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'Ultra'-low-temperature sintering of PZT: A synergy of nano-powder synthesis and addition of a sintering aid

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Abstract

It has been found that under certain conditions, PZT [$Pb(Zr_{0.52}Ti_{0.48})O_3$] can be sintered at a temperature as low as 715 °C, whereas the conventional sintering temperature is around 1200 °C. The conditions for such 'ultra'-low-temperature sintering are the synthesis of PZT nano-powder through autocombustion route and addition of a small amount of $LiBiO_2$ as a sintering aid. Interestingly, the dielectric and piezoelectric properties of such 'ultra'-low-temperature sintered samples are on a par with and in some cases better than those of PZT samples prepared via conventional sintering at a high temperature.

Keywords: Powders-chemical preparation; Dielectric properties; Piezoelectric properties; PZT; Sintering

1. Introduction

The solid solution of $PbZrO_3$ and $PbTiO_3$ with a composition close to morphotropic phase boundary (MPB) between tetragonal and rhombohedral phases [$Pb(Zr_{0.52}Ti_{0.48})O_3$, designated PZT] shows excellent piezoelectric properties and therefore is of great technological importance.[1] Such piezoelectric materials are often used in ultrasonic generators, hydrophones, electronic buzzers and ringers, pressure and stress sensors, etc.[2] The sintering of PZT powder by conventional firing requires a fairly high temperature (1200–1300 °C), which causes a significant loss of PbO by volatilization.[3–6] Other disadvantages of this process are compositional shifting, grain growth, high fuel cost, environmental pollution, etc. The alternatives to get around the problem of high-temperature densification lie in synthesizing nanosized PZT powder, which can be sintered at a low temperature and/or adding sintering aids to lower the sintering temperature. In general, the incorporation of low-melting oxides as sintering aids in PZT reduces the sintering temperature but at the cost of piezoelectric properties. As PZT is an age-old material, there is an extensive amount of published literature and patents available in the public domain [e.g., see Refs.[7–21]] on the low temperature sintering (900–1100 °C) of PZT.

Incidentally, there are a few reports on sintering of PZT below 900 °C. Recently, Banerjee and Bose[22] reported synthesis of PZT by autocombustion technique and the synthesized powder after doping with ZnO can be sintered to 93% of the theoretical density at 900 °C, albeit with inferior piezoelectric properties. Hayashi et al.[23] reported that $LiBiO_2$ could be a useful sintering aid for the densification of PZT at 750 °C. However, to get good dielectric and piezoelectric properties, a small amount of Nb_2O_5 addition was required and saturated hysteresis loops were only observed after sintering at 900 °C. Wang et al.[24] reported that PZT can be sintered at a temperature as low as 800 °C by adding a mixture of $LiBiO_2$ and CuO as a sintering aid. However, useful piezoelectric properties can be achieved by sintering the aforesaid composition above 880 °C. Hayashi et al.[25] also investigated the low temperature sintering characteristics of $(Pb_{0.86}Ba_{0.04}Sr_{0.12})(Zr_{0.56}Ti_{0.44}Sb_{0.02})O_3$ using $Pb_5Ge_3O_{11}$ and $LiBiO_2$ separately as sintering aids. The sintering temperature could be lowered to 800 °C using these additives and the relative density achieved was approximately 96% of the theoretical density. However, the samples showed poor piezoelectric properties and to get acceptable piezoelectric properties, the samples required sintering above 1200 °C. In another study, Hayashi et al.[26] reported sintering of

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$Pb(Ni_{1/3}Nb_{2/3})O_3$–$Pb(Zr_{0.3}Ti_{0.7})O_3$ at 850 °C using $LiBiO_2$ as a sintering aid, and in this case too, to get appreciable piezoelectric properties, the samples required sintering at a higher temperature (1100 °C). Corker et al.[27] studied the effect of Cu_2O and PbO addition on lowering of the sintering temperature of a PZT formulation (commercial hard PZT). The bulk density value of greater than 90% of the theoretical density was achieved for 5 wt% additive (a mixture of Cu_2O and PbO) after sintering at 800 °C. However, to get acceptable piezoelectric properties, the samples needed sintering above 850 °C. Li et al.[28] reported densification of PZT at 800 °C by isostatic hot pressing but the technique is not cost-effective.

