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Phase composition and dielectric properties of spark plasma sintered PbZr$_{0.52}$Ti$_{0.48}$O$_3$

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Abstract

In the present work, lead zirconate titanate PbZr$_{0.52}$Ti$_{0.48}$O$_3$ (PZT) bulk ceramic powders having composition aimed for morphotropic phase boundary (MPB) were synthesized by conventional solid-state reaction and sintered by novel spark plasma sintering (SPS) method. The samples sintered at four different temperatures of 800, 850, 900 and 950 °C are found to have almost same density. The effect of SPS temperature on microstructure, phase constituents and dielectric properties is investigated. Rietveld refinement of XRD patterns of samples was carried out to estimate the phase composition revealing that the enhanced dielectric response is due to the presence of monoclinic phase along with rhombohedral phases with simple cubic structure exist at higher temperature. Among these oxides, ferroelectric Pb$_{1-x}$Zr$_x$O$_3$ has opened up another view for ultra-high dielectric response. The material with composition lying on the MPB shows ultra-high dielectric response. The reason behind such an unusual response is still not resolved, so far. However, researchers have put forward the probable causes, viz. the coexistence of phases [2], the existence of a tricritical point near MPB [3, 4], lattice instability at room temperature [5, 6], softening of elastic modulus [7], availability of more polarization directions [8–13], etc.

1. Introduction

Perovskite oxides have been a very important area of research for ferroelectric and piezoelectric materials over the past 60–70 years because many polar states are found to exist at lower temperature and variety of high symmetry phases with simple cubic structure exist at higher temperature. Among these oxides, ferroelectric PbZr$_{1-x}$Ti$_x$O$_3$ (PZT) solid solutions are important due to the existence of ‘morphotropic phase boundary’ (MPB) separating the tetragonal and rhombohedral phases as reported by Jaffe et al [1]. The material (PZT) composition lying on the MPB shows ultra-high dielectric response. The reason behind such an unusual response is still not resolved, so far. However, researchers have put forward the probable causes, viz. the coexistence of phases [2], the existence of a tricritical point near MPB [3, 4], lattice instability at room temperature [5, 6], softening of elastic modulus [7], availability of more polarization directions [8–13], etc.

Recently, the discovery of a ferroelectric monoclinic phase (F$_m$) with a composition corresponding to MPB of PbZr$_{0.52}$Ti$_{0.48}$O$_3$, has opened up another view for ultra-high dielectric response. The material with composition x = 0.52, leads to tetragonal to monoclinic transition at ~300 K [14]. The polar axis of the monoclinic cell can be rotated along the symmetry plane in response to an external field unlike that in tetragonal, orthorhombic and rhombohedral phases [9, 10]. The discovery of monoclinic phases such as M$_A$ [15, 16] (space group C$_{m}$), M$_B$ [16] (space group C$_{m}$) and M$_C$ [17] (space group P$_m$) in the materials having MPB composition has confirmed that these phases induce ultra-high dielectric performance in PZT, PMN-PT, PZN-PT, etc.

Sintering of PZT materials has been challenging since high sintering temperature of ~1200 °C causes PbO evaporation affecting the dielectric performance of the material and proving to be hazardous to the environment [18]. In addition, the use of dopants in PZT tends to degrade its dielectric performance due to inter-diffusion of constituent elements at high sintering temperature [19, 20]. It is well known that grain size and porosity play a major role in deciding dielectric and electro-mechanical performance. The phase transition from cubic to tetragonal state at below 763 K incorporates a large transformation strain, resulting in crack formation and anisotropic thermal expansion in the sintered samples on cooling from the soaking temperature to ambient...
temperature intermediating through the Curie temperature. This transformation strain has been known to be attributed to grain-grain separation. The stress generated at the grain boundary regions can be minimized by increasing the area of grain boundary. This is accomplished by decrease in grain size i.e. inhibition of grain growth [21].

Energy storage materials concern wide variety of devices such as rechargeable batteries, electrostatic capacitors, electrochemical capacitors, fuel cells etc. Capacitors provide a large amount of energy in a very short time interval. Since capacitors possess low energy density, they form the bulk majority of any device. Therefore, compact size and lightweight capacitors are desirable with high energy storage densities. High energy storage can be achieved by synthesizing materials that produce high dielectric constant and low dielectric loss with large dielectric breakdown strength. Therefore, for a candidate material to be competitive, it is essential to achieve a compromised state wherein these prerequisites are met simultaneously.

