT: Lead zirconate titanate (PZT) nanopowders were synthesized by acid-acetic based sol-gel method. The prepared PZT nanopowders were characterized by XRD, SEM/EDS and TEM technique. Single-phase perovskite PZT nanopowders were obtained after heat treatment at temperature of 700 °C. The effect of calcination temperature on crystal structure of PZT nanopowders has been discussed. The average particle size of PZT powders with spherical-shaped morphology was estimated to be around 20 nm by TEM observations. The optimum values of piezoelectric constant, electromechanical quality factor and a mechanical quality factor are obtained at Sintering temperature 1150 °C: d33=64 pC/N, Kp=0.41 and Qm=34.3.

Keywords: Piezoelectric, PZT nanostructure, perovskite, Electromechanical Coupling Factor

INTRODUCTION

1. Introduction

Pb-based perovskite solid solution of lead zirconate titanates (PZT; Pb(Zr1-x,Tix)O3) have been considered due to its high spontaneous polarization abilities, piezoelectric coefficient, dielectric permittivity and pyroelectricity [1,2]. The highest values for piezoelectric coefficient (d33) and the permittivity (εr) have been observed for chemical composition of x=0.52, the so-called morphotropic phase boundary (MPB), at which the tetragonal (Ti-rich) and rhombohedral (Zr-rich) phases coexist [3,4]. The excellent piezoelectric properties make it a promising material for sensors, optoelectronic and electromechanical transducer application [5]. Nano-sized particles of ferroelectric materials exhibited significant properties which recently motivated many in-depth researches on future applications [6-8]. For example, PZT nanoparticles (PZT-NPs) can also be suspended in PZT sol to serve as seeds to lower sintering temperature and reduction of Pb loss [9]. Currently, there are two approaches to make PZT-NPs. The first way is a top-down approach often used in the industry [10]. The second method is a bottom-up approach that is still underactive investigation by various researchers. Size and quality of PZT-NPs are controlled by various process parameters, such as temperature, time, and mineralizer concentration [11-15]. A wide variety of preparation routes have been employed to produce PZT-NPs such as hydrothermal [16,17], electrodynamics atomization [18,19], ultrasonic spray combustion synthesis (USCs) [20] and sol-gel [21-23]. Among these techniques, sol-gel process provides the advantage of homogenous chemistry in multi-component system, ease of composition variation, and low processing temperature [24]. Acetic acid based sol–gel processing of PZT, introduced by Yi et al. [25], and later developed by Assink and Schwartz [26], offers a simpler preparation route compared to the 2-methoxyethanol based sol–gel. The method was based on the reduced reactivity of transition metal alkoxides by acetic-acid modification. In the present study, PZT precursor solution was prepared from different metallo-organic compounds and different experimental processes. Then, PZT nanopowders were synthesized by acid acetic based sol-gel method. The properties of PZT nanopowders were investigated to evaluate the effect of calcination temperature on the crystal structure of PZT nanopowders by using an X-ray diffraction (XRD). The electromechanical and piezoelectric behavior of PZT were determined by the resonance/anti-resonance method.

MATERIAL AND METHODS

2. Experimental

2.1. Materials

The chemicals used to prepare the PZT sol were: lead acetate trihydrate (Pb(C2H3O2)3× 3H2O, denoted as Pb(OAc)2, 3H2O, Merck.), tetra-iso-propyltitanate (aka titanium-isopropoxide, Ti(OCH(CH3)2)4, denoted as Ti(Opr)4, Sigma-Aldrich Co.), zirconium n-propoxide solution with 70% w/w in n-propanol (ZrO(CH2)2CH3),
denoted as Zr(Opr)_4, Sigma-Aldrich Co.), glacial acetic acid (HOAc, Sigma-Aldrich Co., 99.7% pure) and acetylacetone (C_5H_8O_2, denoted as AcAc, Merck Co.).

