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Low-temperature processing and characterization of single-phase PZT powders by sol-gel method

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Abstract A new sol-gel system using acetoin was developed and employed for the fabrication of PZT powders and films with compositions near the morphotropic phase boundary $Pb(Zr_{0.52}Ti_{0.48})O_3$. Acetoin was used as chelating agent to replace the highly toxic methoxyethanol used in previous formulations. This route simplified the chemical processing of PZT-based solutions. Powders were completely crystallized by about 450 °C and contained the ferroelectric perovskite single phase. The firing temperature and time were to be the most important variables. Metallic lead formed only when excess Pb was incorporated. The precursor and the heat-treated powders have been characterized by using thermal analysis and X-ray diffractometry (XRD) studies. The average particle size, as measured from X-ray line broadening, was ~35 nm.

Introduction

Since their discovery in the late 1950's, PZT-based ceramics are widely investigated and prepared in the form of thin/thick film as well as bulk ceramics. In particular, processing of PZT powder has evolved from a conventional approach where the oxides of the individual components were mechanically mixed to the various chemical methods which significantly improved the homogeneity and as a consequence the quality of the final product. High-temperature solid state reactions, [1–5] hydrothermal, [6, 7] sol-gel, and other related methods have been reported for the preparation of piezoelectric materials [8].

The sol-gel is one of the excessively used route for the preparation of powders, thin, and thick films for electrical applications. This technique is particularly important for the preparation of ceramic powders since the mixing of the reagents occurs on an atomic rather then a particulate scale. This allows control over stoichiometry and is thus advantageous for the synthesis of multi-component oxides. Another advantage comes from the low processing temperatures that facilitate integration with semiconductors.

The most widely employed sol-gel methods fall into one of two general categories [9]: (i) processes based on the use of the solvent 2-methoxyethanol; and (ii) processes based on chelating ligands such as acetic acid [10] or ethanolamine compounds [11]. The alcohol based system using methoxyethanol as both a solvent and a modifier was introduced by Gurkovich and Blum [12, 13]. Despite being largely used by many researchers due to its chelating nature, methoxyethanol is known to be hazardous and toxic. In addition, a sequence of reflux and distillation steps are required. Therefore, uncomplicated and appropriate procedures should be developed in order to render the sol-gel process more practical.

Many chemical preparation routes have been employed to prepare single-phase nano-crystalline PZT powders. Choy et al. [14] employed coprecipitation to produce PZT powder. A calcining temperature as high as 900 °C was necessary to develop the perovskite phase. Similar

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procedure has been used by Taç [15] who synthesized lead zirconate titanate phase from water-soluble chlorides of Pb, Zr, and Ti, following calcination at relatively lower temperature of 500 °C. Das et al. [16] reported a chemical route for the preparation of nanocrystalline single-phase PZT powders using triethanolamine as a complexing agent to keep the metal ions in homogeneous solution. Calcination of the precursors at 450 °C (for 2 h) resulted in the formation of pure PZT phase. The same polymerizing agent (triethanolamine) has been recently used by Faheem et al. [17] to produce the precursor solution. Heat-treatment at slightly higher temperature of 470 °C for 1.5 h lead to a single-phase perovskite structure. Wu et al. [18, 19] have studied the effect of solvent, chemical modifying agents, and zirconium, titanium, and lead starting sources on the crystallization behavior of PZT gel powders. They showed that the effect of the starting chemicals used to introduce the titanium, zirconium, and lead was more determinant than that of the solvents and the stabilizers. Under optimum conditions, pure perovskite phase formed at 600 °C. In a more recent article [20], the same group reported the use of methacrylic acid ($C_4H_6O_2$) in the preparation of PZT fibers. An even lower crystallization temperature of 550 °C could be obtained. Banerjee et al. [21, 22] investigated the synthesis of PZT nanopowder by citrate nitrate autocombustion method. The raw materials used for the PZT preparation were lead nitrate, zirconyl nitrate hydrate, titania powder, and citric acid. Phase pure, free standing PZT nanoparticles were obtained after calcination at 500 °C. The same temperature has been reported by Etin [23] and Chen [24] for sol-gel derived PZT powders.

