Materials Research Express

PAPER

Synthesis of Pb(Zr$_{0.35-x}$Mn$_x$Ti$_{0.65}$)O$_3$, $x = 0.00, 0.02, 0.06, 0.10$ ceramics and their structural, dielectric characteristics

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Keywords: Ceramic, XRD, SEM, Diffusivity

Abstract

The samples of stoichiometry Pb(Zr$_{0.35-x}$Mn$_x$Ti$_{0.65}$)O$_3$, $x = 0.00, 0.02, 0.06, 0.10$ (PZMT) were synthesized by solid state reaction route. For the first time, 35/65 lead zirconate titanate ceramics were modified by manganese (Mn) by replacing zirconium. X-ray diffraction (XRD) study has confirmed the formation of tetragonal phase in samples and no structural change has been observed due to Mn doping. Results of scanning electron microscopy (SEM) showed polycrystalline nature through shape, size and grain distribution in microstructures of all samples. At room temperature, the samples have shown identical nature in variation of dielectric constant ($\varepsilon_r$) and tangent loss ($\tan\delta$) with frequency. At 50 kHz frequency, the value of maximum dielectric constant ($\varepsilon_{\max}$) has been changed from 5440 to 12 562 due to Mn. With increase in doping amount of Mn, the values of Curie temperature ($T_c$) have been decreased from 435 to 373 °C. $\tan\delta$ of samples is decreased with increase in the dopant concentration. The diffusivity of PZT has increased with 2% of Mn doping. But further increase in the Mn concentration has decreased the diffusiveness of the samples.

1. Introduction

Due to good piezoelectric properties, lead zirconate titanate (PZT) is one of the most widely investigated material for sensors and actuators [1, 2]. PZT also possess high dielectric, pyroelectric and electro-optic properties. So it is being used extensively in applications such as oscillators, transducers, and Ferroelectric Random Access Memories (FRAM) and charge storage devices [3]. The ABO$_3$ type perovskite structure of PZT contain lead (Pb) and Zirconium/Titanium (Zr/Ti) atoms residing at A and B sites respectively [4]. Doping of suitable elements at A and/or B sites can strongly affect the physical properties of PZT [5–7]. And the structural properties can be altered by varying Zr/Ti ratio [8]. So modification of PZT has become wide research area in ferroelectrics. The structure of PZT is cubic above $T_c$. But below $T_n$ the structure can be either tetragonal or rhombohedral or mixed phase based on the ratio of Zr/Ti [9, 10]. The Zr/Ti ratio of PZT can be categorized into morphotropic phase boundary (MPB), above MPB (65/35) and below MPB (35/65). Around 52/48 ratio is considered as the MPB of PZT and this composition of PZT shows the optimistic physical properties [11–16]. So PZT with MPB composition is meant for its use in non-volatile memories, piezoelectric actuators, sensors, micro-electro mechanical systems, pyroelectric detector, transducers and photoelectric devices [10, 17–19]. Above MPB, most widely investigated PZT material is of 65/35 ratio [20–28]. Because PZT of this composition possesses high optical transparency, and electro optic effects [29]. But below MPB, very less studies have been reported [30–32]. To alter the physical properties, Mn has been used as a modifier for both (bulk and thin film) forms of PZT [12, 33–36]. For memory and pyroelectric applications, Mn has been doped in PZT thin films and results have indicated improved ferroelectric and pyroelectric properties [33]. Mn modified PZT has shown change in hysteresis properties, $\varepsilon_r$ and $\tan\delta$ [34]. Enhanced fatigue and retention characteristics were reported [35]. It is also observed that dielectric and ferroelectric properties of PZT thin films were deteriorated due to the doping of...
1% of Mn concentration. But the same properties have been improved with the doping of 2% of Mn concentration [36]. Therefore Mn doping can alter the physical properties of PZT.