In the present work we report the synthesis of PZT nanoparticles by citrate–nitrate autocombustion technique and we find that by controlling the citrate to nitrate ratio, the phase formation takes place during the autocombustion stage. Interestingly, the synthesized PZT powder can be sintered at a temperature as low as 715 °C by adding a little amount of lithium bismuth oxide ($LiBiO_2$) as a sintering aid. The piezoelectric properties of our sintered samples are comparable to those of conventionally sintered PZT. To the best of our knowledge, we first time report such "ultra"-low-temperature sintering (at 715 °C) of PZT without sacrificing the piezoelectric properties.

2. Experimental

Reagent grade lead nitrate, zirconyl oxychloride hydrate and titania powder were used as starting materials to make PZT. To prepare a Ti^{4+} solution, titania (TiO_2) powder was dissolved in H_2SO_4 in presence of $(NH_4)_2SO_4$ by constant stirring at 100 °C until a clear solution of titanium sulphate was formed. Ammonium hydroxide in excess was added to the titanium sulphate solution for complete precipitation of titanium hydroxide in an ice bath. The precipitate was washed with distilled water and then dissolved in a nitric acid and water (1:1) mixture to form a clear solution of titanium ion. The strength of the solution was measured gravimetrically. The solution of Ti-nitrate, known to be unstable under normal conditions, was found to be stable by Yamamura et al.[29] for several months when it was prepared by dissolving titanium hydroxide in HNO_3 in an ice bath and storing the resultant solution inside a refrigerator at about 10 °C. To prepare zirconium nitrate solution, zirconium oxychloride hydrate ($ZrOCl_2 \cdot 8H_2O$) was dissolved in distilled water and ammonium hydroxide was added to adjust the pH between 10 and 11 for complete precipitation of zirconium hydroxide. The precipitate was filtered and dissolved in nitric acid and water (1:5) mixture to form a clear solution of Zr^{4+} ion. The strength of the solution was measured gravimetrically. For preparing PZT powders, calculated amounts of zirconium nitrate solution (0.2 M), titanium nitrate solution (0.15 M), lead nitrate, ammonium nitrate and anhydrous citric acid were taken in beakers so that the Pb:Zr:Ti ratio in the final products remains at 1.00:0.52:0.48 and the molar ratios of citrate to nitrate were kept at 0.06 [sample-(a)], 0.14 [sample-(b)] and 0.33 [sample-(c)]. The solutions were concentrated by heating and stirring continuously on a hot plate at 120 °C with a gradual addition of ethylene diamine as a complexing agent. Finally, the solutions set to viscous gels during continuous heating. The stirrers were then removed from the beakers and the gels were further heated. The gels began to foam and swell, and finally burned on its own (autoignition) due to strong exothermic reaction between the citrate and nitrate species. Small amounts of the gels, collected prior to the autoignition, were characterized by TGA and DTA performed on a Shimadzu TGA/DTA-50 at a heating rate of 10 °C/min. The ashes produced after autocombustion were calcined at 500 °C for 5 h to get yellow PZT precursor powders. The powders were characterized using X-ray diffractometer (Philips), thermal analyzer (Shimadzu), specific surface area analyzer using BET method (Micromeretics Gemini 2370) and FESEM (Carl Ziess, Supra 35VP).

