Comparative Structural Analysis of PBZT Nanoceramics Synthesized by Co-precipitation and Sol-gel Method

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In this study, a comparative structural analysis of bismuth doped PZT nanoceramics (i.e. $Pb_{0.98} Bl_{0.02} (Zr_{0.52} Tl_{0.48})_{0.98} O_3$) prepared by chemical co-precipitation and sol-gel methods has been made. Perovskite PZT phase in the compound prepared by sol-gel method can be seen ta the temperature as low as $250\,°C$ whereas the evolution of PZT phase along with small amount of pyrochlore phase take place only after $400\,°C$ temperature in the samples prepared by co-precipitation method. The X-Ray diffractogram of pellets sintered at $1100\,°C$ also confirms that bismuth doping does not affect the crystal structure of the compounds and a tetragonal unit cell structure was formed in both of the cases.

1. INTRODUCTION

Ferroelectric nanoceramics specifically lead zirconate titanate (PZT) has been considered as a material of great technological importance in the development of high-density storage devices. The microstructure and properties of these nanomaterials depend in an extreme manner on the synthesis method as well as on the processing route and it becomes important to select the most appropriate technique for preparation of these materials with desired properties. Classically, PZT powders are produced using high temperature mixed oxide method [1], which eventually proved to be inadequate from the standpoint of chemical homogeneity, purity and uniformity. Presently two wet chemical processes i.e., Chemical coprecipitation [2] and Sol-gel [3,4] are employed to produce ZT nanopowders. In this paper, an attempt is made to synthesize Bismuth doped PZT by sol-gel and co-precipitation method and to compare crystallographic evolution of the compound. The crystallinity and the phase formation study have been completed by powder X-ray diffraction studies. Crystallographic study of PBZT powders calcined at various temperatures shows the different phases occurring during compound formation for both of the cases.

2. EXPERIMENTAL METHODS

The samples of $Pb_{0.98} Bi_{0.02} (Zr_{0.52} Ti_{0.48})_{0.98} O_3$ (PBZT) were prepared by co-precipitation (Sample A) and sol-gel (Sample B) methods. Lead nitrate $[Pb(NO_3)_2]$, lanthanum nitrate $[La(NO_3)_3.6H_2O]$, zirconyl nitrate $[ZrO(NO_3)_2.2H_2O]$, bismuth nitrate $[Bi(NO_3)_3.5H_2O]$ and

titanium isopropoxide $[Ti[(CH_3)_2CHO]_4]$ were used to prepared samples by co-precipitation method (Sample A). The details of powder preparation are given elsewhere [5-10]. Successive calcinations of Oven dried (200°C) powder at 500°C and 800°C followed by intermediate grinding was carried out until a fine powder is achieved. The powder was cold pressed into the form of discs at a pressure of 6×10^7 kg/m^2 using a uniaxial hydraulic press. These pellets were then sintered at 1100°C for 2 hrs. For sol-gel preparation of PZT ceramics $[Pb_{0.98} (Zr_{0.52}Ti_{0.48})_{0.98}O_3]$ lead acetate trihydrate $Pb(CH_3COO)_2.3H_2O$ (99%, S.D. fine chemicals), zirconium propoxide $Zr(C_3H_7O)_4$ (M/s Aldrich Chemicals) and titanium isopropoxide $Ti[(CH_3)_2CHO]_4$ (M/s Aldrich Chemicals) were needed. Bi_2O_3 was used as dopant to make the PBZT ceramic of desired compositional formula $(Pb_{0.98} Bi_{0.02} (Zr_{0.52} Ti_{0.48})_{0.98} O_3$ i.e. sample B). Acetic acid is a key component in the solution preparation process for it acts as a chemical modifier, or chelating agent, replacing essentially all of the alkoxy ligands of the original precursors. Lead acetate and acetic acid (in a ratio of 2: 1) were taken in a vessel and stirrered on a hot plate magnetic stirrer at 110°C. The resultant solution was cooled down to 80°C temperature. Zirconium propoxide was added to above said solution followed by titanium isopropoxide. To get a monolithic gel small amount of ethylene glycol was added strictly after dissolution of zirconium propoxide and titanium isopropoxide otherwise their residues may alcolyze with ethylene glycol to form condense solid. Final sol was obtained after adding small amount of distilled water to above solution. Gel formation took place after keeping the sol at 60°C for 24 Hrs in an oven. This gel converts to a light brown powder by putting it for drying at 100°C for 72 Hrs. This powder was then calcined at 400°C for 4 Hrs to get all the reaction completed and to allow complete phase formation of PZT. Stiochiometric amount of Bi_2O_3 was then added to above powder and recalcined at 800°C. The powder was grinded to assure the homogeneity in the prepared ceramic. Applying the same pressure as in case of sample A, the pellets of sample B were prepared. Sintering was also performed at the same temperature (1100°C) for 2 Hrs. The formation and quality of the prepared ceramics at various calcinations of powders as well as sintered pellets was studied by X-ray diffraction (XRD) measurements using powder X-ray diffractometer (Bruker D8 advance).

3. RESULTS AND DISCUSSIONS

Figure 1(a) and 1(b) shows the XRD patterns for different powders of sample A and sample B obtained after calcination at 250°C, 350°C and 400°C temperature. The XRD pattern after initial calcination (250°C) of sample. A shows mostly peaks of oxides of precursor compounds along with some peak of residual nitrates. As indicated by different symbols in Figure 1(a), it contains peaks of TiO_2, Bi_2O_3, ZrO_2, $PbTiO_3$ and $Pb(NO_3)_2$. These peaks occur due to the partial reaction taking place during initial calcination process. A further change in the spectra is seen at 350°C temperature, which is ascribed to the further decompositions. Perovskite phase could only be observed after 400°C calcinations whereas the similar structure is found at 250°C temperature (Figure 1(b)) in case of sol-gel derived sample (i.e., sample B).