35/65 PZT material has been studied mostly in thin film form [37–42]. Optical properties of 35/65 on PZT thin film have been investigated for solar cell applications [37]. Also the films fabricated by metal organic chemical vapor deposition (MOCVD) has exhibited remanent polarization of 30 μC cm\(^{-2}\) and coercive field of 80 kV cm\(^{-1}\) [38]. 35/65 PZT has been synthesized in the form of smooth and striated films. The optical losses of smooth and striated PZT films are 1.43 dBcm\(^{-1}\) and 2.91 dB cm\(^{-1}\) respectively [39]. This composition of PZT film has also been prepared by sol-gel method. This film has reportedly shown lower \(\varepsilon_r\) and loss compared to 53/47 PZT film [32]. Also 35/65 PZT has been reported as a suitable material ferroelectric memories due to excellent fatigue properties [40]. The films grown by pulsed MOCVD has shown very large value of remanent polarization (30 μC cm\(^{-2}\)) and low coercive field (55 kV cm\(^{-1}\)) [41].

Solid state synthesis is one of the systematic approach to prepare the samples of ceramics and the PZT of various compositions. Humongous value of transduction coefficient was shown by 53/47 PZT ceramic synthesized through this method [42]. Lead antimony niobate-lead barium zirconate titanate (PSN-PBTZ) ceramics, prepared by solid state reaction, have shown improved piezoelectric coefficient \((d_{33})\) and \(T_c\) values [43]. Also the 0.9625\((K_{0.4}O_3,x)_{0.5}O_3\) and \(T_c\) values have been improved piezoelectric properties, large remanent polarization and low coercive field [44]. Similarly a high \(T_c\) value i.e. 546°C has been reported for BiFeO3 - PbTiO3 - BaTiO3 ceramic [45]. Therefore solid state synthesis is a robust technique to prepare the samples of PZT.

Since the Zr/Ti ratio of 35/65 has been studied very less as compared to other two major compositions especially in bulk form, we have prepared the polycrystalline samples of Mn modified 35/65 PZT through solid state reaction method. For the first time, Mn has been doped to 35/65 PZT and the physical properties have been investigated. Therefore in this paper, we report the effect of Mn doping on structure, microstructure and dielectric properties of 35/65. Also presented is the degree of disordering in samples, through diffusivity studies. A systematic investigation on the electrical properties of Pb(Zr\(_{0.35-x}\)Mn\(_{x}\)Ti\(_{0.65}\))O\(_3\), \(x = 0.00, 0.02, 0.06, 0.10\) (PZMT) samples will be presented elsewhere.

2. Experimental section

The high purity chemicals such as lead oxide (99.9%, M/S. LobaChemie Pvt. Ltd., India), zirconium dioxide (99.9%, M/S. Sarabhai Chemicals, India), titanium dioxide (99.9%, M/S. LobaChemie Pvt. Ltd., India), and manganese dioxide (99.9%, M/S. LobaChemie Pvt. Ltd., India) have been used to prepare the samples. The samples of PZMT (Pb(\((\text{Zr}_{0.45-x}\text{Mn}_{x}\text{Ti}_{0.65})\text{O}_3\), \(x = 0.00, 0.02, 0.06, 0.10\)) have been prepared by solid state route. After weighing, the chemicals were mixed in an agate mortar pestle in dry atmosphere for one hour and in acetone for another one hour. And then the mixtures were calcined multiple times with final calcination temperature being 950°C for 4 hours in air atmosphere. In the present study, the x-ray diffraction (XRD) patterns of all compounds have been recorded at room temperature using x-ray powder diffractometer (Rigaku Miniflex, Japan) with wavelength \(\lambda = 1.5405 \text{Å (Cu Kα radiation)}\) in a wide range of Bragg angles, \(2\theta(20° \leq 2\theta \leq 80°)\) at a scanning rate of 3°/min. The operating voltage and current of the x-ray tube are 30 kV and 15 mA respectively. Polyvinyl alcohol (PVA) was added as a binder to the powders. Then the cylindrical pellets were made by cold pressing using a hydraulic press at a pressure of \(4 \times 10^6 \text{N m}^{-2}\). The pellets have approximately 10 mm diameter and 1-2 mm of thickness. Then the pellets were sintered at a high temperature (1100°C for 2 hours) in alumina crucibles. During sintering, PVA was burnt out. The sintered pellets were polished using an air drying silver paste and fired at 150°C for 4 hours. Then the pellets were cooled to room temperature for taking measurements.