$LiBiO_2$ (abbreviated as LBO) was prepared by mixing Li_2CO_3 and Bi_2O_3 in 1:1 molar ratio in an agate mortar and a pestle (by hand for 30 min) and calcining the mass at 600 °C for 1 h followed by grinding in an agate mortar and a pestle. The formation of $LiBiO_2$ phase was confirmed from the XRD analysis. For the study of LBO addition on the sintering of PZT powder, sample-(b) was chosen because, as described later, it showed the optimum properties in comparison to samples-(a) and (c). LBO (1–5 wt%) and ethyl cellulose (1 wt% as a binder) were mixed with PZT powder [sample-(b)] in an agate mortar and a pestle (by hand for 30 min) under acetone and then pelletized under 170 MPa pressure to make 10–15 mm diameter pellets (green density ~56% of theoretical density). The pellets were sintered at 715–750 °C for 6 h in air at a heating and cooling rate of 300 °C/h. For comparison, a few pellets of PZT without any additive were sintered at 1100 °C. The densities of the fired pellets were measured by Archimides' method. The samples for electrical testing were polished and coated with silver paint and cured at 500 °C for 15 min. The piezoelectric strain constant (d_{33}) was measured on a d_{33} meter (Pennebaker 8000 d_{33} tester) after poling the samples in silicone oil at a temp of 120 °C at 3 kV/mm field for 30 min. The dielectric measurements of the fired pellets were made at room temperature in the frequency range of 100 Hz–1 MHz using a Solartron Impedance analyzer. The planer electrochemical-coupling coefficient (k_p) was determined from the resonance (f_r) and antiresonance (f_a) frequencies using the formula:

$$K_p = \sqrt{2.51 \frac{\Delta f}{f_r}} \tag{1}$$

where Δf is equal to $(f_a - f_r)$. Ferroelectric hysteresis loops were obtained for unpoled samples using an LC precision ferroelectric tester.

3. Results and discussion

Fig. 1 shows the XRD patterns of as-burnt (after autocombustion) powders. The sample-(b) showed the formation of phase-pure PZT at the as-burnt state though it contained a small amount of carbonaceous material as evident from the grayish color of the powder. The sample-(c) was of amorphous nature and showed phase formation after calcination at 500 °C and the sample-(a) showed the formation of PZT phase along with other

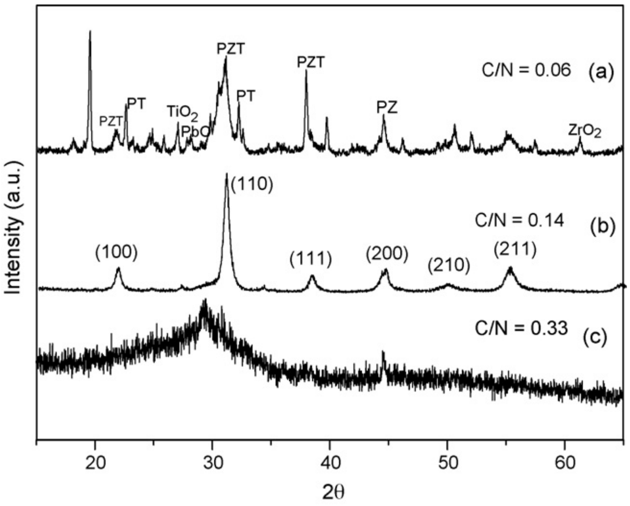

Fig. 1. XRD patterns of as-burnt powders: (a) sample-(a), (b) sample-(b) and (c) sample-(c) (PT is $PbTiO_3$ and PZ is $PbZrO_3$, C/N is the citrate to nitrate ratio).

phases like $PbZrO_3$, $PbTiO_3$, PbO, ZrO_2 and TiO_2. However, for further studies, sample-(b) was also calcined at 500 °C to remove the small amount of carbonaceous matter.

The surface area of the calcined sample-(b) was found to be 25 m^2/g, whereas the surface areas of sample-(a) and sample-(c) were found to be 12 m^2/g and 15 m^2/g, respectively. The FESEM photograph (Fig. 2) depicts the particle size of sample-(b), which is in the range of 70–80 nm.

Fig. 3(a–c) shows the DTA and TGA plots of the gels having different C/N (citrate to nitrate) ratios. Except for C/N = 0.06 [sample-(a)], the gels having C/N ratios equal to 0.33 and 0.14 show double stage decomposition. The first exotherm can be assigned to the decomposition of the metal complexes, and the second peak [for samples-(b) and (c)] can be attributed to the oxidation of the residual carbonaceous matter along with slow crystallization of the amorphous structure.[30] In the TGA plots (Fig. 4) of the as-burnt powders (after autocombustion), sample-(b) shows less than 1 wt% loss indicating complete reaction, whereas samples-(c) and (a) show around 68% and 15%

