



Analysis on the T_c Values of MPB Pb (Zr_{1-x}Ti_x)O₃ Ferroelectric Ceramics

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Abstract

In this communication an attempt has been made to review, in brief, on Curie temperatures (T_c) of lead zirconatetitanate near morphotropical phase boundary. This review also includes 52/48 PZT modified by cadmium (Cd^{+2}) in various amounts such as 5%, 10%, and 15%. We are proposing an easy method of selecting a substitution element for synthesizing modified lead zirconatetitanate (PZT) ceramics. Our investigation revealed that substitution of +3 valence elements will enhance T_c values whereas the substitution of +2 valence elements will decrease T_c . The change in T_c values is also attributed to ionic radii of modifier ions.

Keywords: PZT, Ceramic, MPB, T_c , Ionic Radius

1. Introduction

PZT is an inorganic ferroelectric oxide with perovskite (ABO₃) structure. It is formed by the combination of lead zirconate (PbZrO₃, $T_c = 490$ °C) and lead titanate (PbTiO₃, $T_c = 230$ °C) crystalline solids. Its unit cell consists of lead (Pb^{+2}) atoms at the A-site and zirconium/titanium (Zr^{+4}/Ti^{+4}) atoms at the B-site (Figure1) [1-2]. It is being used widely in several technological applications such as non-volatile memories (due to decent hysteresis properties) [3-4], piezoelectric micromachined ultrasonic transducers (due to lateral strain generated by piezoelectricity) [5-6], micromachined bimorph energy harvester (due to high efficiency in power conversion) [7], hard disk drives (for detecting hard on media) [8], sensors (due to capacitance) [9], etc. Due to the superior physical properties, PZT plays a significant role in the above mentioned applications.

The physical properties of PZT can be varied depending on the type of application. For instance, in the case of fuel injection actuators and shock sensors, high ϵ_r and T_c are required. In contrast, low

ϵ_r is strongly needed for inkjet actuator and loudspeaker applications [10]. Fabrication of capacitors and ultrasonic transducers require materials with high dielectric constant and large coefficient of electromechanical coupling [11]. So tuning the physical properties of PZT is very much necessary to meet the requirements of the above mentioned applications. There are two major ways to alter the physical properties of PZT: (1) varying the Zr/Ti ratio, (2) substitution of suitable elements at A and/or B sites (i.e. cation sites) [12]. PZT ceramics with numerous compositions ($Pb(Zr_{1-x}Ti_x)$ where $0 < x < 100$) can be synthesized through various preparation techniques such as solid state synthesis, RF magnetron sputtering, sol-gel method, etc. Further, the physical properties of the possible PZT composition can be modified in two ways: (1) substitution of the acceptor elements, (2) substitution of the donor elements [10]. Elements are considered as the donors only when their valence is greater than +2 or +4 and are substituted at A or B sites respectively. Elements are known

as acceptors whose valence is less than +2 or +4 and are substituted at A or B sites respectively [3, 13-18].

In any PZT composition, if the amount of titanium is high then the material shows the phase of tetragonal structure. When the zirconium content is high, it shows the phase of rhombohedral structure. Near morphotropical phase boundary (MPB), both tetragonal and rhombohedral phases coexist together. The coexistence of these phases has been attributed to the high value of coefficient of electromechanical coupling. But in 1999, just below the MPB presence of monoclinic phase which is intermediate between tetragonal and rhombohedral is observed. Due to the extensive physical properties, PZT near MPB is widely investigated ferroelectric ceramic material system. Therefore in this work, we have synthesized PZT of MPB composition and modified it with Cd by replacing lead. We present the effect of Cd^{+2} ions substitution on the T_c of PZT. Also presented is the analysis on T_c values of MPB PZT ceramics due to the substitution of +2 and +3 valence elements.

