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The Effects of Sol Gel and Mechanical Milling Process Parameters on the Synthesis of PZT Powders

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Abstract

PZT ceramic powders were successfully prepared from the mixture of PbO, ZrO_2 and TiO_2 or zirconium (IV) propoxide, titanium (IV) isopropoxide and lead acetate trihydrate by mechanochemical and modified sol-gel syntheses under different conditions. The formation of perovskite phase in the calcined PZT powder has been investigated by X-ray diffraction (XRD) technique. The $(Zr_xTi_{1-x})O_2$ powders with nanometer grain size were synthesized at a temperature lower than that required in the conventional process. In the present work, Lead zirconate titanate [Pb $(Zr_{0.52}Ti_{0.48})O_3$, PZT] ceramics were prepared by sol-gel and solid-state reaction methods at a temperature as low as 450°C,600°C respectively with the particle size in the range of 100-150 nm, 30–50 nm,. Fully dense PZT ceramics with 97% of the theoretic density have been achieved from powders at a sintering temperature of 1100°C for 1 h. The dielectric and ferroelectric properties of the sintered PZT ceramic were measured and the results were satisfactoty.

1. Introduction

The lead zirconate titanate solid solution (PZT) has the perovskite structure (general formula, AIIBIVO3) with the A-site (Pb^{2+}) occupying the cube-octahedral interstices described by the BO^{6-}site octahedral [1, 2]. In the practical applications of PZT, various impurities have been added in order to improve the piezoelectric and pyroelectric properties [3, 4]. The additives to PZT have been classified into two groups: 'donor type' additives, which make k31 high and Q_m low (soft piezoelectric) and 'acceptor type' additives that make k_{31} low and Q_m high (hard piezoelectric). As typical examples, Nb^{5+}, Sb^{3+}, Nd^{3+} and La^{3+} belong to the former group, and Fe^{3+}, Mg^{2+} and Al^{3+} to the later group. Manganese, however, does not belong to either group and the Mn addition makes both k_{31} and Q_m high [5, 6]. From the crystal chemical point of view, it seems that the saturation field of perovskite-type ferroelectrics decreases with tetragonality of the lattice, giving rise to the increase in k_{31} at low poling field. The tetragonality is also closely related to the Curie temperature. Roy-Chowdhury and Deshpande [7] reported that the Curie temperature of various perovskite-type ferroelectrics decreased with their tetragonality. It was also reported that most of the softener additives reduced Curie temperature [8]. Therefore, it has been reported that the cause of softening derives from the crystal structure change toward a cubic system rather than whether the additives are donors or acceptors. As for the increase in Q_m, it has been suggested that the oxygen vacancies formed by the charge deficit due to a trivalent B-site ion restrict the movement of ferroelectric domain walls (pinning effect), resulting in hard piezoelectrics [1, 2].

Substitution of two A-site with two aliovalent La^{3+} or Nd^{3+} will result in one vacancy of A^{-} site in the crystal lattice. This substitution and the resulting vacancies in the crystal lattice considerably change the material properties, such as dielectric constant, dielectric loss, elastic modulus, etc [9]. Rare earth ions are donor type substitutions and are other promising way to improve properties of PZT ceramics. i.e., Agrawal et al worked on Mechanical, piezoelectric and dielectric properties of PZT ceramics $(Pb_{0.98}M_{0.02}[(Zr_{0.535}Ti_{0.465})_{0.995}]O_3$, M=Er, Gd, Eu, Nd, La and Bi) [10]. Other Indian group studied sol gel based PZT ceramics with rare earth additives [11]. Sb^{5+} cation is another donor additive that can be substituted in A (Pb^{2+}) sites as Sb^{3+} (0.090 nm radius) or in B sites as Sb^{5+} (0.069 nm radius). Very little information is available on the effect of calcination temperatures on the dielectric constant (ε) and loss factor (tanδ) of PZT ceramics.

In recent years, there has been increased interest in fine crystalline materials, since all properties are strongly related to the microstructure of materials [12]. Fine grain piezoelectrics offer numerous advantages, including low processing temperatures, excellent compositional control, uniform homogeneity, and low cost. Intensive milling in high-energy mills could be a possible way to get fine structure [13]. Mechanical treatment of starting powders can activate powders for sintering and calcination process and consequently reduce temperatures of thermal treatment and decrease contents evaporation.

In this work, PZT powder was successfully synthesized during sol gel, mechanical activation, conventional methods. Calcination temperatures were compared and optimized to improve phase formation and its electrical properties.