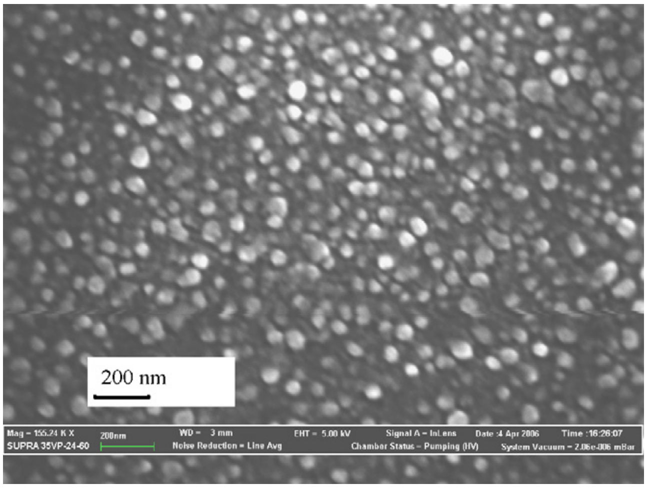

Fig. 2. FESEM photograph of synthesized PZT powder [sample-(b)].

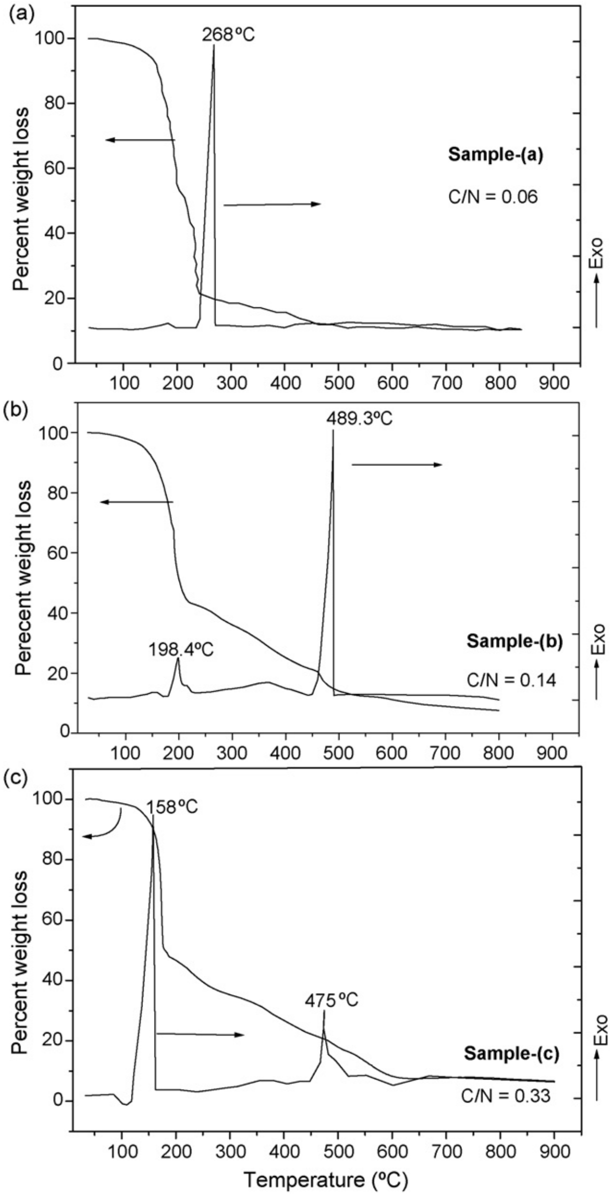

Fig. 3. TGA and DTA plots of the gels with different citrate to nitrate (C/N) ratio sample-(a), (b) sample-(b) and (c) sample-(c).

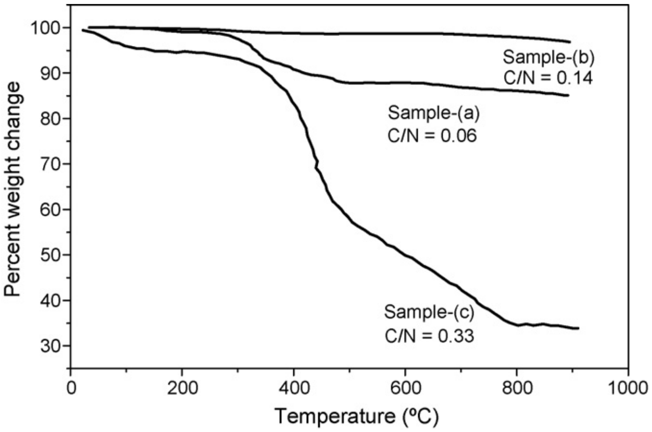

Fig. 4. TGA plots of the as-burnt powders.

