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RESEARCH ARTICLE

DIELECTRIC AND FERROELECTRIC PROPERTIES OF Zn AND Mn DOPED $BaTiO_3$: AFTER OPTIMIZING THE CALCINATION TEMPERATURE

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ABSTRACT

The present work aims to study the effect of calcination temperature on structure and phase formation of $BaTiO_3$ powder. Barium Titanate ($BaTiO_3$) powder was synthesized by mixing high purity $BaCO_3$ and TiO_2 powder using agate mortar in acetone medium for 6 hours. The powder mixture was dried and kept at 60°C. The soft agglomeration was broken and the sample was divided into three portions each weighing 5gm each. These three samples were calcined at 700°C, 800°C and 900° C for 5 h with heating and cooling rates of 10°C/min. Phase transformation and particle size of the calcined powders have been investigated as a function of calcination temperature, by room-temperature X-ray diffraction techniques. It was seen that the perovskite-like phase of $BaTiO_3$ was successfully obtained and this was compared with the standard sample. With increasing calcination temperature, $BaTiO_3$ transformed from the cubic to the tetragonal phase. The X-ray diffraction investigations have revealed that the samples calcined at 900^0C perfectly coincide with original spectrum. After finding the optimum calcination temperature, the second aim was to prepare $Ba_{0.95}Zn_{0.05}TiO_3$, $BaTi_{0.95}Mn_{0.05}O_3$ and $Ba_{0.95}Zn_{0.05}Ti_{0.95}Mn_{0.05}O_3$ under the same conditions and compare with pure $BaTiO_3$. The X-ray diffraction analysis was performed to confirm whether the desired samples were formed. P-E hysteresis loop was analyzed and the hysteresis loop was observed for pure $BaTiO_3$ and $BaTiMnO_3$, due to the formation of oxygen vacancies and exchange interaction-induced polarization. The small area of P-E loop indicates better homogeneity and crystallinity of prepared samples. The dielectric constant of Mn doped sample is increased and Curie temperature is lowered. The samples with Zn dopants are behaving in an entirely different way. They do not exhibit a perfect dielectric behavior but shows a semiconducting property which is confirmed from the band gap measurement.

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INTRODUCTION

Barium Titanate ($BaTiO_3$) has been the first piezoelectric ceramics ever discovered and due to its excellent ferroelectric properties and high dielectric constant at room temperature, it is still widely used in capacitors, thermistors, chemical sensors, electro optic devices and piezoelectric devices (Chandler *et al*., 1993; Millis, 1998; Pena and Fierro, 2001; Potdar *et al*., 1999; Song Wei Lu *et al*., 2000; Yuan Ting Wu *et al*., 2012). It has perovskite structure. Conventional ceramic processing poses problems for the preparation of reproducible high purity $BaTiO_3$ and for the incorporation of small amount of desired impurities. $BaTiO_3$ is conventionally produced by solid state reaction between barium carbonate ($BaCO_3$) and titanium dioxide (TiO_3) at high temperature (700-900^0C). $BaTiO_3$ have been synthesized by using hydrothermal method, sol-gel processing, composite-hydroxide-mediated method, flame assisted spray pyrolysis (FASP), radio-frequency plasma chemical vapour deposition (RF-plasma CVD), one step sol-precipitation route and aqueous chemical route (Song Wei Lu *et al*., 2000; Yuan Ting Wu *et al*., 2012; Hong Liu *et al*., 2006; Bhuiyan *et al*., 2012; Moon *et al*., 2003; SHEN Zhigang *et al*., 2006; Testino *et al*., 2004). Each method has its own advantages and disadvantages. It is known that the properties of BT can be tuned by controlling processing parameter, particle size and doping. Several studies have indicated that the h-Phase could be formed by sintering Barium Titnate in reducing atmosphere or by doping by Mg, Al, Mn, Fe, Zn, Ni, Nb, Ga, Cu etc. It is already reported that the incorporation of Mn in Ti^{4+} site of $BaTiO_3$ lead to decrease the Curie temperature by 10^0C/1%Mn when sintered in an air atmosphere. Mn doped $BaTiO_3$ was found to be most satisfactory dielectric for capacitors. In spite of the fact that zinc components show excellent photoelectric and piezoelectric properties few reports are available on the use of zinc as a dopant in barium titanate. But the detailed studies have not been made. In this paper, we focus on the effect of the calcining temperature, effect of Mn and Zn on phase composition, microstructural evolution,

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dielectric properties and ferroelectric properties of barium titanate fine powders synthesized by the solid state method.

