Low temperature sintering of sol-gel derived PZT ceramics

Chemistry

KEYWORDS : PZT ceramics; Dielectric properties; XRD, SEM and FTIR; characterization; Sintering aids

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ABSTRACT

Lead zirconate titanate ($PbZr^{0.52}Ti^{0.48O3}$) nanocrystalline powder and ceramics were synthesized using a low temperature chemical sol-gel route in the laboratory. The main objective of the present work was to reduce the sintering temperature of PZT ceramics to below 1000°C without compromising on the density, dielectric and piezoelectric properties of the material. PZT powder was synthesized using a sol-gel route using acetate method. As-fired amorphous powder was annealed at two different temperatures at 450°C and 550°C respectively. These powders were co-doped with a novel sintering aid (a mixture of Li^2CO^3, Nb^2O^5 and MnO^2). The resulting powder was then cold-pressed into pellets and sintered below 1000°C (for 2 hours). These pellets were used for further characterization. Structural characterization of powder done using FTIR spectroscopy revealed the existence of TiO_6 octahedral peaks. X-ray diffractograms revealed polycrystalline nature of the ceramics. Positive effect of adding novel sintering aids to lower the sintering temperature and densification of PZT ceramics was reflected as an improvement in the temperature and frequency dependent dielectric properties of ceramics. Scanning electron micrographs showed formation of dense ceramic at low sintering temperature.

Introduction

Lead zirconate titanate perovskite solid solutions $PbZr^{1-x}Ti^{xO3}$ (PZT) are the most important ferroelectric and piezoelectric materials in commercial devices [1]. Ferroelectric to paraelectric phase transition temperature of these ceramics is more than 250°C [2-4]. However, a very high sintering temperature (>1000°C) is a major limitation in the fabrication of PZT ceramics. The final properties depend strongly on the porosity formed during sintering [5,6]. High porosity in ceramics adversely affects the dielectric characteristics such as permittivity and spontaneous polarization which decrease with the increase of porosity [7]. Several sintering aids (inorganic compounds) are added in small quantity as modifying agents to reduce sintering temperature. For instance, it has been reported that Li_2CO_3 addition significantly improves the sinterability of PZT-PZN-PMnN ceramics and reduces the sintering temperature from 1150°C to 930°C [8]. It is a well known fact that this material is a very important member of lead-based relaxor ferroelectric family having high dielectric constant and diffused phase transition temperature [9,10]. However, the sintering temperature of such PZT based ceramics is >1000°C [10-13]. Han et al. [17] showed that 0.1 wt% Li_2CO_3 was quite effective in lowering the sintering temperature of PMN-PFN-PZT ceramics from 1100°C down to 900°C, with the retention of good piezoelectric properties. Hou et al. [18] also showed that Li_2CO_3 could increase the piezoelectric properties and reduce the sintering temperature of 0.5PZT-0.5PZN ceramics from 1100oC down to 950°C. The average grain size of specimens increases with the increasing amount of Li_2CO_3 which was attributed to a liquid phase sintering process. In this process, in the initial and intermediate stages of sintering, Li2CO3 additives with a low melting point of 720°C forms a liquid phase, which wets and covers the surface of grains, and accelerates the growth of grains [15,16,18]. In the later stage, the Li ions are diffused into the lattice and modify the properties of ceramics. With further increase in the Li_2CO_3 content to 0.9 wt %, an abnormal growth of grain boundary is observed, and the average grain size is reduced. This is mainly attributed to the solubility limit of Li ions in PZT–PZN–PMnN structures. When the addition was above the limit, the excessive Li ions would segregate at grain boundary and inhibit the grain growth [18]. The change of Li_2CO_3 content also significantly affects the dielectric, ferroelectric and piezoelectric properties of PZT–PZN–PMnN ceramics. It has been reported that the maximum dielectric constant increased with increasing Li_2CO_3 content, and at x = 0.7 indicated the highest dielectric constant of 20030 and then sharply decreased beyond this point. This was attributed to the increasing grain size [11,19]. Similarly, the Curie temperature of ceramics decreased almost linearly from 253°C to 236°C with an increase in Li_2CO_3 concentration from 0 to 1 wt%,. The coercive field Ec decreased slightly with increasing content of Li_2CO_3 and reached a minimum (8.7 kV/cm) at x = 0.7. For the same concentration, optimized piezoelectric properties were obtained for the same ceramics [19]. Other than $LiCO_3$, MnO_2 and Nb_2O_5 have also been reported to improve the sinterability of PZT based ceramics. Co-doping, i.e. with two or more compounds has ben used to improve piezoelectric properties. It has been reported that MnO_2-Nb_2O_5 co-doped PZT ceramic is better than that of single doping of Nb_{5+} or Mn_{4+} in terms of its high Kp and Qm, low permittivity and its excellent temperature stability [20]. Based on the literature survey given in the preceding section, it was decided to investigate the effect of the addition of a combination of Li_2CO_3, MnO_2 and Nb_2O_5 on the properties of sol-gel derived PZT powders and ceramics, which is being reported in the present paper.