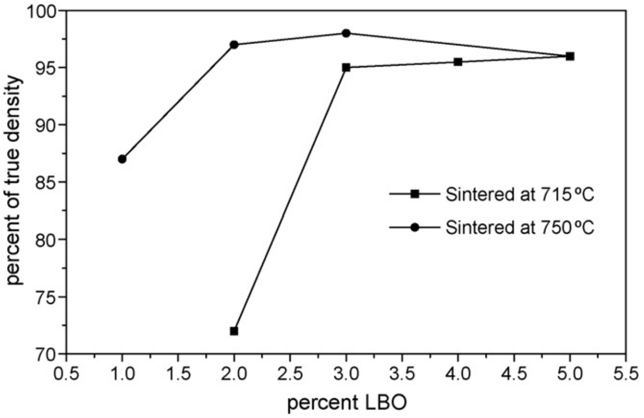

Fig. 5. Variation of bulk density (% of true density) of sintered PZT samples with LBO addition.

weight loss, respectively indicating incomplete combustion during the autocombustion stage. Incidentally, Chakrabarty et al.[10] reported the synthesis of PZT powder by autocombustion route at 800 °C, where the source of Ti was TiO_2 powder directly added to the gel. The surface area of the synthesized powder was 4.7 m^2/g and the particle size was 1.1 μm. Banerjee and Bose[22] also reported synthesis of PZT by citrate–nitrate autocombustion technique where the source of Ti was Ti-nitrate solution, which was prepared by dissolving TiO_2 in HF by 72 h refluxing followed by precipitation of Ti-hydroxide and dissolving the precipitate in HNO_3. The surface area[22] of the calcined powder (500 °C) was 4.6 m^2/g and the particle size was 90–100 nm. Cernea et al.[31] reported synthesis of La- and Nb-doped PZT powder by the gel-combustion method (where the source of Ti was titanium(IV) isopropoxide $Ti[OCH(CH_3)_2]_4$), however, even after calcination at 600 °C, the PZT powder could not be made phase-pure.

Fig. 5 depicts the effect of LBO addition on the sintered density of the pellets at two sintering temperatures, viz., 715 °C and 750 °C. From the figure, it is evident that the bulk density of the pellets [as a % of true density of PZT (7.75 g/cm^3)] increased with an increasing amount of LBO addition up to 3 wt% followed by a decrease or plateau with further addition of LBO. A typical microstructure of a sintered pellet has been shown in Fig. 6. However, without LBO addition, the bulk density of PZT after sintering at 750 °C was only 68%. It may be noted that the weight loss of LBO added PZT after sintering was within 1.3–1.8%, indicating a very little shift in composition (considering 1 wt% ethyl cellulose binder which is lost during heating). Incidentally, LBO in PZT forms a low melting liquid phase (melting point of LBO is 700 °C) that helps in liquid phase sintering. Above the optimum amount of LBO addition (∼3 wt%), the densification decreases because an excess liquid phase formed from a higher amount of LBO addition lowers the densification due to grain and pore growth.[32] It may be mentioned here that, PZT samples without LBO addition can be sintered to 96% of the theoretical density [sample-(s)] (Fig. 7) only after firing at 1100 °C and above. Incidentally, it may be noted that the process of particle rearrangement and densification during liquid phase sintering depends on many parameters[33] like the surface free energy of the liquid–vapor interface, viscosity of the liquid, contact angle, diameter of the capillary and the particle size of the powder. In the present case, further systematic study can find out the role of the aforesaid parameters in imparting LBO the characteristics of an excellent sintering aid for PZT.