Spark plasma sintering (SPS) method utilizes presumed electrical discharge between the particles under pressure of compaction to generate a local high-temperature state. This causes vaporization and melting of the surface of powder particles. The electrical current application creates satisfactory conditions for the removal of impurities and activation of the powder particle surface. This activation ensures direct grain-to-grain contact and promotes densification of the powder compact instead of grain growth. The SPS process enables materials to be sintered to high degree of density at lower temperature than required for conventional sintering process within a few minutes time period. During the sintering process, high temperature (∼2400 °C) and pressure (∼900 MPa) can be applied simultaneously. SPS is characterized by its very high heating and cooling rates of 1000 °C min⁻¹ and short sintering periods (∼min). High mechanical pressure helps in increasing particle to particle contacts and thereby aiding diffusion of the grains and ensuring high densification. SPS is a useful tool to control parameters like grain size and porosity which play a fundamental role in dielectric response. Therefore, SPS method has been widely used to sinter PZT and doped PZT ceramic oxides for electrical applications [22–36]. However, volatilization of PbO at higher temperatures (>600 °C) may disrupt the stoichiometry of synthesized PZT ceramic oxide [22, 27, 31].

The main objective of the present work is to study the effect of spark plasma sintering temperature on PZT ceramic oxide having MPB composition through (i) qualitative and quantitative analyses of crystallographic phases using Rietveld refinement, (ii) temperature dependent microstructural observations, (iii) temperature dependent dielectric performance. The data reveals that the higher dielectric constant of the sample sintered at 900 °C, is due to the higher number of available polarization domains present in its crystallographic phases, but not due to densification. This observation greatly helps to select the sintering temperature of lead-based ferroelectric ceramic systems.

2. Experimental procedure

2.1. Materials synthesis

The raw materials PbO (99.5%, Merck), ZrO₂ (99.5%, Merck), TiO₂ (99.5%, Merck) used were of analytical reagent-grade. The powders were weighed in stoichiometric proportion for the preparation of PbZr₀.₅₂Ti₀.₄₈O₃ phase. The powder mixture was milled in a planetary ball mill using zirconia jar and balls for 8 h at 450 rpm maintaining the ball-to-charge ratio of 10:1 for complete homogenous mixing. The milled powder was calcined at different temperatures varying between 800 and 950 °C for 4 h in a muffle furnace. The grounded powder samples were designated as SPS-800, SPS-850, SPS-900, and SPS-950 in respect of sintering temperature used. The fine powder (~1.5 g) was kept in a graphite die of 10 mm inner diameter with graphite foil wrapped around it and sintered by spark plasma sintering set-up (Dr Sinter SPS-625, Japan) at 800 °C, 850 °C, 900 °C and 950 °C for 5 min under standard vacuum condition of 6 Pa. Initially, only contact pressure was applied to the powder sample and was heated at a heating rate of 100 °C min⁻¹ from room temperature to a high temperature which is below 100 °C of the sintering temperature and thereafter heating was done at 33 °C min⁻¹ till the soaking temperature of sintering. Just before soaking, uniaxial pressure was increased to 30 MPa and the sample was kept for 5 min for soaking. For cooling the sample, complete pressure was first released to prevent cracking of ceramic samples and the sample was naturally cooled to room temperature. Thereafter, all samples were heat-treated at 800 °C for 4 h to compensate for oxygen deficiency generated due to prior treatment in the reducing atmosphere in SPS chamber and to eliminate carbon residue. In order to minimize the PbO evaporation, a PbO rich atmosphere was set-up by using double crucibles during the heat treatment. All the samples were polished down to 0.5 mm in thickness and 10 mm in diameter followed by silver pasting on the flat surfaces of the samples for electrodng required for dielectric properties measurement.
2.2. Materials characterization

The bulk density of the samples were measured using Archimedes principle. Morphological features and elemental distribution were analyzed by field emission scanning electron microscope (FE-SEM) (200 FEG Quanta FEI, Netherland). The average grain size of the sintered samples was measured from the photomicrographs of the samples using linear intercept method. The crystalline phase identification of all samples was performed by using x-ray diffractometer (Rigaku Smart Lab, Japan) using Co Kα radiation (λ = 1.7819 Å) at a scanning rate of 0.5° min−1 with a step size of 0.02° in the scanning range of 2θ = 20°–70°. Rietveld refinement was carried out using PDXL software with PDF4 + ICDD database. Dielectric properties were determined by using an impedance analyzer (HIOKI 3532–50 LCR HiTester) in the frequency region of 42 Hz—5 MHz and over the temperature range 30 °C–500 °C.

3. Results and discussion

3.1. SEM analysis

Figure 1(a) shows the scanning electron micrograph of PbZr0.52Ti0.48O3 powder calcined at 900 °C for 4 h. The particles of the powder have largely faceted shape along with some particles having irregular appearance. The average particle size varies from as low as 100 nm to 350 nm. However, there are some larger particles having size ~650 nm also. Energy-dispersive x-ray spectroscopy (EDS) spectrum of the compound along with its elemental composition is shown in figure 1(b) confirming that the composition of the compound has targeted stoichiometry.