2.2. Synthesis of PZT nanopowders

First, 13.9 g Pb(OAc)_2.3H_2O was dissolved in HOAc on a 1:3 molar ratio while stirred and refluxed at 110 °C during 3 h for dehydration and homogeneity purposes (solution A). Subsequently, 0.48 g Ti (Opr)_4 was mixed with (2.52 g) acac in order to avoid fast hydrolysis of reactants and continuously stirred at room temperature for 4 h. Then 14.8 g Zr(Opr)_4 was added into the mixture of Ti(Opr)_4/AcAc, which will be referred hereafter as solution B. Pb and Zr/Ti precursor solutions were then mixed and refluxed for 3 h at 85 °C. For hydrolysis, 1.8 g of distilled water was added to it and pH value was adjusted using Hydrochloride acid to allow the nanoparticle precursor to slow grow. The solution was stirred overnight at room temperature to get slightly yellowish clear transparent sol and then heated at 70 °C to obtain the gelation of Zr-rich PZT sol. The gel was dried at 120 °C and heat treated in two stages. The first heat treatment was carried out at 400 °C/2 h with a heating rate of 5°C/min. The obtained powder agglomerates were manually milled and then calcined at 700°C for 2 h (5°C/min) to promote the formation of the perovskite structure of PZT. After this second heat treatment, the carbon compounds were eliminated leading to nano-sized PZT powders with high purity. The colomic synthetic route employ is shown schematically in Fig.1.

Nano-sized PZT powders obtained were plasticized by 4 wt.% polyvinyl alcohol (PVA) addition, granulated and cold-pressed to disc-pellets at 120 MPa. Green ceramic discs (diameter (D): 10 mm & thickness (t): 4.5 mm) were sintered (5°C/min) in PbZrO_3 rich atmosphere, at various temperatures.

2.3. Characterization

Density (ρ) of sintered discs was measured by the liquid displacement technique based on the Archimedes’ principle. Silver paste was applied on both sides of ceramic discs as electrodes to provide a better ohmic contact for electrical measurements. Polarization was done at 120 °C/30 min in a silicon oil bath under a DC electric field of 15 kV/cm. The piezoelectric strain coefficient (d_33) of each disc was measured 24 h after poling, by a quasi-static d_33-meter (RM3500, KCF Tech). Coupling factor (k_p) and mechanical quality factor (Q_m) were determined by the resonance/anti-resonance method using an Agilent 4294A impedance analyzer (hp Hewlett Packard). The parameters k_p and Q_m were related to the resonance frequencies by means of the following expressions [14,29,30]:

\[ k_p = \left( \frac{f_a - f_r}{0.395 \cdot f_r + 0.574(f_a - f_r)} \right)^{1/2} \]

\[ Q_m = \frac{f_a}{2\pi Z_m C f_r(f_a^2 - f_r^2)} \]

where \( f_a \) is the resonat frequency and \( f_r \) is the anti-resonant frequency in the fundamental vibration mode. \( Z_m \) and \( C \) represent the resonant impedance and the capacitance on the mechanical branch of the equivalent circuit, respectively.
RESULTS AND DISCUSSION

3. Result and discussion
3.1. DTA-TG analysis
Thermal decomposition behavior of PZT gel was examined by thermo gravimetry (TG) and differential thermal analysis (DTA), shown in Fig. 2. At temperature of up to 400 °C, endothermic (Ed) and exothermic (Ex) reactions may be attributed to the volatilization and burnout of residual solvent in the sol [5]. The Ed peak at around 70 °C is due to the evaporation of water absorbed in the PZT solution (rate of weight loss: 4.173%). Also, the vaporization of light molecular organics occurs between 210-310 °C which corresponds to Ed, accompanied by a 27.492% weight loss. As a result, the exothermic peaks at 390, 480 and 530 °C were considered to be related to progressive decomposition of an organic group from Pb-Zr-Ti alkoxide and due to crystallization of metal oxide phase [3,5]. Therefore, crystallization of PZT powders takes place at 480 °C, and perovskite structure is established above 530 °C.

![Fig. 2. TG/DTA curves of PZT gel powders](image)

3.2. XRD patterns
X-ray diffraction patterns of PZT nano-powders calcined at various temperatures are shown in Fig. 3. A series of characteristic peaks: (012), (110), (202), (024) and (018) crystal planes at 2θ values are observed of nanopowders, which can be indexed based on rhombohedral phase (ICDD No. 1-070-0740).