2.0 Materials and methods

2.2.1 Synthesis of PZT powder and ceramic

Various chemicals that are used in the preparation of the samples are mentioned in Table 2.1. The starting materials were Lead Acetate Trihydrate [$Pb(CH_3COO)_2.3H_20$ ≥99%], Zirconium isopropoxide [$Zr(OC_3H8)_4$] and Titanium tetrabutoxide (97%). Glacial acetic acid [CH_3COOH ≥ 99.7%] and butyl alcohol [C_4H_9OH > 99.5%] were used as solvents. Calculated amounts of Lead acetate trihydrate and Zirconium propoxide were weighed to synthesize compositions of ($PbZ_{1-x}Ti^xO^3$) (where molar concentration x = 0.48) [(Zr+Ti):Pb = 1:1] powders. The weighed amount of these compounds were mixed together in glacial acetic acid and refluxed for 0.5h using a sand bath. The Pb-Zr solution was cooled down to the room temperature and the calculated amount of Titanium Tetrabutoxide mixed with butyl alcohol was added and the resulting solution was stirred again using a magnetic blender for 0.5h at room temperature. Small amount of acetylacetone ($CH_3COCH_2COCH_3$) was added as stabilizer. After stirring, the sol was hydrolysed using 10-15ml of distilled water. The sol was relatively clear and stable. The sol was covered with aluminium foil and kept in a dessicator to avoid air contamination. The sol was left in open for gelation and it gelated in 12 hours. The obtained gel was fired at 350°C in air for 3-4 hrs. As–fired powder obtained was amorphous in nature. This powder was calcined at 850°C for 3 hrs in a muffle furnace to obtain a poly-crystalline powder. The PZT powder so obtained was milled and die-pressed into thick pellets under a pressure of 300MPa. The samples were finally sintered at 950°C for 2h. The powder and the ceramics were prepared using a procedure given in the flow chart (Fig. 2.1).

2.2.2 Synthesis of sintering aids doped PZT powder and ceramic

The crystalline PZT powder was mixed with appropriate amount of sintering aids such as lithium carbonate (Li_2CO_3), Niobium Pentoxide (Nb_2O_5) and manganese dioxide (MnO_2). The powder was milled and mixed homogeneously in a mortar and pestle. The powder was then die-pressed into thick pellets under a pressure of 300MPa. The samples were finally sintered at 950°C for 2h.

2.3 Material Characterization

2.3.1 Structural Characterization

XRD diffractograms

X-ray diffractograms of undoped PZT ceramics and sintering aids (Li_2CO_3, MnO_2 and Nb_2O_5) doped PZT ceramics are shown in Fig. 2.2. These diffractograms reveal a polycrystalline nature of ceramics and the peaks were assigned hkl values using JSPDS card.

FT-IR spectroscopy

Structural characterization of polycrystalline PZT powder annealed at 450°C and 550°C for 2 hours was done using FT-IR spectrometer. FT-IR spectrograms of the three samples are shown in Fig. 2.3. The peaks around 580-600 cm^{-1} show polycrystalline nature and confirm the formation structure of TiO_3 octahedral.

Morphological characterization

Morphological characterization of undoped and doped PZT ceramics was done using scanning electron microscope (SEM). Photomicrographs of the samples are shown in **Fig. 2.4**.

2.3.2 Dielectric characterization

AC frequency dependent values of parallel capacitance (Cp) and loss tangent or dissipation factor (tan δ or D) of the ceramics pellets were measured by using Agilent 423B precision LCR meter. The actual thickness of samples was measured using a micrometer before electroding by application of conductive silver plate using a paint brush. Electroded samples were placed in a sample cell between two electrodes and voltage was applied.

The parallel capacitance (Cp) was measured on the LCR meter. Dielectric constant was calculated using the formula:

$$(\epsilon)=C/C_0.$$

where, $C_O(={}_{\epsilon o}A/d)$ is the capacitance with vacuum between parallel plates and $\epsilon o=8.85\times10^{-12}$ F/m) is the permittivity of free space, A is the area of electrodes, and d is the thickness of the sample. Dissipation factor (D or tan δ) was directly measured on the LCR meter.