3.2. XRD analysis

Figure 2 presents the XRD patterns of PbZr0.52Ti0.48O3 powders calcined at 800, 850, 900 and 950 °C for 4 h. The analysis of the patterns indicates that all the samples show the typical perovskite structure and are indexed as tetragonal crystal system having P4mm space group matching with PDF file no. 04–011–8847. It can be observed that samples calcined at 800 °C and 850 °C have pyrochlore as impurity phase [37] and sample calcined at 950 °C has unreacted ZrO2 phase, which remains due to volatilization of PbO at higher temperature. The calcination temperature 900 °C appears to be the optimum temperature to get pure perovskite phase with no detectable traces of the pyrochlore phase. Tetragonal and rhombohedral MPB structures were expected and identified by the split of XRD peaks {001}, {101}, {002}, {102} and {112} [38]. As the sample calcined at 900 °C shows the relevant phases, the same material was further studied for other investigations.

3.3. Temperature and pressure profiles used in Spark plasma sintering

The samples calcined at 900 °C were sintered by spark plasma sintering method at different temperatures varying between 800 and 950 °C. The same profile was used for sintering the samples. The profile is depicted in figure 3 for SPS-950 sample. The temperature profile is divided into three stages: (i) T1 over which a heating rate of 100 °C min−1 was applied from room temperature to the temperature which is 100 °C below the sintering temperature; (ii) T2 over which a heating rate of 33 °C min−1 was applied up to sintering temperature; (iii) T3 over which soaking was done. At stage T1, higher heating rate was chosen to reduce grain growth leading to higher bulk density of the samples [39]. At stage T2, lower heating rate is applied to allow sufficient time for atomic diffusion (mainly through grain boundary and the initiation of lattice diffusion). The pressure profile is
also divided into three stages namely P1, P2, and P3. At stage P1, the pressure is just sufficient to maintain powder particles in contact which is maintained until the sintering temperature is attained to allow the liquid phase to flow (PbO liquid phase) to aid the sintering process. At P2, the pressure is increased to 30 MPa at the beginning of the sintering stage. The increased pressure tends to closure of the remaining pores in the samples. At P3, the pressure is released just before the cooling process begins so as to prevent cracking of ceramic samples [39].

Table 1 shows the density data of all SPS sintered samples calcined at 900 °C. It can be observed that the sample has been densified even at 800 °C (ρ = 7.14 g cm⁻³). The difference between density data for the samples sintered at different temperatures (between 800 and 950 °C) is negligibly small. However, the phase composition of the samples sintered at different temperatures is different and this has been discussed in section 3.4. The composition change in the phase diagram corresponds to changes in the crystal structure which has a direct influence to the dielectric performance of the compound as the polarization vectors of the different phases are different.

![Figure 2. XRD patterns of PZT powders calcined at different temperatures.](image)

![Figure 3. Spark plasma sintering profile used for sample SPS-950.](image)
3.4. Structural analysis
The crystal structures of Pb(Zr$_x$Ti$_{1-x}$)O$_3$ ceramics at room temperature are found tetragonal for $x \leq 0.52$ and rhombohedral for $x \geq 0.53$. While for $x = 0.52–0.53$, both the tetragonal phase (T phase) and the rhombohedral phase (R phase) coexist corresponding to morphotropic phase boundary (Mishra, Pandey et al) [3, 5]. The coexistence of R and T phases was complemented by the doublet nature of (111) and (200)/(002) reflections on the powder XRD patterns. However, Noheda et al (1999) [15] postulated that the MPB composition also has a monoclinic phase. Thereafter, Ragini et al (2002) [14] stated that earlier established phase composition of tetragonal and rhombohedral is actually tetragonal and monoclinic phases.

In order to get a clear view on phase composition, Rietveld refinement of the XRD patterns was done using PDXL software with PDF4+ ICDD database. The reference CIF files mapped were of tetragonal, rhombohedral and monoclinic symmetry of PZT. In addition, the CIF file of PbO phase was also incorporated to account for any impurity phase present in the sample. The XRD patterns along with difference plots are shown in figure 4. In addition, the nature of variation of diffraction peaks (110), (111), (200) with sintering temperature is shown in figure 5. The refinement data clearly reveals that the sample SPS-800 has a tetragonal structure (P4mm).