The present work describes a novel and simple route that can be used to prepare pure and highly sintered PZT powders at relatively low processing temperature. Acetoin is used for the first time as a stabilizing ligand instead of methoxyethanol and other chelating organic ligands, which are routinely utilized.

Experimental procedure

Solution synthesis

PZT precursor solutions were prepared by first premixing the appropriate amounts of zirconium (IV) butoxide [$Zr(OC_4H_9)_4$] (80 wt.% in 1-butanol, Aldrich) with titanium (IV) isopropoxide [$Ti(OC_3H_7)_4$] (97%, Aldrich) in isopropanol [$(CH_3)_2CHOH$] (99.5%, Sigma-Aldrich) under nitrogen atmosphere. The optimum amount of acetoin [$CH_3COCH(OH)CH_3$] (Aldrich) (4 and 2 mol, with respect to the Zr and Ti ions, respectively), was then added as stabilizing agent with constant stirring. Finally, Lead acetate trihydrate [$Pb(OCOCH_3)_2 \cdot 3H_2O$] (≥99%, Aldrich) was stoichiometrically added based on the formula $Pb(Zr_{0.52}Ti_{0.48})O_3$ and the solution was stirred for about 10 min until complete dissolution of the lead precursor. The dissolution of zirconium, titanium and lead resulted in a clear, yellow solution. Here it is worth to note that lead acetate alone could not be dissolved in isopropanol using acetoin as the chelating ligand. Therefore the preparation sequence shown in the flow diagram, Fig. 1, should be respected in order to get a stable and clear solution. The effect on microstructure of adding excess lead to the starting sols to compensate for an eventual evaporation was examined using 20 mol% excess lead acetate.

Gel and powder preparation

Gels were dried overnight in air under a lamp to remove most of the organic material. The resulting amorphous solid was ground into a fine powder using a mortar and pestle. Powders were placed in combustion alumina boats and heat-treated in air for 3 h at a heating rate of 5 °C/min. The temperature ranged from 300 to 800 °C. The heat treatment was followed by air quenching to room temperature.

In general, for a given composition and set of deposition parameters, the structure of the PZT was observed to be a function of both annealing temperature and time. Figure 2 shows that maintaining the heat-treatment procedure for 3 h at 350 °C (as an example) was enough to evaporate~95% of the organic compounds susceptible to be released. Therefore, a heating time of 3 h was adopted throughout this study unless otherwise noted.

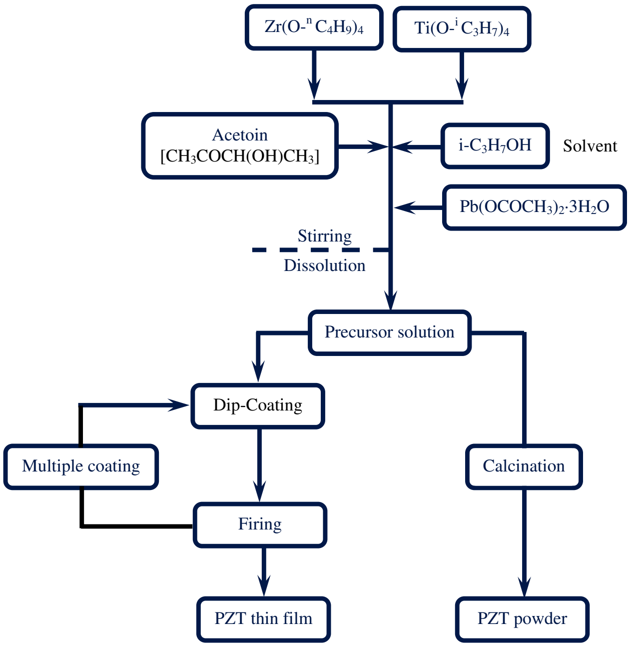

Fig. 1 Flow diagram of a processing route for the PZT precursor solution, powder, and films