It is clear from Figure 1(b) that the peaks become sharper and well separated on further calcinations. This concludes the better homogeneity of sol-gel prepared compounds at much lower temperatures in comparison to the ceramics prepared by chemical co-precipitation method. Figure 2 combines the XRD graphs of both of the ceramics sintered at 1100°C, which reveals that both of the ceramics belong to tetragonal system.

1(a)   **1(b)**
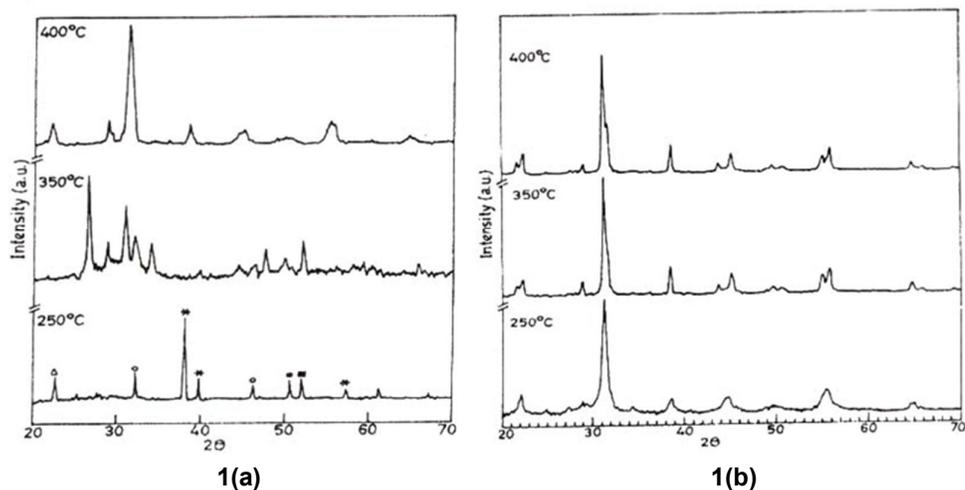
Fig. 1: XRD patterns at various temperatures for **(a)** sample A: (⋆)TiO_2, (Δ) $Pb(NO)_3$, (o) Bi_2O_3, (■) ZrO_2 **(b)** sample B.
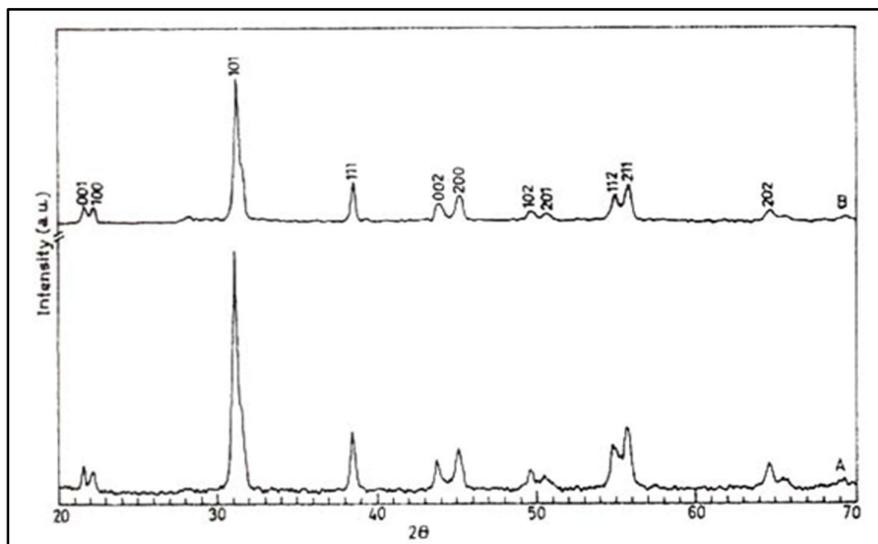
Fig. 2: XRD pattern of sintered ceramics.

A small change in the d values is observed due to a change of lattice parameters. The peaks were indexed by using a computer program (Powdmult). Lattice parameters and d values were also calculated and refined (by least square fitting method) using this program. A good matching has been found in calculated and observed d values (Table-1).

Table 1. Comparison of observed and calculated d values

d values in Á (Sample A)		d values in Á (Sample A)		h k l
Observed	Calculated	Observed	Calculated	
4.128	4.129	4.113	4.114	0 0 1
4.018	4.019	4.004	4.005	1 0 0
2.876	2.880	2.872	2.870	1 0 1
2.344	2.341	2.334	2.333	1 1 1
2.064	2.064	2.063	2.057	0 0 2
2.008	2.009	2.006	2.002	2 0 0
1.836	1.836	1.836	1.830	1 0 2
1.8080	1.807	1.801	1.800	2 0 1
1.6730	1.670	1.668	1.664	1 1 2
1.647	1.648	1.646	1.642	2 1 1
1.440	1.440	1.437	1.435	2 0 2

Table 2, which lists all the lattice parameters, confirms that a larger unit cell formed in case of sample A with same tetragonal distortion (a/c) in both the cases.

Table 2. Comparison of lattice parameters

Sample	System tetragonal			Vol. of unit cell (Å^3)
	a (Å)	c (Å)	a/c	
A	4.0197	4.1298	1.0274	66.73
B	4.0057	4.1148	1.0272	66.02

4. CONCLUSIONS

We have examined and compared the structural properties of PBZT ceramics near the morphotropic phase boundary (52/48) prepared by coprecipitation and sol-gel method. In the conclusion we may w rite that the formation of Perovskite phase in the sol-gel derived

ceramics take place comparatively lower temperature which is an important tool in the property optimization and device performance

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