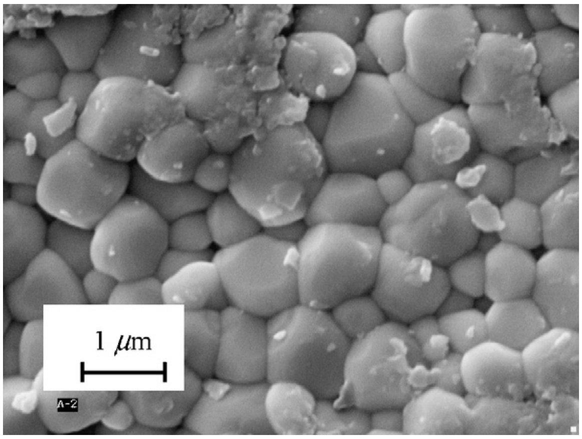

Fig. 6. Typical micrograph of a sintered LBO added-PZT pellet.

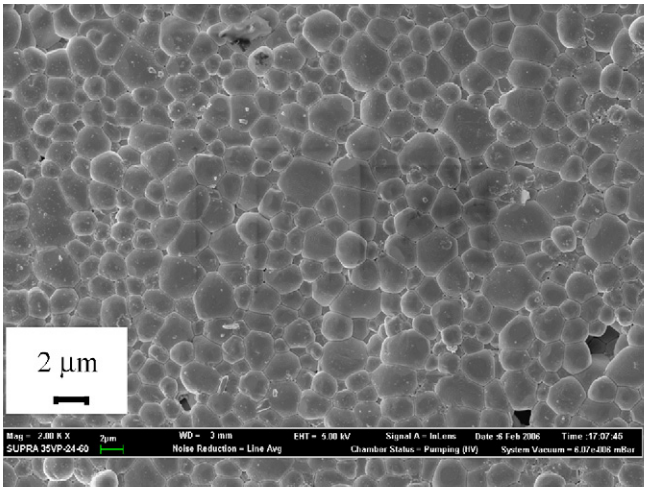

Fig. 7. FESEM photograph of a PZT pellet sintered at 1100 °C.

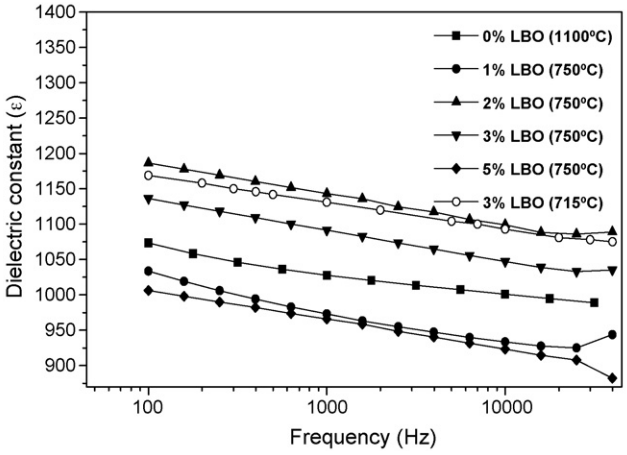

Fig. 8. Dielectric constant vs. frequency for PZT samples sintered under different conditions.

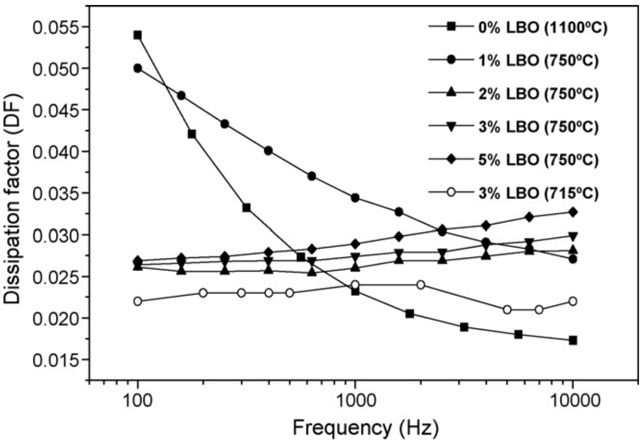

Fig. 9. Variation of dissipation factor with frequency for PZT samples under varying sintering conditions.