To calculate ac conductivity, parallel capacitance (Cp) and dissipation factor (D or tan δ) from 100 Hz up to 100 kHz was measured. $_{ac}(\omega)$ was calculated by using following expression :

$$_{ac}(\omega) = 2f_{\epsilon o}\epsilon''=2f_{\epsilon o}\epsilon'\epsilon'' \tan\delta$$

where, tan δ is the dissipation factor, $\omega=2f$ is the angular frequenc, ϵo is the permittivity of free space (=8.85x10-12 F/m), ϵ' is the dielectric constant, ($\epsilon''/\ \epsilon'= \tan\delta$), and ϵ'' is the dielectric loss.

2.5 Electrical characterization

Temperature dependent electrical properties of the samples were measured using a direct measurement method. Electric current (I) was measured using a Keithley Electrometer keeping the voltage constant. The sample was heated at a constant heating rate of 2°C/min using a furnace and temperature controller. A plot between electric current and temperature was drawn.

3.0 Results and discussion

Fig. 3.1a shows the temperature and frequency dependent dielectric constant of PZT ceramics prepared using powders annealed at 550°C. With increasing temperature, dielectric constant increased consistently, however, no Curie temperature (T_c) was observed till 400°C. It is clear from the figure that the value of dielectric constant overlapped at room temperature at all frequencies. However, with increasing temperature, the difference in the values of dielectric constant became more prominent at all frequencies. Low values of dielectric constant and no evidence of T_c were attributed to the porous nature of ceramics. Due to a low sintering temperature, dense ceramics could not be formed. There was no evidence of grains or growth of grains as is clear from the micrograph of ceramic shown in Fig. 2.4a. Fig.3.1b shows the temperature dependent dielectric loss of the same ceramics. Dielectric loss was found to be below 0.1 at all frequencies. However, at Tc the dielectric loss was also the maximum.

3.1.1 Effect of sintering aids on dielectric behavior of PZT ceramics

Temperature and frequency dependent dielectric constant and dielectric loss of the sintering aids doped PZT ceramics are shown in Fig. 3.2a and b respectively. These ceramics were also sintered at 950°C for 2 hrs. In contrast to Fig. 3.1a, a diffused Curie temperature was clearly evident around 250°C. Though the magnitude of dielectric constant was not very high, it was higher compared to that of the undoped ceramic. This improvement in the dielectric properties was attributed to the reduction in the porosity of ceramic and initiation of grain growth as is visible in the micrograph shown in Fig. 2.4b. Lower values of dielectric constant are also attributed to a contrasting combination of dopants Nb_2O_5 and MnO_2. Nb_{5+} ions with an ionic radius of 0.069 nm is regarded as a soft dopant for PZT which helps in achieving higher permittivity values. In contrast, Mn_{2+} ions are regarded as hard dopants which occupy the B-sites in the perovskite structure. Unlike soft doping, hard doping increases the hardness of PZT properties but lowers dielectric constant. However, both the dopants help in the formation of dense PZT ceramics. Variation of current with respect to temperature at a constant heating rate of 2°C/min is shown in Fig. 3.3. It is evident from the figure that till a temperature of 150°C the current was almost constant. However, with further increase in temperature it started increasing and no drop in the current was observed till 300°C.

4.0 Conclusions

Bulk ceramics of Lead zirconate titanate (PZT) prepared using nanocrystalline powders derived from sol-gel method showed that porous ceramics are formed when they are sintered at 950oC. However, when a combination of sintering aids such as Li, Nb and Mn are added, dense ceramics are formed at a sintering temperature of 950°C. Dielectric properties are improved and the ferroelectric-paraelectric phase transition temperature (T_c) also shifts to a lower temperatures. With a very small addition of sintering aids, a very high dielectric constant and a low dielectric loss is obtained at room temperature.

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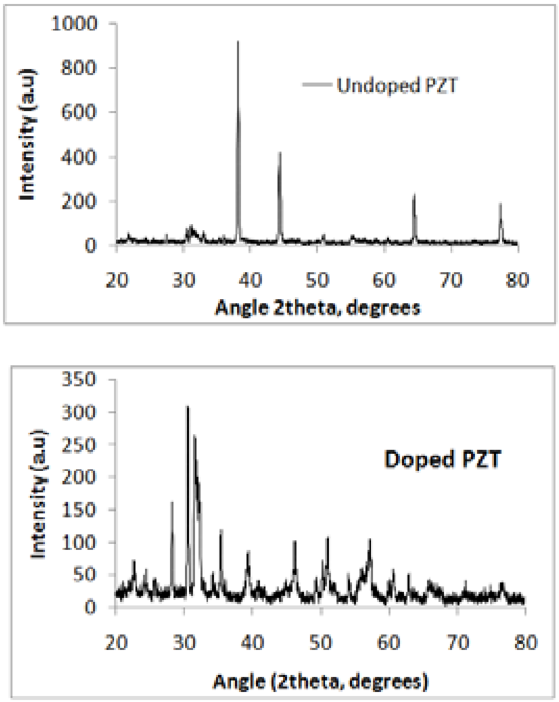