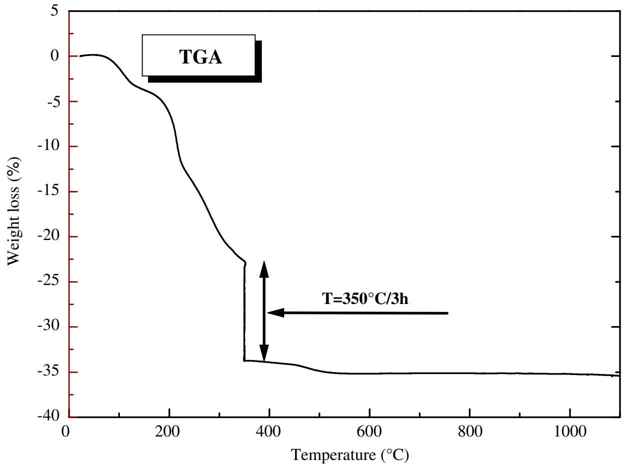

Fig. 2 Thermogravimetric analysis curve recorded at a heating rate of 5 °C/min for PZT gel powder. The temperature was temporary maintained at 350 °C for 3 h

The dielectric and piezoelectric properties of PZT solid solutions are known to be sensitive to structure as well as composition, and are a maximum near the morphotropic phase boundary separating the tetragonal and rombohedral phases [25]. In the present study it was possible to prepare PZT powders of any desired composition by simply adjusting the metal concentrations in the precursor solution. A series of PZT powders were prepared via the heat-treatment at different temperatures.

Characterization

Crystalline phase development of gel-derived powders with heat treatment (400–800 °C) was analyzed by X-ray diffraction (XRD) using a Rigaku Diffractometer. Scans were taken from 20 to 70° 2θ, sampling every 0.02° at a continuous rate of 2°/min. Simultaneous thermogravimetric-differential thermal analysis (TG-DTA) was performed to analyze the thermal decompositions and transformation of precursor solution. The solutions were thoroughly dried prior to TG-DTA to evaporate the solvent. TG-DTA runs were made up to 1000 °C; some runs were terminated at intermediate temperatures by rapid cooling to identify the phases at those temperatures. Samples were removed, crushed in a mortar, and subjected to X-ray analysis.

Discussion

Thermal decomposition

TG-DTA data for PZT powders pyrolyzed in air (100 cm^3/min, 5 °C /min) are presented in Fig. 3. The TGA curve shows that the gel exhibited a weight loss of ~35% in the temperature range of 20–500 °C. The product decomposed exothermically through three successive processes. An initial large exothermic peak characterized by an abrupt weight loss on TGA occurs at ~180–300 °C and corresponds to pyrolysis and the oxidation of the residual carbonaceous mass. For the higher temperature exotherms, XRD of DTA samples removed from the instrument before and after the exotherms showed that the lower temperature peak corresponds to the crystallization of pyrochlore from the amorphous powder, and the higher temperature exotherm is the transformation to perovskite. These two peaks overlap indicating that the crystallization and transformation occurred at very similar temperatures; as will be shown later, XRD data showed complete conversion of pyrochlore to perovskite with heat-treatment at 450 °C for 3 h.