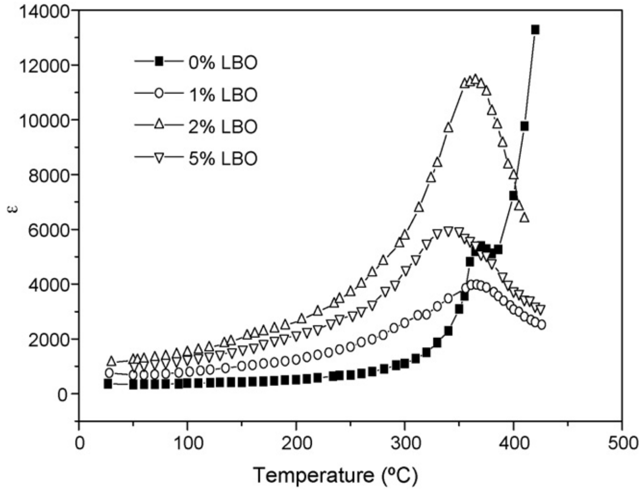

Fig. 10. Temperature dependence of dielectric constant (ε) of PZT with varying LBO addition (all the samples were sintered at 750 °C, except for 0% LBO, which was sintered at 1100 °C).

Figs. 8 and 9 show the dielectric constant and dissipation factor versus frequency curves for PZT samples sintered under varying conditions. From Fig. 8, it is noteworthy that the ε values of LBO added samples (for 2 wt% and above) are much higher than those of the conventionally sintered sample (at 1100 °C). Normally, for higher LBO addition, ε should decrease, which may be understood by considering the formation of non-ferroelectric low-ε LBO rich grain boundaries, as Wang et al. showed by XPS analysis that some LBO remains at the grain boundaries of the sintered ceramics.[24] Also with LBO addition, the dissipation factor (at low frequencies) decreases due to the formation of non-ferroelectric LBO rich grain boundaries. Besides, some amount of lithium and bismuth doping in PZT due to LBO addition is possible, as Li^+ can replace Pb^{2+} in PZT (acceptor doping).[11] Also owing to its small ionic radius, Li^+ can stay in the interstices[11] and some Bi^{3+} can also replace Pb^{2+} (donor doping).[11] In the present case, some LBO incorporation into the PZT structure is confirmed from the variation of c/a ratio (Table 1), which increases with LBO addition and then plateaus. Also the shifting of T_c with LBO addition (Fig. 10) vindicates our former assertion. Yadav and Choudhary[34] reported similar lowering of T_c with an addition of Li in La-doped PZT and Mahato et al.[35] also reported lowering of T_c with Na doping in PZT. However, in the present case, further studies are required to understand the doping process in detail for different concentrations of LBO addition. Fig. 11 depicts the variation of d_{33} and k_p of sintered PZT samples with varying LBO addition. We found the maximum values of d_{33} to be 400 pC/N and k_p to be 0.62 for PZT samples with 2 wt% LBO addition after sintering at 750 °C. The d_{33} and k_p values for 715 °C-sintered sample (for 3 wt% LBO addition) were found to be 347 pC/N and 0.52 respectively, whereas, the d_{33} and k_p values for 1100 °C sintered PZT (without LBO addition) were 170 pC/N and 0.4, respectively (for conventionally sintered PZT, the literature reported values are $d_{33} = 223$ pC/N and $k_p = 0.51$).[1] The g_{33} (piezoelectric voltage constants) and Q_M (mechanical quality factor) were in the range of $27–39 \times 10^{-3}$ V m/N and 23–54, respectively for 750 °C-sintered samples and the same for 715 °C-sintered samples were 15–30 V m/N and 15–40, respectively. The g_{33} and

Table 1
Variation of c/a ratio of $Pb(Zr_{0.52}Ti_{0.48})O_3$ with varying LBO addition