2.1. SEM and electrical characterization

After making the pellets flat and parallel, The micrographs at different magnifications were taken using JEOL JSM-5800 and LEICA S440i scanning electron microscopy at 20 kV. HIOKI 3532 LCR Hi-TESTER with an ac signal of 1.3 volts, sample holder and heating set up were used for the characterization of materials. At various temperatures (room temperature – 500°C), dielectric characteristics were determined as a function frequency (1 kHz–1 MHz). Temperature was measured by chromel-alumel thermocouple and digital multimeter. Measurements were recorded within a small temperature interval.

3. Results and discussion

This section provide an insight into the structural, microstructural and dielectric studies of the Mn modified 35/65 PZT electroceramics.
3.1. Structure and microstructure analysis

XRD patterns of Pb(Zr_{0.35−x}Mn_{x}Ti_{0.65})O_{3}, x = 0.00, 0.02, 0.06, 0.10 (PZMT) samples are given in figure 1.

The patterns of all the samples have shown peaks indicating the perovskite structure. The peaks were observed at 2\theta of 21.868 (1 0 0), 31.138 (1 1 0), 38.268 (1 1 1), 44.528 (2 0 0), 50.038 (2 1 0) and 55.418 (2 1 1). (1 0 0), (1 1 0), (1 1 1), (2 0 0), (2 1 0), (2 1 1), (2 2 0), are the reflections that get indexed as per the tetragonal phase of perovskite PZT [32, 38, 46–48]. The appearance of those peaks have confirmed the polycrystalline nature of samples. No pyrochlore phase was observed in the samples. The splitting of the peaks at 2\theta of 21.7°, 31.2°, 44.8° and 55.5° clearly indicated the formation of tetragonal phase in the material system. The observed split peaks are naturally the result of tetragonal crystallographic structures of the compounds. For tetragonal structure, (1 0 0) and (0 0 1) is the splitting of the peaks at 2\theta near 22°; (1 1 0) and (1 1 1) 31.5°; (2 0 0) and (0 0 2) 44.5°; (2 1 0) and (2 0 2) 50°; (2 1 1) 56° [49]. No big changes were found in structures of Pb(Zr_{0.35−x}Mn_{x}Ti_{0.65})O_{3}, x = 0.00, 0.02, 0.06, 0.10 samples. But some minor peaks have been disappeared with increase in the concentration of Mn and some reduction in splitting of the peaks can be seen. A clear intense patterns with distinguishable peaks of diffraction were observed in XRD showing crystallization and uniformity of the samples. Table 1 presents the values of crystallite size (P) of Pb(Zr_{0.35−x}Mn_{x}Ti_{0.65})O_{3}, x = 0.00, 0.02, 0.06, 0.10.

Scherer’s formula i.e., $P = \frac{0.489\lambda}{\beta_2 \cos \theta}$ has been used to find P of the samples. The ICDD cards numbered 01-070-4263 shows rhombohedral; 01-070-4265 shows rhombohedral, and 01-070-4262 shows tetragonal phase of PZT. Figure 2 provides SEM micrographs of Mn modified PZT samples.

Dense and undifferentiated distribution of grains can be seen from the surfaces of all compounds. Our samples are said to possess the polycrystalline characteristics because of the grains distribution, size and shape in SEM micrographs. But the grains of 53/47 PZT ceramics, doped with Lanthanum and Niobium, have shown some pores in their micrographs and no uniform distribution of grains was observed [42]. The size of the grains (G) of all compounds is given in table 1.

| x    | P(Å) (XRD) | G(μm) (SEM) |
|------|------------|-------------|
| 0.00 | 292        | 3.3         |
| 0.02 | 239        | 1.6         |
| 0.06 | 273        | 1.3         |
| 0.10 | 227        | 1.5         |

3.2. Dielectric studies

3.2.1. Study of $\epsilon_r$ and $\tan \delta$ with frequency at room temperature

In figure 3, $\epsilon_r$ and $\tan \delta$ variation of PZMT at room temperature is shown. A material is said to possess polar dielectric behavior if $\epsilon_r$ and $\tan \delta$ decreases with increase in frequency [50]. Irrespective of composition of

![Figure 1. Comparison of x-ray diffraction pattern of calcined powders of Pb(Zr_{0.35−x}Mn_{x}Ti_{0.65})O_{3}, x = 0.00, 0.02, 0.06, 0.10.)](image-url)
Figure 2. SEM micrographs of Pb\((Zr_{0.35-x}Mn_xTi_{0.65})O_3, x = 0.00, 0.02, 0.06, 0.10\) ceramics.