MATERIALS AND METHODS

A). Preparation of pure barium titanate

The barium titanate powder was synthesized from commercially available $BaCO_3$(99% Purity) and TiO_2 (99.9% Purity). The equimolar dried $BaCO_3$ and TiO_2 powders were weighed accurately and mixed in a agate mortar and pestle for 6h in acetone medium. The powder mixture was dried and kept at 60^oC. The soft agglomeration was broken and divides the sample into three batches of 5g each. These three batches were calcined at 700^oC, 800^oC and 900^o C for 5 h with heating and cooling rates of 10^oC/min. All the experiments were done in air. The crystalline structure of the calcined powder was investigated by X-ray diffraction (Rigaku Japan/Ultima-IV) using CuK_α (λ= 1.5406 Å) in the range 10^o to 80^o with a scanning step of 0.02^o. The pellets with diameter 12 mm and 2 mm thickness were prepared by adding 3% PVA (binder). Pressing is done using a hydraulic press under constant pressure of 250 mpa. The green pellets were heated to 400°C for 3h in a covered Al_2O_3 crucible for binder burnout, and then ramped at 3°C/min to a sintering temperature between 500 to1000°C with a 2h hold time at and a cooling rate of 5°C/min.

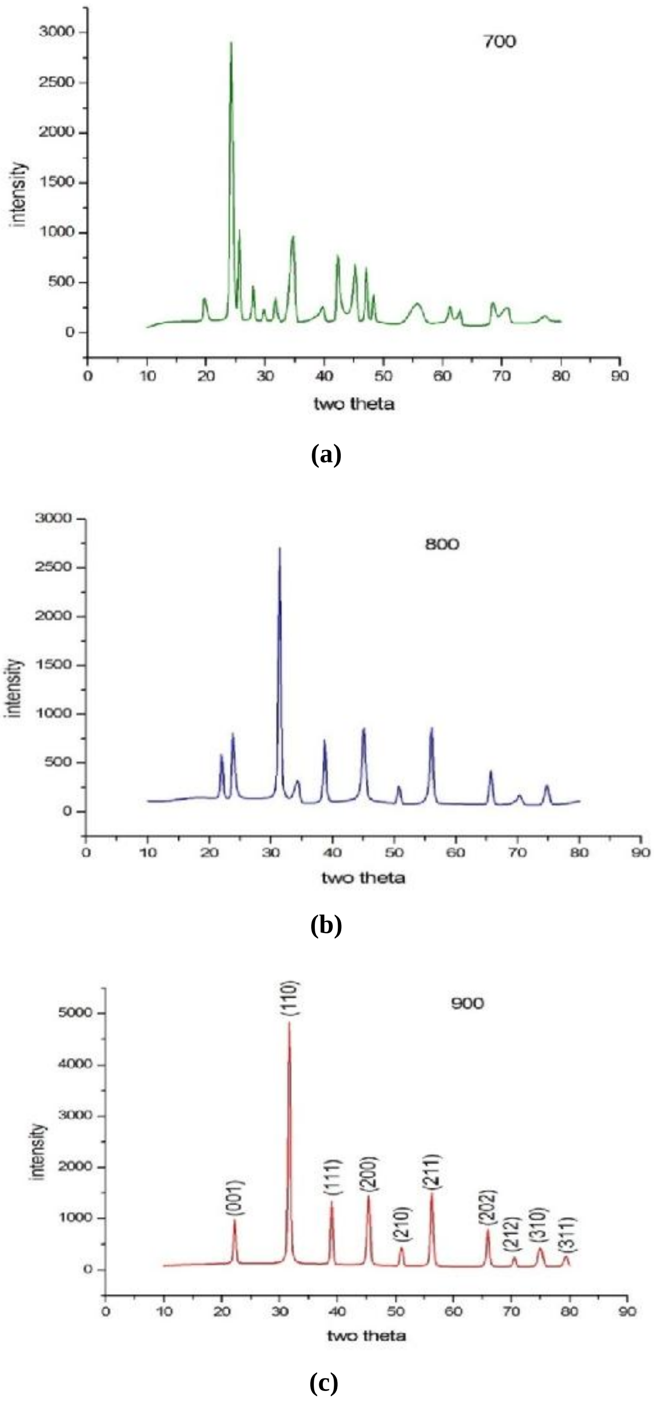
(B)Preparation of doped $BATIO_3$

After selecting the optimum calcinations temperature polycrystalline samples of $BaTiO_3$, $Ba_{0.95}Zn_{0.05}TiO_3$, $BaTi_{0.95}Mn_{0.05}O_3$ and $Ba_{0.95}Zn_{0.05}Ti_{0.95}Mn_{0.05}O_3$ were prepared by the conventional solid state reaction technique. High-purity (99%) $BaCO_3$, TiO_2, $MnCO_3$, and $ZnCO_3$ powders were taken to have stoichiometric quantities according to the formula $BaTiO_3$, $Ba_{0.95}Zn_{0.05}TiO_3$, $BaTi_{0.95}Mn_{0.05}O_3$ and $Ba_{0.95}Zn_{0.05}Ti_{0.95}Mn_{0.05}O_3$ mixed thoroughly by using agate mortar and pestle mixed powders were calcined in air at 900^oC for 5 h. Calcined powders were pressed into pellets and pellets were sintered at 1000^oC for 2 h. The circular electrical contact of known diameter was prepared by applying aluminum coating on both sides of the sintered pellets. The dielectric properties of the pellets were determined using Hewlet Packard (Model 4192A) Impedance Analyzer from 100 HZ to 13 MHZ at room temperature. The spontaneous polarization (P_s), coercive field (E_c) and the breakdown voltage (E_b) were obtained from the ferroelectric hysteresis loop observed at 1to10 Hz on an using a ferroelectric tester system (Radiant Technologies, Inc., RT66A)

RESULTS AND DICUSSION

X-ray diffraction

The Figure 1 (a-c) given below shows the X-ray diffraction patterns of the mixture of $BaCO_3$ and TiO_2 calcined at temperatures 700^0C, 800^0C and 900^0C respectively. The absence of peak at 21.6^0C and 26.8^0C indicates that there is no intermediate phase like $Ba_2Ti_2O_5.CO_3$. Crystalline $BaTiO_3$ is found to form at a temperature of 700^0C along with some impurities like $BaCO_3$ and TiO_2. The gradual decomposition $BaCO_3$ and subsequent formation of phase pure $BaTiO_3$ is clearly seen from the XRD pattern in samples calcined at different temperatures. As the calcination temperature increases, the peaks become sharper and the phase pure $BaTiO_3$ is found to be formed at 900^0C, which is completely devoid of any impurity phases.



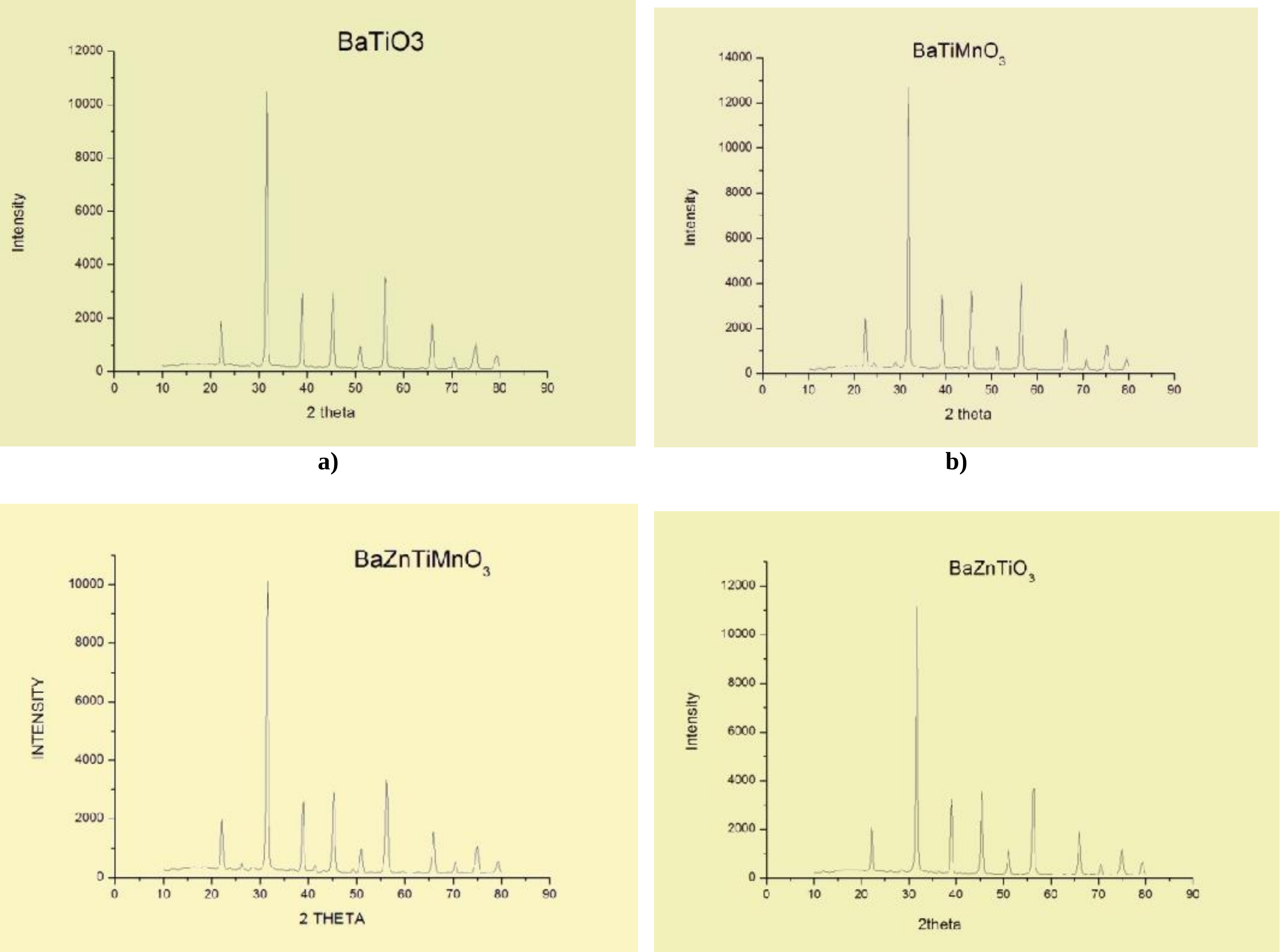
(a)