2. Experimental Procedure

The starting materials were commercially available PbO(99.9%, Merck), ZrO_2 (99.9%, Merck), TiO_2(99.9%, Merck)for solid state methods and Trihydrated lead acetate $[Pb(CH_3COO)_2\text{-}3H_2O]$(analytical grade, Merck), zirconium n-propoxide $[Zr(OCH(CH_3)_2)_4]$(assay 70% in propanol, Fluka) and titanium iso-propoxide $[Ti(OCH(CH_3)_2)_4]$ (for synthesis, Merck)for sol-gel method. According to chemical formula $Pb_{1.1}(Zr_{0.52}Ti_{0.48})O_3$, approximate amonts of starting materials were weighed.

In solid state methods, oxides mixed in a alumina jar for 24 h in etanol and for activation further milled in plantary ball mill. Milling conditions were the following: Stainless steel jar and balls, ball to powder weigh ratio was 20:1, powder quantity was 20 g, air atmosphere, rotation speed of discs was 350 min^{-1}, milling time was 900 min.

In the sol gel method, lead acetate trihydrate was dissolved in heated acetic acid. The solution was dehydrated at 105°C for 2 hand after cooling to 80°C it was mixed with the acetate solution of zirconium and titanium propoxide in the required ratio of compounds. By polycondensation of the formed orange lead zirconyl titanyl acetate after adding a hydrolyzing agent [ethylene glycol, H_2O and NH_3 (aq)] with the temperature of 80°C, an yellow sol was formed, which was converted to a gel at the given temperature. Polycondensation took placein closed flasks. After polycondensation (12 h), it was dried at 100°Cin 8 h.

All powders calcinated at 450-850°C with steps 50° for 2 h. Calcinated powders were subsequently examined by room temperature X-ray diffraction(XRD; SIEMENS 500), using CuK_α radiation, to identify phase formation and optimum calcinations conditions for the manufacture of perovskite PZT powder.

The mixtures were pressed in to grain pellets and sintered at 1100°C for 2 h. the density of PZT ceramics was measured by using Archimedes principle. The dielectric property of the sintered samples was measured using impedance analyzer. The value of kp, planar coupling factor be determined via the resonance and antiresonance method by measuring the frequencies corresponding to the minimum and maximum impedance of the sample, $kp=\sqrt{(1.265(fa^2-fr^2)/fa^2)}$, where fr and fa are resonance frequency and antiresonance frequency, respectively.

3. Results and Discussions

XRD patterns of the calcinated PZT powders are shown in Figure. 1. X ray diffractograms contain of broadened peaks, indicating reduction in crystallite size and some intermediate phases and lead loss for conventional powder. In the case of actived powders, perovskite phase is formed in 600°Cand lead loss and intermediate phaseand crystallite size are reduced(100-150nm), andin the case of sol gel derived powders amorphous phase was identified and in lower temperature proveskite phase is formed with fine cyrstallte size(30-50nm). Crystallite size and lead loss is increased with temperature increase.

The sintered density (relative density: % theoretical density) of PZTs synthesized by 15 h of mechanical activation and sol-gel and conventional methods as afunction of calcinating temperature is shown in Figure. 2. The sintered density increases with increasing temperature initially and peaks at anoptimum temperature, before a decrease is observed with further increase in temperature. For example, the sintereddensity of the sol gel-derived PZT increases with rising temperature over the range from 450 to 600°C, where it maximizes at 97.6% theoretical density. Further increasing the temperature (above 700°C) results in a slight fall in sintered density, due to lead loss and the exaggerated graingrowth. The PZT derived from solid state is much less sintering reactive and exhibits a much lower sintered density than that of the activation or sol-gel -derived PZT powder at each temperature. It can be related to formation of finally phase as seen in X-ray analyses. Calcinations temperature has negligible effect on the bulk density, because lead content [14], phase formation and grain size [15] have different effect in sintering mechanism. The main sintering mechanism of PZT ceramics is lattice diffusion of vacancies that named coble's model [16]. After optimum condition at nano powders processes, the diffusion coefficient by bounding vacancies, so that they inhibit the mass transport and reduce the density. The macro sized PZT powder is much less sintering reactivity and exhibits a much lower sintered density than that of the nano sized PZT ceramic at each temperature and composition.

The grain size as a function of the calcination temperature indicated that a decrease in grain size as the temperature reduced. The defects are effective grain growth inhibitors and routs for densification. The vacancy can concentrate near the grain boundaries and decrease their mobility. Activation of PZT powders by milling or sol gel methods accelerating sintering and causes small grain size.