Figure 3. Variation of \(\varepsilon\) and \(\tan\delta\) of Pb\((Zr_{0.35-x}Mn_xTi_{0.65})O_3, x = 0.00, 0.02, 0.06, 0.10\) ceramics with frequency at room temperature.
specimens, PZMT samples are also said to possess polar dielectric behavior. Because at room temperature, the value of $\varepsilon_r$ and $\tan\delta$ of samples have been decreased with increase in frequency. At this ratio of Zr/Ti of 35/65, a step wise decrease was observed between 1—10 kHz for both $\varepsilon_r$ and $\tan\delta$, for all the samples. For a given frequency, $\varepsilon_r$ shows an increasing trend with increase in Mn concentration, and $\tan\delta$ also shows a similar trend with maximum at $x = 0.06$ and then shows a decreasing nature. It was also observed that, both $\varepsilon_r$ and $\tan\delta$ shows an identical nature of variation with frequency, at room temperature. There is increase in the value of $\tan\delta$ with increase in concentration of Mn at room temperature.

3.2.2. Variation of dielectric constant with temperature

In figure 4, the $\varepsilon_r$ variation of PZMT with temperature is shown at selected frequencies. $T_c$ is known as the phase transition temperature of ferroelectric materials. It is a definite temperature at which a ferroelectric material transitions from ferroelectric phase to non-ferroelectric (paraelectric) phase [51]. From figure 4, we can see that the value of $T_c$ decreases with increasing Mn concentration, from 435 to 373 °C. Our $T_c$ is significantly a higher value compared to $T_c$ values of thin films such as 50/50 PZT ($T_c = 392.6$ °C), 45/55 PZT ($T_c = 405.5$ °C), and 40/60 PZT ($T_c = 392.6$ °C)[52]. For all the samples, the value of $\varepsilon_r$ has increased gradually on increasing temperature to its maximum value ($\varepsilon_{max}$), and then decreased [51]. On further increase of temperature, the $\varepsilon_r$ was decreased for all the compositions. Within a sample, almost all the samples show single (very less deviation) $T_c$. The normal dielectric behavior of a ferroelectric was confirmed when it was found that within a sample $\varepsilon_{max}$ decreases with increase in frequency. The value of $\varepsilon_{max}$ of Mn modified samples is more than that of pure PZT, and shows an increasing trend with increasing Mn concentration, from 5440 to 12 562 for 1 kHz. Likewise, PZT of both 52/48 and 65/35 also shown increase in dielectric constant due to Mn modification [12, 53] but the PZT thin films deposited on Ti-Pt alloys have shown value of 1224.25 [54].

3.2.3. Study of $\tan\delta$ with temperature

In figure 5, the $\tan\delta$ variation of PZMT with temperature is shown at selected frequencies.

The value of $\tan\delta$ remains negligible up to 300 °C for $x = 0.00$, 375 °C for $x = 0.02$ and 0.06, and 275 °C for $x = 0.10$ respectively. But above these temperatures $\tan\delta$ has been increased rapidly up to 500 °C. This increase in the value of $\tan\delta$ at higher temperatures is due to space charge polarization [50]. So loss of PZMT samples has been reduced due to Mn doping. But 65/35 PZT has shown increase in the loss due Mn substitution [53].
Therefore we conclude that PZMT samples of 35/65 ratio show low tangent loss compared to 65/35 PZT. All the samples in loss spectrum show anomalies at their respective Curie temperatures. The dielectric properties of PZMT samples are given in table 2. The dielectric properties of Pb\((Zr_{0.35-x}Mn_xTi_{0.65})O_3, x = 0.00, 0.02, 0.06, 0.10\) ceramic samples are given in table 2.