(b)

(c)

Figure 1 (a-c): X-Ray Diffraction pattern of $BaTiO_3$ ceramics sintered at various temperatures

Figure 2(a-d) shows X-ray diffraction pattern of the samples ($BaTiO_3$, $Ba_{0.95}Zn_{0.05}TiO_3$, $BaTi_{0.95}Mn_{0.05}O_3$ and $Ba_{0.95}Zn_{0.05}Ti_{0.95}Mn_{0.05}O_3$). X-ray diffraction pattern confirm that $BaTiO_3$ has perovskite structure. There are many peaks in the spectrum which indicates the presence of undecomposed precursors. The spectrum of doped $BaTiO_3$ is exactly similar to that of pure $BaTiO_3$. So it is evident that the addition of small quantities of dopant will not change the perovskite structure of $BaTiO_3$. Therefore, doping $BaTiO_3$ with minute quantity of some suitable elements like Zn, Mn etc can improve their crystal qualities.



a) b)

c) d)

Figure 2(a-d): The x-ray diffraction (XRD) patterns of $BaTiO_3$, $Ba_{0.95}Zn_{0.05}TiO_3$, $BaTi_{0.95}Mn_{0.05}O_3$ and $Ba_{0.95}Zn_{0.05}Ti_{0.95}Mn_{0.05}O_3$

The exhibited peaks can be indexed as tetragonal lattice of pure and doped $BaTiO_3$. On comparison with the standard XRD pattern of $BaTiO_3$ powder, the peaks at 22.25^0, 31.52^0, 38.97^0, 45.31^0, 50.95^0, 56.61^0, 66.31^0, 70.61^0, 75.13^0 and 79.43^0 can be attributed to the Miller indices of (001), (110), (111), (200), (210), (211), (202), (212), (310) and (311), respectively.

Dielectric behaviour of samples

The dielectric constant of the phase pure $BaTiO_3$, formed at a calcination temperature of 900^0C, is measured to compared the prepared sample with the standard value. Figure 3 shows the variation of dielectric constant as a function of temperature .Up to 131^0C, the dielectric constant of $BaTiO_3$ increases as the temperature increases. Beyond 131^0C, the dielectric constant decreases as the temperature increases. Therefore, the Curie temperature of $BaTiO_3$ was found to be 131^0C. The corresponding value of dielectric constant is 3109. This value of curie temperature and dielectric constant is very much matching with the standard value. Similarly Figure 4 show the effect of dopant on the dielectric property. It is clear from the figure that in pure Mn-doped $BaTiO_3$, the dielectric constant at all temperatures is lower than that of pure $BaTiO_3$. For Zn-doped $BaTiO_3$, dielectric constant is not varying with temperature. This implies that Zn-doped barium titanate does not show a perfect dielectric property and from the available data it is assumed to be shifted to semiconductor behaviour.