2. Experimental Section

The oxides of high purity such as lead oxide (99.9%, M/S. LobaChemiePvt. Ltd., India), zirconium dioxide (99.9%, M/S. Sarabhai Chemicals, India), titanium dioxide (99.9%, M/S. LobaChemiePvt. Ltd., India), and cadmium oxide (99.9%, M/S. LobaChemiePvt. Ltd., India) have been used to prepare the samples. The samples of PCZT ($\text{Pb}_{1-x}\text{Cd}_x(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$, $x = 0.00, 0.05, 0.10, 0.15$) have been prepared by solid state route. The detailed step by step procedure and the complete process parameters are similar to that which has been reported elsewhere [14-16]. The experimental condition for calcination of powders: 950 °C for 6 hours in air atmosphere. The experimental condition for sintering of pellets: 1100 °C for 4 hours in alumina crucibles. A detailed method of extracting the electrical measurements has been reported elsewhere [14].

3. Results and Discussion

3.1 Study of temperature dependent dielectric constant

Figure 2 shows the variation of dielectric constant (ϵ_r) of PCZT ceramics with temperature.

For all samples, ϵ_r value increased with increase in temperature up to its maximum value (ϵ_{max}) and then showed a decrease at all frequencies except at 1 kHz where a further increase has been observed. Space charge polarization (scattering/transportation of space charges due to thermal activation) or some defects may be responsible for the increase of ϵ_r at higher temperatures [17-18].

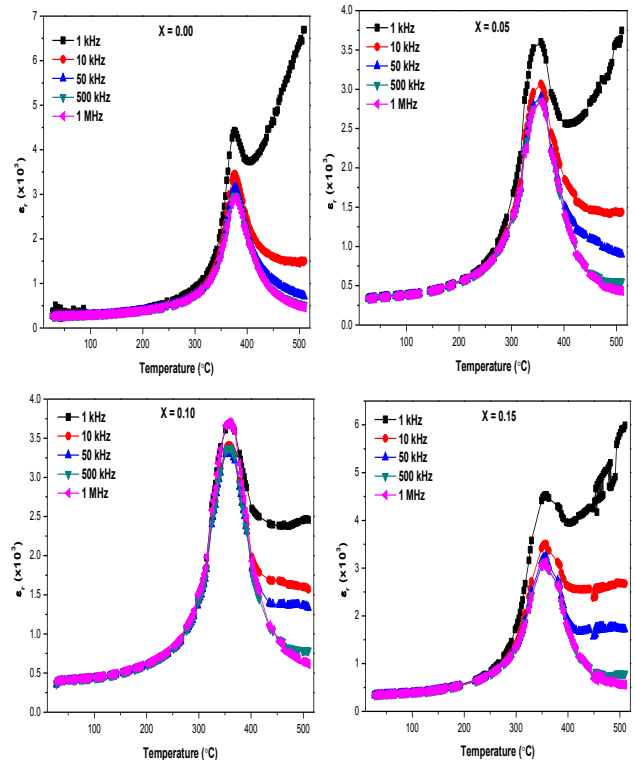


Fig.1. Variation of dielectric constant with temperature

It is observed from the figure that there is a point of Curie temperature (T_c) at which the transition of phase has been occurred. The occurrence of phase transition is generally from the ferroelectric to non-ferroelectric phase (paraelectric phase).[27-32] In each composition, an identical T_c has been observed at the given frequencies (value of T_c has not changed much with change in frequency). The change in the value of T_c is due to the Cd substitution at the Pb-site. Substitution of 5% amount of Cd has decreased the value of T_c from 375 °C to 356 °C where the further increase in the concentration of Cd has not changed much the value of T_c . The decrease in value of ϵ_{max} with increase in frequency has been clearly observed in $x = 0.00, 0.05, 0.15$ samples, indicating the presence of normal dielectric behaviour of a

ferroelectric material [19]. But for $x = 0.10$ sample, an initial decrease followed by constancy in the value of ϵ_{max} is observed. Widened dielectric peaks were not observed in the samples, suggesting the absence of disordering in the material perovskite structure. This means that all the cations are arranged orderly in the material system.

3.2 Effect Substitution of +2 and +3 Valence Elements by Replacing Lead

T_c is a specific temperature that helps to identify the phase transition of ferroelectric materials from the ferroelectric to the non-ferroelectric phase. This value of PZT will be maximum at MPB due to the high polarization of material [20-26]. The T_c values of modified MPB PZT ceramics are given in Table 1.1 in continuation with the use of Table 1, and in Table 2.2 in continuation with the use of Table 2.