The perovskite -type structure emerged at a higher temperature of 400 °C which is due to large grain size and high extent of crystallinity [2-5]. The relative intensity of pyrochlore peak (29.4°) at calcination temperature of 400 °C with respect to PZT peak (30.62°) is much stronger. At temperature of 500 and 600 °C, the pyrochlore and perovskite phases coexisted, which is consistent with the results reported elsewhere [2,3,12]. However, the pyrochlore phase at 29.4° of 2θ was transformed into perovskite phases at temperatures of 700 °C. By comparison, it can be found from Fig. 3: (i) At 400 °C the powders calcined were already crystalline, and composed of phases of cerussite (PbCO3; Ref. code 5-417), hydrocerussite (Pb3(3CO3)2(OH)4; Ref. code 13-131), and laurionite (PbClOH; Ref. code 31-680), monoclinic zirconia (ZrO2; Ref. code 5-543), and anatase titanium oxide (TiO2; Ref. code 2-387). (ii) Following calcination at 500-600 °C, the PZT precursors were composed of phases of litharge (PbO; Ref. code 1-796), PbZrO3 (Ref. code 1-75-1607) and PbTiO3 (Ref. code 1-75-1605). Lead hydroxycarbonate phases (i.e., cerussite and hydrocerussite) were mostly converted into their oxides (i.e., litharge). (iii) Upon calcination at 700°C, the phases of litharge and pyrochlore completely disappeared, and the initial formation of rhombohedral PZT (Ref. code. ICDD 1-70-740) was observed. The average particle size (Sp) was calculated by the Debye– Scherrer formula [17]; 

$$ S_p = \frac{0.89\lambda}{\beta \cos \theta} $$

where \( \lambda \) is the X-ray wavelength (1.54
˚A), θ is the diffraction angle and β is the peak width of half maximum (the $S_p$ of PZT nano-powders calcined at various temperatures are shown in Fig. 3).

Fig. 3. XRD images of PZT nanopowders calcined at various temperatures

3.3. SEM and TEM morphology

Typical TEM micrographs of represent PZT nano-powders calcined at 700 °C are shown in Fig. 4. From Fig. 4, nearly spherical shape particles, highly crystalline nature and size distribution less than 20 nm can be observed which is a relatively agglomeration state due to high surface energy of particles in nano-scale.

Fig. 4. TEM images of PZT nano-powders calcined at 700 °C

The surface morphology of PZT nano-powders nanocrystals was analyzed by scanning electron microscopy. Fig. 5 present the SEM photographs of PZT nano-powders calcined at 700 °C. Though the SEM images did not show well dispersed PZT nano-powders, but the PZT aggregated particles appear to be composed of much smaller crystallites. Also, to better identification of elemental composition of the synthesized material, Energy dispersive X-ray measurements were carried out by the EDX spectrometer attached to SEM. The EDS pattern of PZT is shown in Fig. 5f, which confirms the existence of Pb, Zr and Ti elements.
3.4. Piezoelectric study

To determine piezoelectric property of ceramics, resonant vibration spectrum of samples were measured at room temperature. Fig. 6 shows the impedance-phase spectra on frequency for piezo-ceramics sintered at 1150 °C. From these results, the resonant ($f_r$) and anti-resonant ($f_a$) frequencies, the minimum impedance $Z_{\text{min}}$, electromechanical coefficients $K_p$, mechanical quality factor $Q_m$ and dielectric loss tanδ are defined and the value are listed in table 1.

![Fig. 6. The frequency spectra of piezo-ceramic sintered at 1150 °C](image)

Table 1. Piezoelectric properties of ceramic samples sintered at various temperatures.