Similarly, for SPS-850, the tetragonal symmetry (P4mm) with pyrochlore phase shows good fit ($\chi^2 = 3.59$) to the experimental data. The tetragonal nature of both SPS-800 and SPS-850 samples can also be inferred by visualizing the singlet nature of (111) and doublet nature of (200) as depicted in figure 5. It is interesting to note that, although the calcined powder was of desired stoichiometry, the composition of the sample sintered in SPS differs from that of calcined powder signifying the effect of sintering temperature on PZT composition.

| Calcination temp. (°C) | Sintering temp. (°C) | Annealing temp. (°C) | Density (g cm$^{-3}$) | Relative density (%) |
|------------------------|----------------------|----------------------|-----------------------|----------------------|
| 900                    | 800                  | 800                  | 7.14 ($\pm$0.1)       | 99.17                |
| 900                    | 850                  | 800                  | 7.15 ($\pm$0.2)       | 99.30                |
| 900                    | 900                  | 800                  | 7.17 ($\pm$0.1)       | 99.58                |
| 900                    | 950                  | 800                  | 7.16 ($\pm$0.1)       | 99.44                |

Figure 4. Observed, calculated and difference profiles generated in Rietveld refinement.
Rietveld refinement of SPS 900 sample was carried out using tetragonal (P4mm space group) but the profile fitting was not found to be proper on the basis of tetragonal symmetry alone. The coexistence of tetragonal and monoclinic phases can be clearly seen for the sample sintered at 900°C, through peak splitting observed with (111) and (200) peaks. (200) peak clearly splits into three for SPS 900 sample which is a characteristic of pseudo-tetragonal monoclinic phase with space group Cm\[14\]. After mapping both tetragonal (P4mm) and monoclinic (Cm) symmetry, the fit improves drastically with the corresponding $\chi^2 = 3.19$. This coexistence of the phases has also been reported by Noheda et al\[12\] and Ragini et al\[14\]. Noheda et al\[12\] mentioned that the monoclinic structure of PbZr\(_{0.52}\)Ti\(_{0.48}\)O\(_3\) is derived from the tetragonal structure by shifts of the Pb and Zr/Ti atoms along the tetragonal [110] axis and suggested that the local monoclinic structure forms a bridge between the tetragonal and rhombohedral phases. Since the monoclinic cell permits rotation of the polar axis along its symmetry plane, a high dielectric response is expected from the material/chemical compound possessing the monoclinic phase and thereby from SPS-900 sample.

For SPS-950, the split (200) peaks tend to merge and become almost a singlet with a full width at half maximum (FWHM) greater than that of (200) peaks of other samples. Further, the (110) and (111) peaks are still doublets which suggest pseudorhombohedral tetragonal phase as found by Ragini et al\[14\]. Accordingly, Rietveld refinement was carried out by considering the coexistence of tetragonal (P4mm) and rhombohedral (R3c) phases. The fit between the observed and calculated profiles is satisfactory with $\chi^2 = 3.39$. Thus, the `morphotropic phase' transitions from tetragonal phase to the mixed phases of tetragonal (P4mm) with monoclinic (Cm) at 900°C and tetragonal with rhombohedral (R3c) at 950°C with increase in sintering temperature from 800 to 950°C. The refined parameters of crystal structures for each sample are given in table 2.

### 3.5. Microstructural analysis of spark plasma sintered samples

SEM micrographs of the spark plasma sintered samples, which were annealed at 800°C for 4 h for compensation of oxygen deficiency that occurred on sintering, are illustrated in figure 6. The grain size distribution of each sample is depicted in figure 7. It can be seen that sintering leads to very small grained (15–40 nm) microstructure and the grains are smaller than that of conventionally sintered samples for which the grain size range is 1–3 μm [40]. The average grain size of the samples increases from 15.47 ± 0.35 nm to 19.41 ± 0.41 nm with the increase in sintering temperature for SPS-800, SPS-850 and SPS-900 implying that the grain size increase with increase in sintering temperature is insignificant. However, the average grain size of SPS-950 (37.26 ± 0.42 nm) is almost the twice of that of the other three samples. The macroscopic driving force operative during sintering of powders is the reduction of excess energy associated with surfaces of the powder particles. This can happen by (a) reduction of total surface area by increase in the average size of particles, leading to coarsening and/or (b) the elimination of solid interfaces and the creation of grain boundary area, followed by grain growth, causing

![Figure 5. Room temperature XRD profiles of the (110), (111) and (200) peaks of SPS-800, SPS-850, SPS-900 and SPS-950.](image-url)
Table 2. Refined structural parameters of all spark plasma sintered samples.