| x  | f (kHz) | \(\varepsilon_{RT}\) | \(\varepsilon_{RT}\tan^\delta_T\) | \(\varepsilon_{RT}\) | \(T_c(°C)\) |
|----|---------|----------------------|----------------------|----------------------|-------------|
| 0.00 | 50     | 165                  | 0.027                | 5440                  | 435         |
|     | 100    | 164                  | 0.024                | 4793                  | 434         |
|     | 500    | 163                  | 0.015                | 3894                  | 434         |
| 0.02 | 50     | 306                  | 0.116                | 9223                  | 412         |
|     | 100    | 303                  | 0.083                | 8530                  | 412         |
|     | 500    | 301                  | 0.046                | 7482                  | 411         |
| 0.06 | 50     | 320                  | 0.142                | 10092                 | 379         |
|     | 100    | 308                  | 0.119                | 9355                  | 381         |
|     | 500    | 297                  | 0.097                | 7985                  | 384         |
| 0.10 | 50     | 378                  | 0.173                | 12 562                | 373         |
|     | 100    | 348                  | 0.146                | 10 954                | 373         |
|     | 500    | 318                  | 0.109                | 8395                  | 373         |

Therefore we conclude that PZMT samples of 35/65 ratio show low tangent loss compared to 65/35 PZT. All the samples in loss spectrum show anomalies at their respective Curie temperatures. The dielectric properties of PZMT samples are given in table 2. The dielectric properties of Pb\((Zr_{0.35-x}Mn_xTi_{0.65})O_3, x = 0.00, 0.02, 0.06, 0.10\) ceramic samples are given in table 2.

4. Diffusivity studies

In figure 6, the study variation of \(\ln \left(\frac{1}{\varepsilon_T} - \frac{1}{\varepsilon_{\text{min}}}\right)\) with \(\ln(T - T_c)\) of PZMT ceramics at different frequencies is shown.
Here the broadening of dielectric peaks doesn’t clearly indicate the diffusiveness of this material system. Diffuseness in the phase transition can be obtained from the following expression

\[ \ln\left(\frac{1}{\epsilon} - \frac{1}{\epsilon_{\text{max}}}\right) \propto (\ln(T - T_c))^\gamma \]

From the graphs slopes, diffusivity was computed which is shown in each figure. All the values of \( \gamma \) lies between 1 (for general or ideal ferroelectric material systems) and 2 (for totally disordered ferroelectric material systems). The higher value of exponent \( \gamma (> 1) \) confirms that materials exhibit some features of diffuse phase transition. The broadening or diffuseness of dielectric peaks occurs mainly due to statistical composition fluctuations, which must occur if crystallographically equivalent sites are occupied randomly by different cations. Since the value of \( \gamma \) is within 1 and 2, a deviation from Curie-Weiss behavior is concluded and therefore the occurrence of disordering in the samples is confirmed. In the PZT systems, the diffuse phase transition can be explained by the presence of certain non-equivalent position in the elementary cell \([55]\). From the diffusivity values, it can be seen that \( \gamma \) value decreases with introduction of Mn and as the concentration of Mn further increases the value of \( \gamma \) increases indicating that the disordering in the modified systems decreases.

5. Conclusions

Using solid state route, the polycrystalline samples of \( \text{Pb}(\text{Zr}_{0.35-x}\text{Mn}_x\text{Ti}_{0.65})\text{O}_3, x = 0.00, 0.02, 0.06, 0.10 \) (PZMT) were prepared under high temperature. For the first time, 35/65 PZT ceramic has been doped with Mn element. The structure of PZT has not changed with the introduction of Mn. But the size and density of particles on surface has been changed. With the doping of Mn, the value of \( \epsilon_{RT} \) has changed significantly from 5440 to 12 562. The values of \( \tan\delta \) were decreased with increase in the concentration of Mn. Doping of Mn has resulted in the decrease of \( T_c \) values of the compounds.
Acknowledgments

We (authors) would like to thank IIT Kharagpur for its support to the experimental work. We are also thankful for the partial financial support provided by DST-SERB.

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