Fig. 2.2 XRD diffractograms of undoped and doped PZT ce-

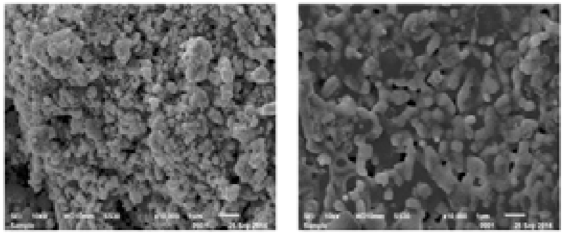


Fig. 2.4 SEM of (a) undoped PZT ceramic and (b) doped PZT ceramic (sintered at 950ºC for 2 hr)

Fig. 2.3 FT-IR spectrograph of sol-gel derived PZT powder annealed at 450ºC and 550ºC.

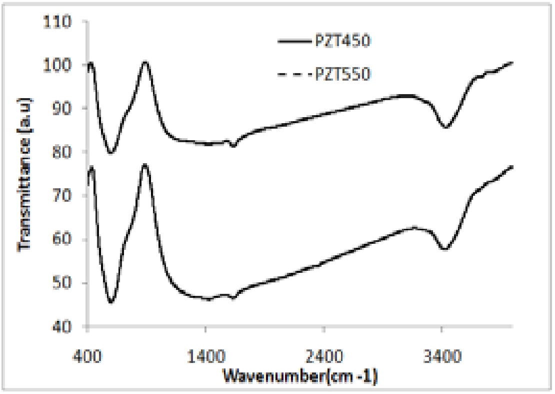


Table 2.1: PROFILE OF THE CHEMICALS AND REAGENTS USED FOR THE PREPARATION OF PZT

S.No	CHEMICAL NAME	MOLECULAR FORMULA	MOLECULAR WEIGHT(g/mol)	CAS No.	PURITY/ASSAY (%)
1.	Lead acetate trihydrate	$Pb(CH_3COO)2.3H_2O$	379.33	6080-56-4	≥99.99
2.	Lithium carbonate	Li_2CO_3	73.89	554-13-2	-
3.	Acetic acid	CH_3COOH	60.05	64-19-7	≥99.7
4.	Titanium tetrabutoxide	$Ti(OC_4H_9)_4$	340.32	5593-70-4	97
5.	Zirconium isopropoxide	$Zr(OC_3H_8)_4$	327.57	23519-77-9	
6.	Butanol	C_4H_9OH	-	71-36-3	>99.5
7.	Acetylacetone	$CH_3COCH_2COCH_3$	100.12	123-54-6	≥99
8.	Niobium pentoxide	Nb_2O_5	265.81	1313-96-8	-
9.	Manganese dioxide	MnO_2	86.9368	1313-13-9	-

Fig. 2.1 a: Flow chart for sol-gel synthesis of PZT powder and ceramics

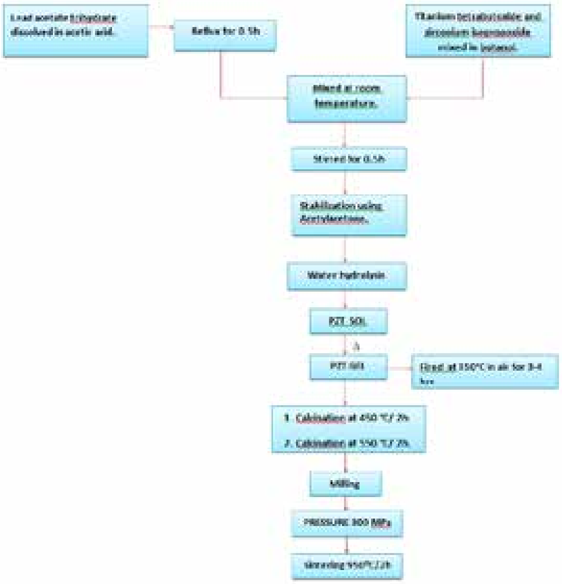
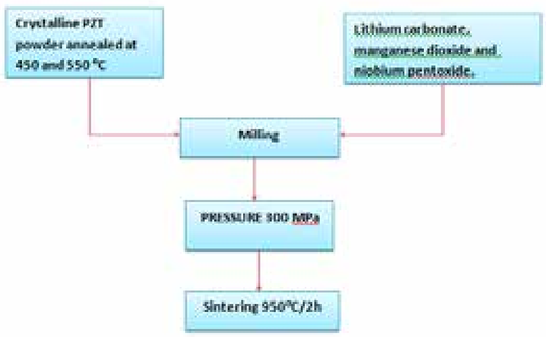