| Sintering temperature | 800 °C | 850 °C | 900 °C | 950 °C |
|-----------------------|--------|--------|--------|--------|
| Space group           | P4mm   | P4mm   | P4mm   | R3c    |
| a (Å)                 | 4.000054 | 4.019(2) | 3.9617(14) | 5.723(2) | 4.0326(10) | 5.757(7) |
| b (Å)                 | 4.000054 | 4.019(2) | 3.9617(14) | 5.6935(16) | 4.0326(10) | 5.757(7) |
| c (Å)                 | 4.090632 | 4.104(3) | 4.139(2)   | 4.1061(8)  | 4.1347(12) | 14.12(3) |
| β (deg.)              | 90.0   | 90.0   | 90.0   | 90.0   | 90.0   |
| Pb(x/y/z)             | 0/0/0 | 0.5/0.5/0.5224 | 0.5/0.5/0.473 | 0.5/0.5/0.51 | 0/0/0.031(15) |
| Zr(x/y/z)             | 0.5/0.5/0.5281 | 0/0/0.00(18) | 0/0/0.00(2) | 0.52(2)/0.04(3) | 0.5/0.5/0.571(6) | 0/0/0.031(15) |
| Ti(x/y/z)             | 0.5/0.5/0.5281 | 0/0/0.00(18) | 0/0/0.00(2) | 0.52(2)/0.04(3) | 0.5/0.5/0.571(6) | 0/0/0.031(15) |
| O1(x/y/z)             | 0.5/0/0.613 | 0.5/0/0.1(17) | 0.5/0/0.02 | 0.49(17)/0.04(8) | 0.5/0/0.51(5) | 0.22(2)/0.32(17)/0.086(8) |
| O2(x/y/z)             | 0.5/0.5/0.134 | 0/0/0.66(11) | 0/0/0.35(4) | 0.33(3)/0.02(2) | 0.51(12) | 0.06(3) |
| Phase fraction        | 100    | 100    | 69(5)  | 31(5)  | 58.8(12) | 41.2(11) |
| Rwp                   | 5.1    | 5.4    | 5.43   | 5.92   |
| χ²                    | 3.21   | 3.59   | 3.19   | 3.39   |

Figure 6. Microstructures of PbZr0.52Ti0.48O3 samples spark plasma sintered at different temperatures (a) 800 °C, (b) 850 °C, (c) 900 °C, (d) 950 °C.

densification. These two mechanisms are usually in competition. It may be considered that atomic processes that lead to densification reaches saturation up to the temperature of 900 °C (as observed in the density values in table 1) and grain coarsening is largely effective above 900 °C which may explain the surge in grain size for SPS-950 sample [41].

Figure 8 illustrates the EDS spectra of different samples obtained following area scan method. The results indicate that the atomic ratios of Pb/Zr:Ti/O for SPS-800 is 97:44:56:290 and for SPS-850 is 95:46:54:280 which is approximately consistent with the composition of PZT that exhibits a tetragonal perovskite structure. The atomic ratio for the sample SPS-900 and SPS-950 are 96:53:47:280 and 95:57:43:269 respectively. The elemental
composition of SPS-900 and SPS-950 are closest to the desired MPB composition of (100:52:48:300). It is noteworthy to mention that the EDS analysis is in agreement with the findings of Rietveld refinement pertaining to the coexistence of phases as discussed in section 3.4. As a result, higher dielectric performance is expected for SPS-900 and SPS-950 due to increased number of available polarization directions. The peaks in the EDS spectrum at about 0.1 keV corresponding to oxygen element is not labelled in the auto-generated EDS spectrum.

3.6. Dielectric measurements

Figures 9(a) and (b) represent the frequency-dependent behaviour of dielectric constant and dielectric loss tangent ($\tan \delta$) of all four spark plasma sintered ceramic samples in the frequency range 42 Hz to 5 MHz. Figure 9(a) reveals that the plateau in the dielectric spectra extends from 42 Hz to 100 kHz. The plateau region is followed by dielectric dispersion at the frequency range from 100 kHz to 1 MHz. Thereafter, dielectric constant reaches to static values at frequencies higher than 1 MHz. Such dispersion behaviour can be explained by Maxwell-Wagner type interfacial polarization involving Koop’s theory [42, 43] for ferroelectric materials. Different types of polarization namely ionic, electronic, orientation, and space charge may be induced by interfacial dislocations, grain boundary charge defect, oxygen vacancies in ABO$_3$ type of perovskite structure, etc. Dielectric constant falls drastically at higher frequencies since only ionic and electronic polarization act and the charge carriers cannot follow the applied electric field [44]. The dielectric constant of SPS-900 sample is the highest among the different samples studied, which is in agreement with the phase analysis by Rietveld refinement results. In figure 9(b), dielectric loss is nearly constant up to 10 kHz. The relaxation peak is observed at frequencies below 1 MHz for SPS-800 and SPS-850 specimens. It can be clearly observed that the relaxation frequency shifts to higher value for samples SPS-900 and SPS-950 [45–47].

The dependence of dielectric constant on temperature for PZT has been examined over the temperature range from room temperature to 500°C. Figure 10 illustrates the variation of dielectric constant with the temperature observed at a frequency of 100 kHz and confirms the ferroelectric nature of PZT samples. The dielectric constant increases with increase in temperature and peaks at a particular temperature known as Curie temperature after which it decreases due to the transition from ferroelectric phase to paraelectric phase. The
Curie temperature is found to be 320 °C for SPS-950 and 335 °C for other samples. For comparison, Geetika et al obtained a dielectric constant of ∼6000 at 100 kHz for conventionally sintered PbZr0.5Ti0.5O3 at the transition temperature [48]. It is noteworthy to mention that both SPS-900 and SPS-950 show higher dielectric constant at

Figure 8. Energy-dispersive spectrometry analysis of various grains.