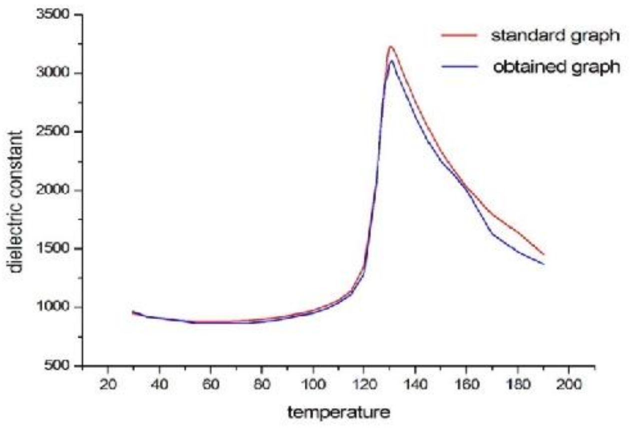


Figure 3. Variation of dielectric constant as a function of temperature of pure $BaTiO_3$ sample and is compared with standard value

Table 1(a). Curie temperature and dielectric value of $BaTiO_3$ and is compared with the standard value

	Curie temperature	Dielectric constant
Standard value	130^0C	3225.2814
Obtained value	131^0C	3109.0613

Table 1(b). Curie temperature and dielectric value of $BaTiO_3$ and $BaTiMnO_3$

Property	$BaTiO_3$	$BaTiMnO_3$
Curie temperature	131^0C	64^0C
Dielectric constant	3109.0613	4853.2861

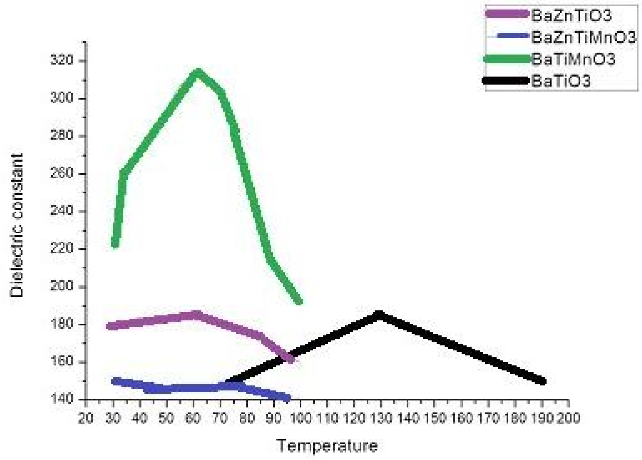


Figure 4. Dielectric vs temperature graph for $BaTiO_3$, $Ba_{0.95}Zn_{0.05}TiO_3$, $BaTi_{0.95}Mn_{0.05}O_3$ and $Ba_{0.95}Zn_{0.05}Ti_{0.95}Mn_{0.05}O_3$

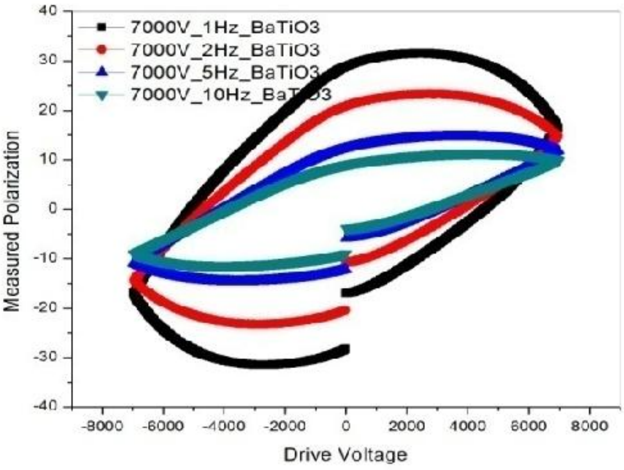
The dielectric constants of all temperatures are noted for all the samples. For pure $BaTiO_3$, as mentioned before the dielectric constant is increasing with temperature up to 131^0C and beyond 131^0C, the dielectric constant is decreasing. When it is doped with Mn, sample exhibits the same dielectric behaviour as that of pure $BaTiO_3$ but with an increased dielectric constant. But the Curie temperature is shifted to a low value of about 62^0C. The samples with Zn dopants are behaving in an entirely different way. They do not exhibit a perfect dielectric behaviour, since the plot shows an irregular variation in dielectric constant with temperature. Their measured band gap energy corresponds to that of a semi conductor. Thus, it can be inferred that $BaTiO_3$ with Zn dopant is no more an insulating material and its further study is going on.