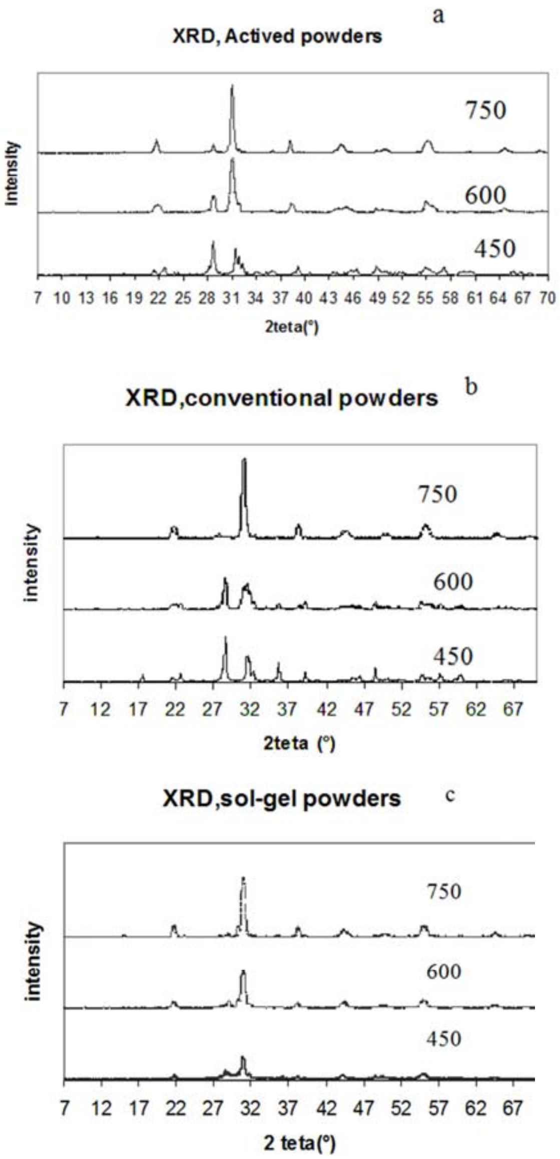

Figure 1. *Room temperature X-ray diffractograms using CuKα(0.151418 nm) radiation.(a) XRD patterns of PZT powders obtained fromconventional powder at 450,600,750°Ctemperatures.(b) XRD patterns of PZT powders obtained from actived powders at 450,600, 750°Ctemperatures.(c) XRD patterns of PZT powders obtained from sol-gel precursor calcined at 450,600,750°Ctemperatures.*

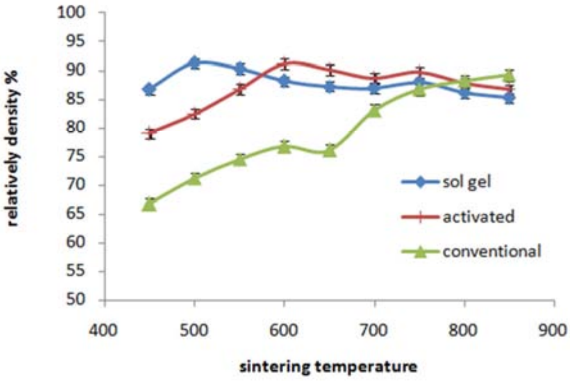

Figure 2. *A graph of the relative density against calcination temperatures.*

The dielectric constant of the PZT ceramics was measured at 1kHz(Table 1) Results imply that the dielectric constant increases and loss factor decreases with the increase of grain sizeand density of the PZT ceramics. It is well accepted, in ferroelectric ceramics, that the coupling effect of the grain boundaries exerts a restraining influence on the domain reorientation and domain wall mobility and for actived and sol gel powders densification is occurred in low temperature and they reached to full density that improved dielectric constant. As seen in Table 1, dielectric constant of sol gel and milled samples which calcinated at 750°C are twice time higher (~1100) than conventional sample (~ 650), loss factor and density of samples indicated that fully densification and crystallite, lower porosity, smaller crystalline size cause this advantage.

Table 1. *Dielectric constant(ε) and loss factor(tanδ) of samples with defferent calcination temperatures.*

	450, ε	**450, tanδ**	**600, ε**	**600, tanδ**	**750, ε**	**750, tanδ**
Conventional	-	-	-	-	667	27
Activated	1020	1.1	1053	1.2	1107	0.9
Sol-gel	1105	1.3	1134	0.9	1174	0.8

4. Conclusion

PZT ceamics have been fabricated from sol-gel and mechanical activation are nanosized powders, both the phase formation and sintering temperatures are much lower than those obsereved in the conventional method. The PZT ceramics calcinated in low temperature exhibit electrical property(k~1100, loss factor ~1) for sol gel and mechanical activation, which are in good agreement with the widely reported values for PZT samples that prepared in high temperature or with different additives.

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