Figure 9. Variation of (a) dielectric constant, (b) dielectric loss tangent with frequency for different samples.
the Curie temperature relative to the other two samples. This is in close agreement with the coexistence of phases confirmed through Rietveld refinement.

Dielectric performance of SPS-900 and SPS-950 are significantly enhanced relative to other samples. The variation in grain size of spark plasma sintered samples other than SPS-950 depicted in figure 7 is minimum. In addition, all samples have been successfully densified by spark plasma sintering as shown in table 1. Considering the above points, the dielectric properties depends considerably on the presence of phase constituents. Rietveld refinement reveals the existence of monoclinic phase in SPS-900 and rhombohedral phase in SPS-950 samples, which lay emphasis on importance of sintering temperature on the phase composition. Coexistence of phases has been known to induce ultra-high dielectric response due to an increase in the availability of polarization domains [2]. In addition, monoclinic phase permits rotation along the symmetry plane [16] whereas polarization vector in tetragonal phase and rhombohedral phase lies along fixed [001] and [111]. Therefore, similar enhancement is observed in SPS-900, which shows the highest dielectric performance due to the presence of monoclinic phase. It is essential to mention that the increased grain size of SPS-950 may also be a contributing factor for its enhanced dielectric performance [49].

4. Conclusion

The bulk nanocrystalline PbZr0.52Ti0.48O3 synthesized by spark plasma sintering method has been investigated thoroughly by FESEM, XRD and EDS analyses. It is suggested that optimum calcination temperature of 900 °C is needed for complete single perovskite phase formation above which PbO volatilization leads to the formation of impure phases. The fine-grained ceramics obtained by spark plasma sintering at four different temperatures 800, 850, 900 and 950 °C have grain sizes in the range of 15–37 nm for which increase in grain size was observed with increase in sintering temperature. It is proposed that the compositional fluctuation occurred due to sintering at a faster rate has a significant effect on dielectric performance. Since the grain size variation is not very significant for the samples sintered at different temperatures, the factor affecting dielectric performance is perhaps the stoichiometry/composition. Rietveld refinement reveals that SPS-900 having a mixture of both monoclinic and tetragonal phases shows highest dielectric performance due to the higher number of available polarization directions. The phase transformation from tetragonal to cubic state occurs at a Curie temperature of 320 °C. Rietveld refinement and EDS analysis results are in good agreement suggesting the formation of MPB phase in SPS-900 and SPS-950 in which the former shows the highest dielectric response.

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References

[1] Jaffe B, Cook W R and Jaffe H 1971 Piezoelectric Ceramics (London: Academic) (https://doi.org/10.1016/B978-0-12-379550-2.50011-9)

[2] Isupov V A 1968 Properties of Pb(Ti, Zr)xO3 piezoelectric ceramics and nature of their orientational dielectric polarization Sov. Phys. Solid State, U.S.S.R. 10 4985

[3] Mishra S K, Singh A P and Pandey D 1997 Thermodynamic nature of phase transitions in Pb(Zr,Ti1−x)O3 ceramics near the morphotropic phase boundary I. Structural studies, Philos. Mag. B. 76 213–26

[4] Solanki R S, Mishra S K, Kuroiwa Y, Moriyoshi C and Pandey D 2013 Evidence for a tricritical point coinciding with the triple point in (Pb0.34Sr0.66)0.75(Zr0.85Ti0.15)O3: a combined synchrotron x-ray diffraction, dielectric, and Landau theory study Phys. Rev. B 88 184109

[5] Mishra S K, Pandey D and Singh A P 1996 Effect of phase coexistence at morphotropic phase boundary on the properties of Pb(Zr,Ti1−x)O3 ceramics Appl. Phys. Lett. 69 1707–9

[6] Singh A K, Mishra S K, Ragini D, Pandey S, Yoon S B and Shin N 2008 Origin of high piezoelectric response of Pb(Zr,Ti1−x)O3 at the morphotropic phase boundary: Role of elastic instability Appl. Phys. Lett. 92 022910

[7] Cordero F, Craciun F and Galassi C 2007 Low-temperature phase transformations of PbZr1−xTiO3 in the morphotropic phase-boundary region Phys. Rev. Lett. 98 255701

[8] Fu H and Cohen R E 2000 Polarization rotation mechanism for ultra-high electromechanical response in single-crystal piezoelectrics Nature 403 281–3