Ferroelectric properties of barium titanate and doped barium titanate

Figure 5 shows the P-E curves of (a) BaTiO3, (b) $BaTi_{0.95}Mn_{0.05}O_3$ ceramics at room temperature. It is observed that with the addition of Mn the value of maximum polarization decreases as well as the area of the loop also decreases. The details of maximum polarization and coercive field (Ec) for each sample are shown in Table 2. The P-E loop is not observed for the samples with Zn and are typical of a lossy linear dielectric rather than for a ferroelectric material. This behaviour suggests that either the doped ceramics are still in the sub-switching regime or the ferroelectricity is largely suppressed. This may be attributed to the formation of hexagonal phase. Since the hexagonal phase of BTO is not ferroelectric (Moon *et al.*, 2003), the formation of the hexagonal phase weakens the ferroelectricity of $BaTiO_3$ to a large extent (Du *et al.*, 2010). The stability of the ferroelectric phase can be determined by structural transition with additional factors like incorporation of foreign atoms (Zhao *et al.*, 2004). It is evident that persistence of ferroelectricity results from the long-range polar orders of dipoles (Kuehn and Kliem, 2009). Any disruption in the polar order would affect the ferroelectricity. Generally, reduction of polarization occurs due to reduction in grain size (Zhao *et al.*, 2004), the presence of structural imperfections such as oxygen vacancies and dislocations (Zhao *et al.*, 2004). It is also observed from Table 2 that the value of coercive field (Ec) remains high and the maximum polarization value reduces sharply (*P*-max). The above fact indicates that all the samples are highly insulator. Here, the reasons for degradation of ferroelectricity may be due to formation of hexagonal phase along with the creation of oxygen loss by co-substitution of Mn.

Table 2. Values of P_r, P_s and E_c for $BaTiO_3$ and $BaTi_{0.95}Mn_{0.05}O_3$ at 7kV _1Hz

Sample	P_R	P_S	E_C
$BaTiO_3$	9.944	9.108	2913.35
$BaTiMnO_3$	3.527	2.0527	2349.47



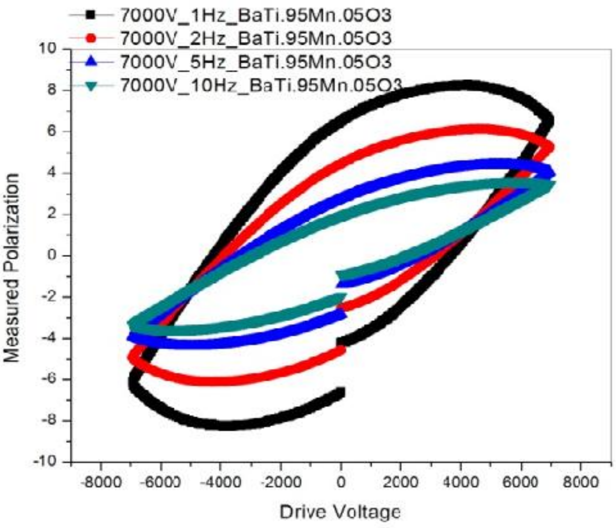


Figure 5. The room temperature P–E loops of (a) BaTiO3, (b) $BaTi_{0.95}Mn_{0.05}O_3$ ceramic samples

Zn-doped barium titanate and both Mn and Zn-doped barium titanate does not show P-E hysteresis as well as a perfect dielectric behaviour but shows a semiconducting property which is confirmed from the band gap measurement. Further detailed investigation is required and the work is in progress.

Conclusion

In this study, will get a clear picture of calcination temperature at which the phase pure $BaTiO_3$ is formed. Another important result is the room temperature multiferroicity is observed for the typical composition $BaTi_{0.95}Mn_{0.05}O_3$. Peculiar magnetic behaviors are shown by Mn-doped ceramic compositions in which magnetic hysteresis loops are narrowed near the origin. Such a magnetic effect may be attributed to the coexistence of antiferromagnetic and ferromagnetic exchange interactions between Mn3+ and Mn4+ ions. Although the ferroelectric polarization decreases in Mn-doped compositions, the ferroelectricity shown by mn-doped compositions is present well above room temperature. This type of ferroelectric behavior observed in Mn-doped BTO is due to the presence of a hexagonal structural phase. Zn-doped shows a semiconducting property which is confirmed from the band gap measurement. Further detailed investigation is required to confirm this.

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