<table>
<thead>
<tr>
<th>Sintering Temperature (°C)</th>
<th>1000</th>
<th>1050</th>
<th>1100</th>
<th>1150</th>
<th>1200</th>
<th>1250</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/cm³)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$d_{33}$ (pC/N)</td>
<td>54</td>
<td>63</td>
<td>67</td>
<td>64</td>
<td>57</td>
<td>40</td>
</tr>
<tr>
<td>$\epsilon_r$</td>
<td>384</td>
<td>349</td>
<td>303</td>
<td>320</td>
<td>334</td>
<td>295</td>
</tr>
<tr>
<td>Tgδ (%)</td>
<td>2</td>
<td>3</td>
<td>2</td>
<td>1.5</td>
<td>2</td>
<td>1.5</td>
</tr>
<tr>
<td>$K_p$</td>
<td>0.28</td>
<td>0.3</td>
<td>0.32</td>
<td>0.41</td>
<td>0.39</td>
<td>0.31</td>
</tr>
<tr>
<td>$Q_m$</td>
<td>23.7</td>
<td>29.4</td>
<td>20.4</td>
<td>34.3</td>
<td>28.4</td>
<td>25.3</td>
</tr>
</tbody>
</table>

The variation of ceramic density as a function of sintering temperatures ($T_{\text{sint}}$: 1000-1250 °C) is shown in Fig. 7. A relative density of 7.53 g/cm³ was achieved at sintering temperature of 1150 °C, which is close to the
theoretical density (~95%). At higher $T_{\text{sint}}$, the density of ceramic samples strongly decreases which can be attributed to the evaporation of excess PbO.

Fig. 7. The variation of ceramic density at sintering temperatures.

The electromechanical properties of PZT ceramics as a function of sintering temperatures are shown in Fig. 8. Both $d_{33}$ and $Q_m$ show a similar variation trend with increasing temperatures. The optimized values of $d_{33}$ (64 pC/N) and $Q_m$ (34.3 pC/N) were obtained at 1150 °C. The $K_p$ value of piezo-ceramics initially increases with increasing $T_{\text{sint}}$ until it reaches a maximum value of 0.41 at 1150 °C, and then decreases for high temperature, which may be due to the evaporation of lead oxide. In addition, with decreasing $T_{\text{sint}}$, dielectric constant ($\varepsilon_r$) increased continuously. This phenomenon is common for polycrystalline ferroelectric ceramics. In the past decades, effect of grain size on the relative permittivity has been extensively reported and different theoretical models have been introduced to describe the physical origin of this effect [27]. For example, in BaTiO$_3$, it is now widely accepted that $\varepsilon_r$ increases with decreasing grain size, reaching a value of 5000, or higher, as the grain size approaches 1µm. Below 1µm, however, $\varepsilon_r$ of BaTiO$_3$ decreases markedly with further decreasing grain size [28]. In our work, the maximum value (384) of $\varepsilon_r$ was obtained for specimen with mean grain size of 1.84 µm sintered at 1000 °C. Further lowering the sintering temperature to obtain smaller grain size is impossible, because the sample is difficult to be densified.

Fig. 8. The variation of (a) $d_{33}$ (b) $Q_m$ (c) $K_p$ (d) $\varepsilon_r$ and (e) tanδ as a function of sintering temperatures.

Fig. 9a demonstrates the variations of the dielectric properties, i.e., dielectric constant ($\varepsilon_r$) and loss tangent (tanδ) as a function of frequency. It can be seen for piezo-ceramic sintered at 1150 °C that both $\varepsilon_r$ and tanδ are nearly independent of frequency and measured about 388 and 1.5% at 1 kHz, respectively. The dielectric
constants decrease slowly at low frequency regime (Fig. 9b; ϵ_r < 390), which is may be attributed to the dielectric relaxation of PZT nanoparticles. Besides, the dielectric constants climb markedly with increasing frequency beyond 550 kHz (Fig. 9c). Dielectric relaxation of the ferroelectric ceramics could originate from the alternations of the elastic and electric behavior and the movement of the domain walls at high frequency regions [29].

Fig. 9. The variation of dielectric constant (ε_r) and loss factor (tanδ) versus frequency.

4. Conclusion
The PZT nanopowders were synthesized by the sol-gel method using acetic acid as a complexing reagent. The PZT nanopowders with spherical-shaped morphology, perovskite structure and an average size of 20 nm are synthesized. The single PZT phase starts to form at a calcination temperature of 500 °C. The optimum piezoelectric parameters are obtained at sintering temperature 1150 °C: d33=64 pC/N, K_p=0.41 and Q_m=34.3.

REFERENCES