[9] Bellaiche L, Garcia A and Vanderbilt D 2000 Finite-Temperature Properties of Pb(Zr1−x)TiO3 Alloys from First Principles Phys. Rev. Lett. 84 5427–30

[10] Bellaiche L, Garcia A and Vanderbilt D 2001 Electric-field induced polarization paths in Pb(Zr1−x)TiO3 alloys Phys. Rev. B 64 086103

[11] Vanderbilt D and Cohen H M 2001 Monoclinic and triclinic phases in higher-order Devonshire theory Phys. Rev. B 63 094108

[12] Guo R, Cross I E, Park S-E, Noheda B, Cox D E and Shirane G 2000 Origin of the High Piezoelectric Response in PbZr1−xTiO3 Phys. Rev. Lett. 84 5423–6

[13] Park S-E and Shrouf T R 1997 Ultra-high strain and piezoelectric behavior in relaxed ferroelectric single crystals J. Appl. Phys. 82 1004–11

[14] Ragini R, Ranjan S K and Mishra D 2002 Pandey, Room temperature structure of Pb(Zr1−x)TiO3 near the morphotropic phase boundary: a rietveld study J. Appl. Phys. 92 3236–74

[15] Noheda B, Cox D E, Shirane G, Gonzalez J A, Cross I E and Park S-E 1999 A monoclinic ferroelectric phase in the Pb(Zr1−x)TiO3 solid solution Appl. Phys. Lett. 74 2059–61

[16] Noheda B, Gonzalez J A, Cross I E, Guo R, Park S-E, Cox D E and Shirane G 2000 Tetragonal-to-moniclinic phase transition in a ferroelectric perovskite: The structure of PbZr0.52Ti0.48O3 Phys. Rev. B 61 8687–95

[17] Singh A K and Pandey D 2003 Evidence for M4 and M3 phases in the morphotropic phase boundary region of {1−x}[Pb(Mg1/3Nb2/3)O3−xPbTiO3] A Rietveld study Phys. Rev. B 67 064102

[18] Ryu J, Choi J-I and Kim H-E 2001 Effect of heating rate on the sintering behavior and the piezoelectric properties of lead zirconate titanate ceramics J. Am. Ceram. Soc. 84 892–4

[19] Neumeister P, Ellinger S, Gebhardt S, Schönecker A and Flossel M 2014 Effect of mechanical constraints in thin ceramic LTCC/PZT multilayers on the polarization behavior of the embedded PZT Int. J. Appl. Ceram. Technol. 11 422–30

[20] Zhang W and Eltel R E 2013 Sintering behavior, properties, and applications of Co-Fired piezoelectric/low temperature co-fired ceramic (PZT-SKN/LTCC) multilayer ceramics Int. J. Appl. Ceram. Technol. 10 354–64

[21] Ueda I 1972 Effects of additives on piezoelectric and related properties of PbTiO3 ceramics Jpn. J. Appl. Phys. 11 450–52

[22] Wu Y J, Uekawa N, Kakegawa K and Sasaki Y 2002 Compositional fluctuation and dielectric properties of Pb(Zr0.52Ti0.48)O3 ceramics prepared by spark plasma sintering Mater. Lett. 57 771–5

[23] Chen C, Liang K, Zhou Z, Zhang W and Dong X 2018 Enhanced bipolar fatigue resistance in PMN–PZT ceramics prepared by spark plasma sintering Ceram. Int. 44 3563–70

[24] Mesquita A, Godart C, Michalowicz A and Mastelaro V R 2012 Pb50Ba500Zr0.6Ti0.4O3 nanostructured ceramisferic ceramics prepared by spark plasma sintering Ferroelectrics 429 69–74

[25] Han B, Zhao C, Zhu Z X, Chen X, Han Y, Hu D, Zhang M, Thong H C and Wang K 2017 Temperature-insensitive piezoelectric performance in PbZr0.52Ti0.48Sn0.02Nb0.06O3 ceramics prepared by spark plasma sintering ACS Appl. Mater. Interfaces 9 34078–84

[26] Ciomaga C E, Paduraru L, Curecheriu I P, Lupu N, Liseckii I, Deluca M, Tascu S, Galassi C and Moseriu L 2014 Using multi-walled carbon nanotubes in spark plasma sintered Pb(Zr0.52Ti0.48)O3 ceramics for tailoring dielectric and tunability properties J. Appl. Phys. 116 09–10

[27] Kakegawa K, Wada M, Wu Y J and Uekawa N 2005 Change in compositional fluctuation in Pb(Zr0.52Ti0.48)O3 soluid solution during spark plasma sintering Advances in Applied Ceramics 104 55–88

[28] Wang D, Guo H, Morandi C S, Randall C A and Trolle-R-Mckinstry S 2018 Cold sintering and electrical characterization of lead zirconate titanate piezoelectric ceramics APL Mater. 6 016101