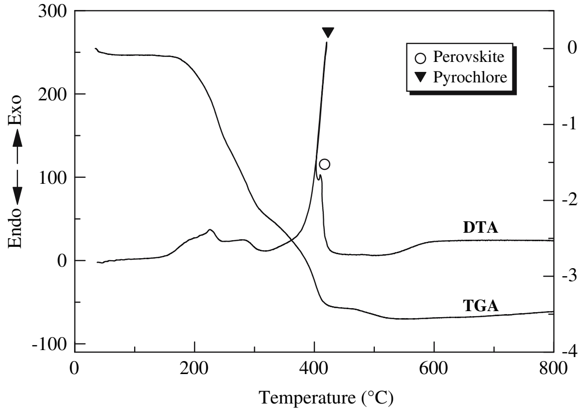

Fig. 3 Thermogravimetric and differential thermal analysis data for powders prepared from PZT solutions

Crystalline phase development

Sol-gel-derived PZT can form in two crystalline phases during the gel to ceramic transformation: a metastable cubic pyrochlore phase of the form $A_2B_2O_{7-x}$($Pb_2(Zr_{1-x}Ti_x)_2O_6$) [26] and a perovskite phase of the form ABO_3. The name pyrochlore originally comes from the mineral $CaNaNb_2O_6F$ which has a cubic structure and which can be represented by three-dimensional network of B_2O_6 oxygen octahedra. The pyrochlore phase does not exhibit the desired electrical properties of the perovskite.

The formation of crystalline phases in the powders was studied by XRD analysis with samples subjected to varying final temperature treatments up to 800 °C. Figure 4 shows the X-ray diffraction patterns for PZT powders that were calcined up to a selected temperature then quenched to room temperature. Below 400 °C powders were X-ray amorphous. It may be seen that at 400 °C, the crystallization was initiated; however, a broad peak corresponding to the formation of a pyrochlore phase appeared with concurrent crystallization of perovskite. Further heating

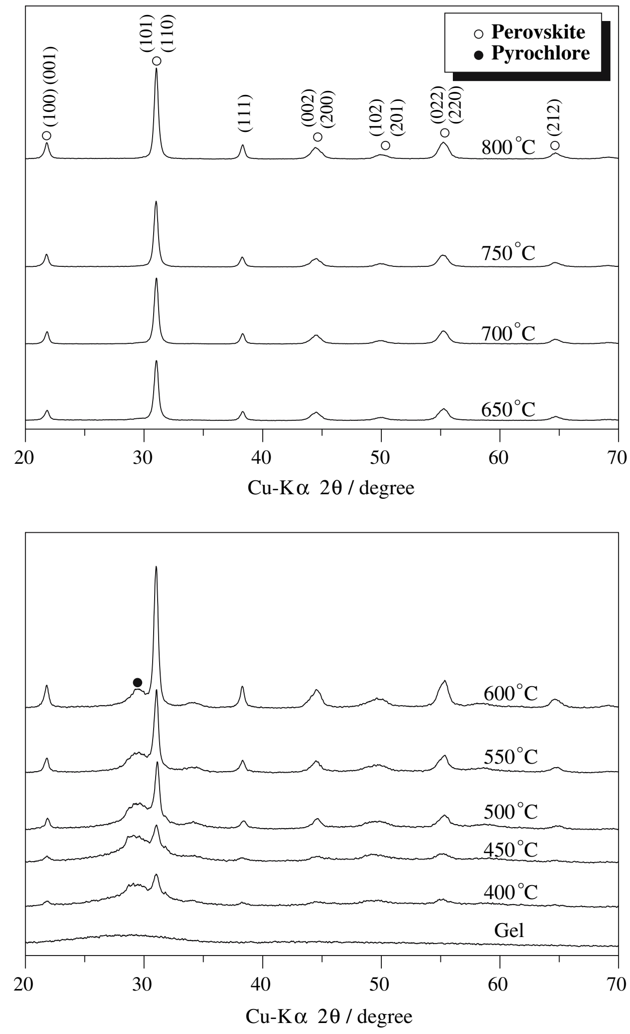

Fig. 4 Room temperature powder X-ray diffractograms of the PZT precursor powders prepared from PZT solutions and heat-treated in air at 5 °C/min up to the temperatures indicated then quenched to room temperature