Fig. 2.1 b: Flow chart for synthesis of doped PZT powder and ceramics



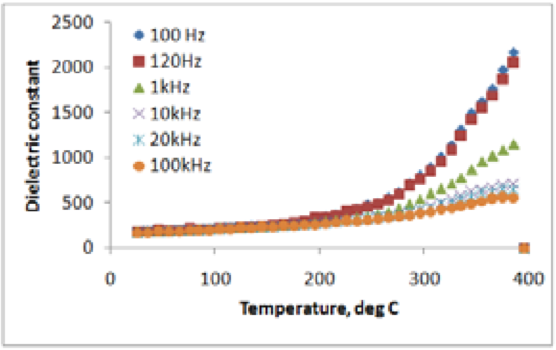


Fig.3.1a: Frequency and temperature dependent dielectric constant of PZT ceramics prepared using powder annealed at 550$^{oC.}$

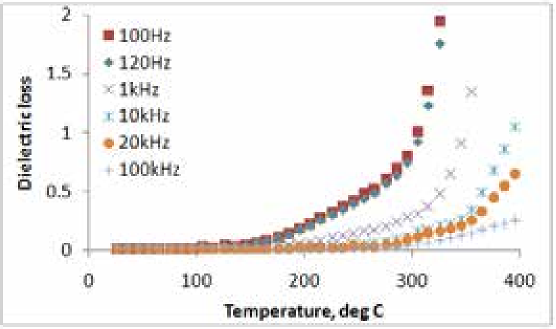


Fig.3.1b: Frequency and temperature dependent dielectric constant of PZT ceramics prepared using powder annealed at 550°C.

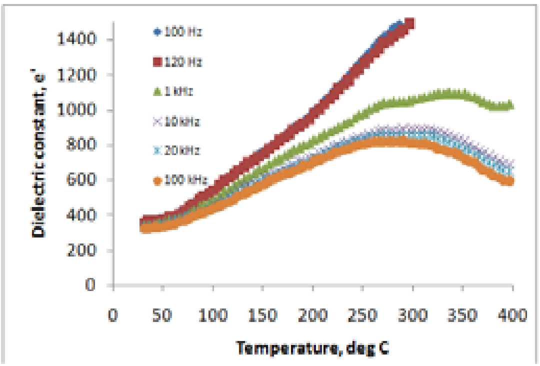


Fig. 3.2 a: Frequency and temperature dependent dielectric constant of doped PZT ceramics prepared using powder annealed at 550°C.

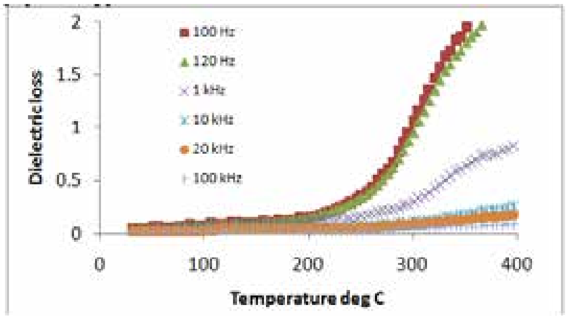


Fig. 3.1 b: Frequency and temperature dependent dielectric loss of doped PZT ceramics prepared using powder annealed at 550°C.

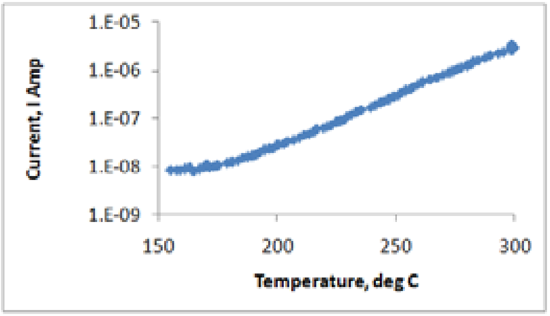


Fig. 3.3: Variation of current with respect to temperature at a constant heating rate of 2°C/min for doped PZT ceramic.

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