Table.1. T_c Values of MPB PZT Ceramics due to +3 Valence Modifiers Substitution

S. No	Composition	Modifier (of +3 Valence)	Concentration of Modifier (%)			
1	PZ ₄₈ T ₅₂	Gallium	0	6		
2	PZ ₅₂ T ₄₈	Lanthanum	0	2		
3	PZ ₅₂ T ₄₈	Neodymium	0	2		
4	PZ ₅₂ T ₄₈	Dysprosium	0	2		
5	PZ ₅₀ T ₅₀	Bismuth	2	13	27	
6	PZ ₅₂ T ₄₈	Ytterbium	0	5		
7	PZ ₅₅ T ₄₅	Gadolinium	0	6	9	
8	PZ ₅₅ T ₄₅	Lanthanum & Bismuth	0	3	5	7

Table.1.1. T_c Values of MPB PZT Ceramics (continuation to Table 1)

T_c (~ °C)				Reference
385		432		21
323		353		22, 23
323		325		22, 24
323		275		22, 24
405	410	450		25
323		393		22, 26
380	410	420		27
457	542	545	548	28

The increment/decrement in T_c is found to be dependent on the valence of the modifier. The T_c values are increased when ceramics were modified with +3 valence ions. But when the ceramics were modified with +2 valence ions, the T_c values are decreased.

Table.2. T_c Values of MPB PZT Ceramics due to +2 Valence Modifiers Substitution

S. No	Composition	Modifier (of +2 Valence)	Concentration of Modifier (%)			
1.	PZ ₅₃ T ₄₇	Calcium	0	1	5	8
2.	PZ ₅₂ T ₄₈	Calcium	2		6	10
3.	PZ ₅₃ T ₄₇	Strontium	0	1	5	10
4.	PZ ₅₆ T ₄₄	Strontium	12.5		20	
5.	PZ ₅₃ T ₄₇	Barium	0	2	4	6
6.	PZ ₅₅ T ₄₅	Samarium	0	3	6	9
7.	PZ ₅₂ T ₄₈	Cadmium	0	5	10	15

Table.2.1 T_c Values of MPB PZT Ceramics (continuation to Table 2)

T_c (~ °C)				Reference
385	385	385	360	29
325		315	300	30
385	385	360	290	29
265		242		29
395	410	405	410	31
390	352	349	320	32
375	356	358	358	Our sample

Table 3 presents the ionic radii (r) of the +2 valence modifiers and Table 4 shows ionic radii of +3 valence modifiers.

Table.3. ' r ' of +2 Valence Elements (<http://abulafia.mt.ic.ac.uk/shannon/ptable.php>)

S.No	Element	r ($\times 10^{-10}$ m)
1.	Calcium	1
2.	Strontium	1.21
3.	Barium	1.38
4.	Samarium	1.22

Table.4. 'r' of +3 Valence Elements (credit: <http://abulafia.mt.ic.ac.uk/shannon/ptable.php>)

S.No	Element	r (x10 ⁻¹⁰ m)
1.	Gallium	0.76
2.	Lanthanum	1.032
3.	Neodymium	0.983
4.	Dysprosium	0.912
5.	Bismuth	1.03
6.	Ytterbium	0.868
7.	Gadolinium	0.938

From Tables 3 and 4, it can be observed that the r-value is lesser (<1.04) and greater (≥ 1) for +3 and +2 valence elements of coordination number 6 respectively. So the substitution of higher ionic radii elements will reduce the T_c whereas the substitution of lower ionic radii elements can enhance the T_c . This may be due to the mismatch between ionic radii of substitute and substituent. In PZT, Pb (r~0.98) atoms get replaced by modifier atoms due to the substitution at A-site. When ionic radii of both Pb and modifier ion are approximately similar, then the material may show the high T_c values.

Conclusions

The samples of PCZT have been prepared by solid state synthesis. These ceramics are suggested for high T_c applications, due to their high T_c . The higher is the valence of a modifier, the greater is the T_c value and vice versa. The higher is the ionic radius of a modifier, the lower is the T_c value and vice versa. Therefore it is recommended that, to enhance the T_c of MPB PZT, it is worth choosing a modifier whose ionic radius matches with lead ionic radius.

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