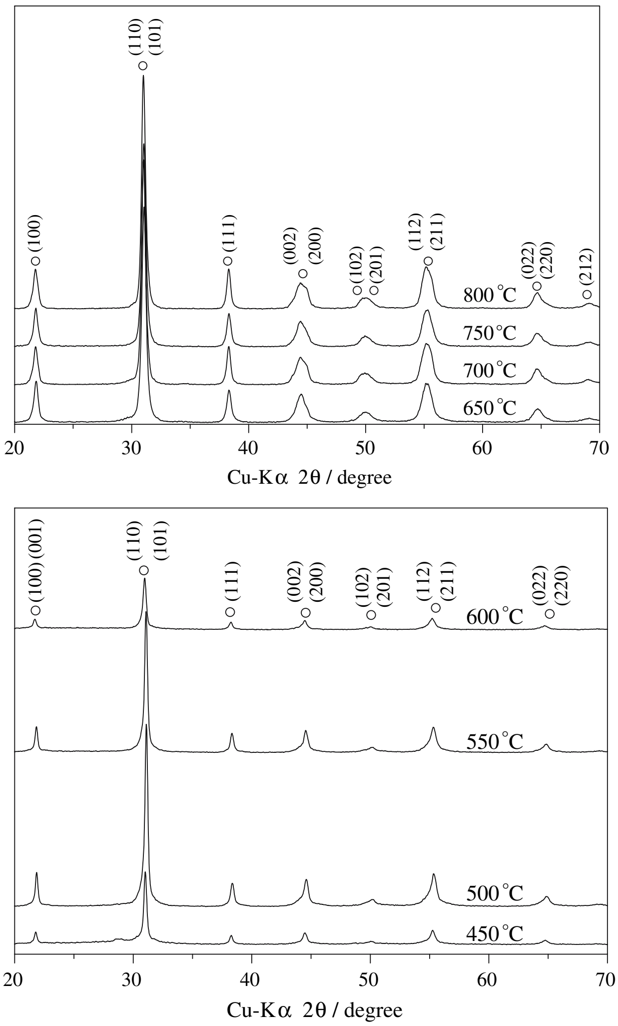

Fig. 5 Room temperature powder X-ray diffractograms of the PZT precursor powders after heat treatment in air for 3 h at the temperatures indicated

promotes the development of the perovskite phase so that by 650 °C cristallinity is enhanced and pyrochlore phase has completely transformed as shown by the X-ray spectra, which exhibit single-phase perovskite. Figure 5 shows that prolonged heating (3 h) increases the fraction of the perovskite phase at the expense of pyrochlore. Pure perovskite phase could be obtained at relatively low external temperature of 450 °C. No tetragonal split was observed due to the fact that the composition of the powders is near the morphotropic phase boundary in the $PbZrO_3$–$PbTiO_3$ phase diagram. It has been reported in the literature [27, 28] that the pyrochlore phase is converted to the PZT equilibrium perovskite phase at high temperatures in a slow kinetic process. This explains the need for a prolonged heating to accomplish the transformation pyrochlore–perovskite. The low-temperature heat treatment of the precursor mass resulted in high in-situ temperatures, because of the exothermic decomposition of the carbonaceous residue. This phenomenon facilitated a solid-phase reaction between the constituent ions [16]. As a result, the PZT phase formation occurred at relatively lower external temperatures. In addition, the low phase transformation temperature of pyrochlore-to-perovskite may also be attributed to weak chemical bonding and high degree of homogeneity in solution. These studies also reflected the growth of crystallinity in the powders with the increasing heat-treatment temperatures.