LBO (wt%)	c/a
0	1.006
2	1.008
3	1.011
5	1.010

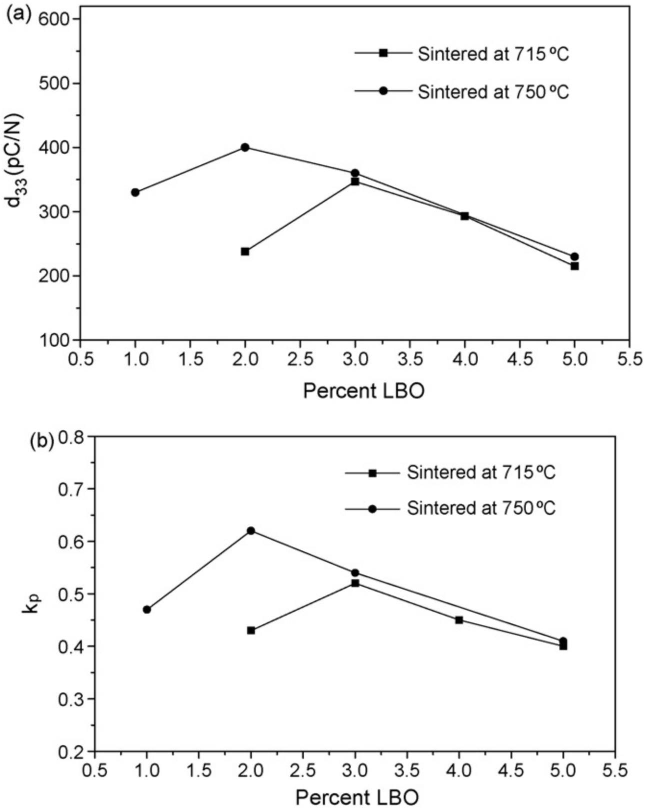

Fig. 11. Variation of (a) piezoelectric constant (d_{33}) and (b) k_p of PZT samples sintered under varying condition.

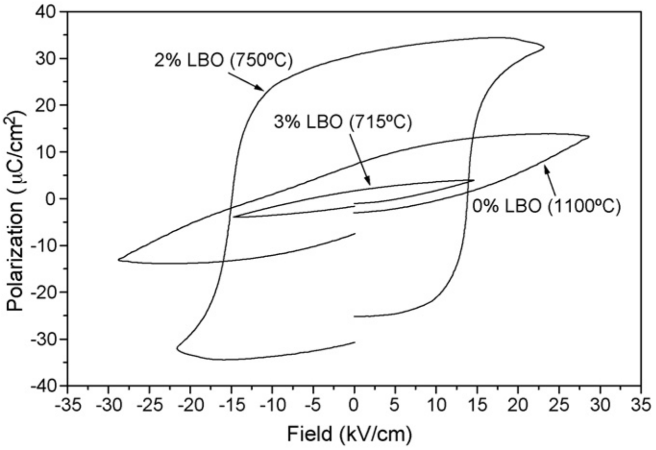

Fig. 12. P–E hysteresis loops (at room temperature) of PZT samples sintered under varying conditions.

Q_M values were calculated from the following relations:

$$g_{33} = \frac{d_{33}}{\varepsilon_0 \varepsilon_{33}} \tag{2}$$

$$Q_M = \frac{1}{2\pi f_r R_1 C_f \{1 - (f_r/f_a)^2\}} \tag{3}$$

where ε_0 is the permittivity of the free space, ε_{33} the material permittivity, R_1 the resonant resistance, C_f the free capacitance across the electrodes, and f_r and f_a denote the resonance and antiresonance frequencies, respectively. Fig. 12 shows the P–E loops for different PZT samples indicating the saturation polarization of 2% LBO added PZT sample (sintered at 750 °C) to be higher than that of 1100 °C-sintered PZT without any LBO addition.

4. Conclusion

Nanoparticles of PZT have been synthesized successfully using citrate–nitrate autocombustion method. By controlling the citrate to nitrate ratio, it is possible to synthesize phase-pure perovskite PZT during the autocombustion process. The synthesized powder can be sintered to around 95% of the theoretical density at a temperature as low as 715 °C by adding 3 wt% $LiBiO_2$ as a sintering aid and the density improved to 97% of theoretical density, when sintered at a temperature of 750 °C by adding 2 wt% $LiBiO_2$. The dielectric and piezoelectric properties of the LBO added sintered samples are on a par and in some cases better than those of high-temperature conventionally sintered PZT without $LiBiO_2$ addition.

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