[29] Liu K, Wang W, Liu Q and Song L 2019 Y. wen Guo, F. Ye, Phootostriiction properties of PLZT (4/52/48) ceramics sintered by SPS Ceram. Int. 45 2097–102

[30] Zheng M, Hou Y, Ai Z and Zhu M 2017 Nanocrystalline build-up, relaxor behavior, and polarization characteristics in PZT-PNZN quaternary ferroelectrics J. Am. Ceram. Soc. 100 3033–41

[31] Kakegawa K, Uekawa N, Wu Y J and Sasaki Y 2005 Change in the compositional distribution in perovskite solid solutions during the sintering by SPS Mater. Sci. Eng. B 99 11–4

[32] Mulinepalii V R and Leng F 2019 Dielectric and ferroelectric studies on high dense Pb(Zr0.52Ti0.48)O3 nanocrystalline ceramics by high energy ball milling and spark plasma sintering Ceramics. 2 13–24
[33] Zhou L, Rixecker G, Aldinger F, Zuo R and Zhao Z 2006 Electric fatigue in ferroelectric lead zirconate stannate titanate ceramics prepared by spark plasma sintering J. Am. Ceram. Soc. 89 3868–70

[34] Hungria T, Amorín H, Galy J, Ricote J, Algueró M and Castro A 2008 Nanostructured ceramics of 0.92PbZn1/3Nb2/3O3−0.08PbTiO3 processed by SPS of nanocrystalline powders obtained by mechanosynthesis Nanotechnology 19 155609

[35] Chen K-P, Li C, Lei C, Zhang X and Huang Y 2002 Preparation and electric properties of dense Lead Nickel Niobate–Lead Titanate (Pb(Ni1/3Nb2/3)O3−PbTiO3) ceramics by spark plasma sintering J. Mater. Sci. Lett. 21 1785–7

[36] Peng P, Hu Y-Y, Liu Y, Chen S, Shi J, Xiong R and Zhang Y 2015 Magneto-electric effect of CoFe2O4/Pb(Zr,Ti)O3 composite ceramics sintered via spark plasma sintering technology Ceram. Int. 41 6676–82

[37] Vittayakorn N, Rujijanagul G, Tunkasiri T, Tan X and Cann D P 2003 Perovskite phase formation and ferroelectric properties of the lead nickel niobate–lead zinc niobate–lead zirconate titanate ternary system J. Mater. Res. 18 2882–9

[38] Joshi S and Acharya S 2016 Infl uences of liquid-phase sintering on structure, grain growth, and dielectric behavior of PbZr0.52Ti 0.48O3 ceramics Int. J. Appl. Ceram. Technol. 13 753–62

[39] Stanciu L A, Kodash V Y and Groza J R 2001 Effects of heating rate on densification and grain growth during field-assisted sintering of α-Al2O3 and MoSi2 powders Metall. Mater. Trans. A 32 2633–8

[40] Cao W and Randall C A 1996 Grain size and domain size relations in bulk ceramic ferroelectric materials J. Phys. Chem. Solids 57 1499–505

[41] Barsoum M W 2002 Fundamentals of Ceramics (Boca Raton, FL, USA: CRC Press) (https://doi.org/10.1201/9781498708166)

[42] Wagner K W 1913 Zur Theorie der unvollkommenen Dielektrika Ann. Phys. 345 817–55

[43] Koops C G 1951 On the dispersion of resistivity and dielectric constant of some semiconductors at audiofrequencies Phys. Rev. 83 121–4

[44] Rani A, Kohle J and Gopalan P 2015 Phase formation, microstructure, electrical and magnetic properties of Mn substituted barium titanate Ceram. Int. 41 14057–63

[45] Rawat M and Yadav K L 2014 Study of structural, electrical, magnetic and optical properties of 0.65BaTiO3−0.35Bi0.5Na0.5TiO3–BiFeO3 multiferroic composite J. Alloys Compd. 597 188–99

[46] Yu Z and Ang C 2002 Maxwell–Wagner polarization in ceramic composites BaTiO3−(Ni0.5Zn0.5)Fe2O4 J. Appl. Phys. 91 794–7

[47] Ahmed M A, Bishay S T and Abdelatif G 2001 Effect of ytterbium on the electrical properties of Li–Co ferrite J. Phys. Chem. Solids 62 1039–46

[48] Srivastava G, Goswami A and Umarji A M 2013 Temperature dependent structural and dielectric investigations of PbZr0.55Tl0.45O3 solid solution at the morphotropic phase boundary Ceram. Int. 39 1977–83

[49] Kamel T M and de With G 2008 Grain size effect on the poling of soft Pb(Zr,Ti)O3 ferroelectric ceramics J. Eur. Ceram. Soc. 28 851–61