Effect of lead content

The change in composition and in particular the level of Pb in the solution is reported to have important effects on the

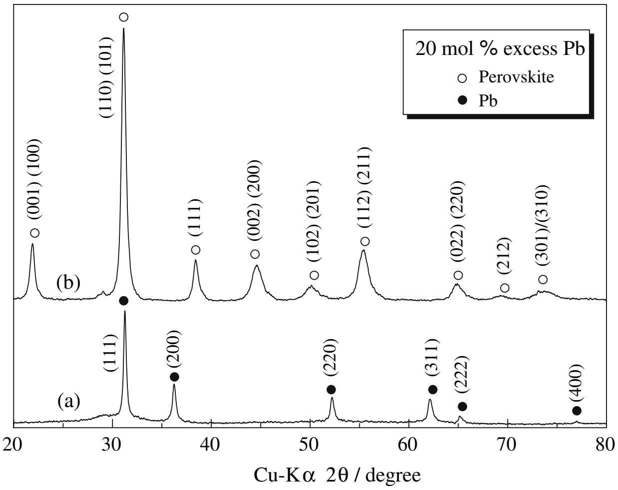

Fig. 6 Room temperature powder X-ray diffractograms of the PZT precursor powders that were prepared with 20 mol% excess lead after heat-treatment at (a) 400 °C and (b) 500 °C for 10 h

microstructure of PZT powders and films. In general, it has been observed that the presence of excess lead favors perovskite-phase formation, as would be expected, because of the volatility of lead species. The preferential loss of lead compounds, which occurs during the heat-treatment, may cause some deviation from stoichiometry. An intermediate pyrochlore phase that does not exhibit the desired electrical properties of perovskite is often reported when lead deficient sols were used. Therefore, efforts have been deployed to minimize the level of this phase using lead-rich precursor systems. However, excess lead increases the risk of the retention of PbO at grain boundaries or as a second phase [29]. This may negatively affect the ferroelectric properties of the final product. In addition to concerns about lead toxicity, substantial degassing due to Pb and/or PbO evaporation may leave voids resulting in less dense material.

In the present study, the lead oxide content in the powders was altered by adjusting the relative concentrations of Pb, Zr, and Ti elements in the precursor solutions. The XRD patterns for PZT powders modified with excess Pb are shown in Fig. 6. The crystalline phase development for PZT powder modified with excess Pb and fired at 400 °C showed the presence of metallic lead. In contrast, we have found no evidence of such a phase in any of the XRD patterns of stoichiometric samples. This result is particularly important since it shows that only the part of lead that has been added in excess is reduced to metallic Pb. This indicates that the large part of lead is well incorporated within the gel structure, thereby limiting its evaporation.

The gases such as CO, which were liberated during the decomposition of the organic reagents present in the gel reduces the Pb^{2+} ions to the metallic state, which is highly volatile (melting temperature = 204 °C). Hence, Pb release may be enhanced especially when its level exceeds the stoichiometric composition.

Conclusion

The lead zirconate titanate single phase has been synthesized from alcoholic solution, following calcinations at 450 °C in air atmosphere. This study showed for the first time that it is possible to dissolve the lead, zirconium, and titanium precursors in isopropanol containing acetoin. The use of acetoin in the reported method is simple and innovative; the chemical processing steps involved in this route are more straightforward than the widely used methoxyethanol process. The optimum amount of acetoin in the system provided the dissolution of the metal ions and prevented precipitation. Through this route, the crystallization of single-phase PZT occurred at a relatively low temperature in comparison to all other reported methods except hydrothermal synthesis. This result is due to the low boiling point of acetoin combined to its exothermic decomposition. In the formation of PZT, the pyrochlore phase forms first or most rapidly. Very weak broad pyrochlore reflection was only detected below 450 °C for the powders that were calcined for very short time at the detection level of XRD analysis; up on further heat-treatment the pyrochlore completely decomposed to reform perovskite PZT. Excess lead was found to be unnecessary for the perovskite phase stabilization. Addition of excess lead acetate led to the formation of crystalline Pb at 400 °C. Above this temperature, the resulting microstructures were similar to those produced with stoichiometric composition. The different parameters involved in the PZT powder processing have to be judiciously adjusted in order to synthesize the single PZT phase at low temperature.

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