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Ferroelectric and dielectric properties of sol-gel processed barium titanate ceramics and thin films

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Ferroelectric and dielectric properties of barium titanate ($BaTiO_3$) bulk ceramics and thin films have been investigated. The bulk ceramics and thin film samples have been prepared from barium acetate [$Ba(CH_3COO)_2$] and titanium(IV)isopropoxide [$Ti(CH_3)_2CHO)_4$] precursors by sol-gel technique. The as-grown bulk powder and thin films were found to be amorphous, which crystallized to tetragonal phase after annealing at 700 °C in air for one hour. The values of the spontaneous polarization (P_s), remanant polarization (P_r) and coercive field (E_c) of the bulk ceramics were found to be 19.0, 12.6 $\mu C\,cm^{-2}$ and 30 $kV\,cm^{-1}$ respectively. In the case of the film, the values of P_s, P_r and E_c were respectively found to be 14.0, 3.2 $\mu C\,cm^{-2}$ and 53 $kV\,cm^{-1}$. The capacitance-voltage (C-V) characteristics of the film also showed polarization hysteresis. The values of the dielectric constant (ϵ) of the bulk ceramic and thin film at 1 kHz were found to be 1235 and 370 respectively. Both the films and ceramics showed dielectric anomaly peaks at 125 °C, showing ferroelectric to paraelectric phase transition. © *1999 Kluwer Academic Publishers*

1. Introduction

Ferroelectric bulk ceramics and single crystals have found wide applications in many electronic, acousto-optic, piezoelectric devices [1, 2]. Recently there has been considerable interest in the ferroelectric thin films due to possible applications in integrated devices [3–6]. The advantages of thin film devices include low operating voltages, high switching speeds and possible integration with the existing semiconductor technology. With the advancement of the thin film technology, attempts have been made to prepare near bulk quality ferroelectric thin films for device applications. However, the properties of the films such as dielectric permitivity, polarization etc. showed a sharp decrease as compared to their bulk ceramic counterparts. The properties of ferroelectric bulk ceramics and thin films have been widely investigated [1, 7]. However, there is hardly any report on the studies on the basic properties of the bulk ceramics and thin films prepared by the same technique. In this paper, we report the ferroelectric and dielectric properties of sol-gel processed $BaTiO_3$ ceramics and thin films.

The most common method for making $BaTiO_3$ ceramics is the conventional solid state reaction method [7]. Recently the sol-gel technique has been utilized for the fabrication of ferroelectric $BaTiO_3$ bulk powder and ceramics [8]. The advantages of sol-gel technique include fine particle size, easy compositional control and low processing temperature. Various deposition techniques such as sputtering [9], evaporation [10], metaloorganic chemical vapor deposition (MOCVD), sol-gel [11] etc. have been utilized for the fabrication of ferroelectric $BaTiO_3$ thin films. Among the various techniques, sol-gel is gaining interest for the fabrication of ferroelectric films due to low equipment cost and ease of integration with the already existing semiconductor technology.

2. Experimental details

The source chemicals containing the metal components (Ba and Ti) were 99.99% barium acetate [$Ba(CH_3COO)_2$, BDH] and titanium(IV)isopropoxide [$Ti((CH_3)_2CHO)_4$, Aldrich]. Barium acetate was first dissolved in acetic acid [CH_3COOH] and then diluted with 2-methoxyethanol [$CH_3OCH_2CH_2OH$]. An equimolar amount of $Ti(CH_3)_2CHO)_4$ was then added drop wise to the above solution, keeping it constantly stirred and filtered using microfibre glass filter paper. The filtrate was used as the stock solution for the preparation of the $BaTiO_3$ bulk ceramics and thin films. For the preparation of the bulk ceramics, the stock solution was set aside (for about 24 h) until a white opaque gel was obtained. The gel was converted to white powder after drying at 350 °C. The resulting powder was then annealed at 700 °C in air for one hour for crystallization. The ceramic samples were prepared by pressing the powder, using a pressure of 1.25×10^3 kg cm^{-2}, in the form of circular discs (1 cm diameter and 0.1 cm thick) and sintering at 1300 °C for 2 h. Thin films were prepared on quartz and $Pt/Ti/SiO_2/Si$ (PS) substrates by spin casting of the stock solution at 4000 rpm for 30 s. Following the deposition, the films were heat treated for 5 min at 350 °C in air ambient. Thin films of thickness 0.4 μm were prepared by repeating the deposition cycle (the thickness of each coating was being

0.125 μm). The films were then annealed at 700 °C in air for one hour by using a conventional furnace.

The structure of the bulk ceramics and thin films were characterized by X-ray diffraction technique using a Phillips (model PW 1840) X-ray diffractometer. The microstructure of the samples was investigated by using a Jeol (model JSM 840) scanning electron microscope. The dielectric properties were measured by using HP4192A impedance analyzer. The polarization-field hysteresis was measured at 50 Hz by using a Sawyer-Tower circuit. The capacitance-voltage and conductance-voltage characteristics were measured using a Parc CV plotter (model 410). All the electrical measurements were carried out in the metal-ferroelectric-metal (MFM) configuration. Bulk ceramic samples were prepared by electroding the sintered discs with silver paint and poling in oil at 150 °C for 2 h using a poling field of 30 kV cm^{-1}. Thin film samples having a thickness of 0.375 μm deposited on PS substrates. Gold circular electrodes of area 1.96×10^{-3} cm^2 were deposited by vacuum evaporation on the top of the films.

3. Results and discussion

3.1. Structure and microstructure

The as-fired powder was found to be amorphous and had a particle size <1 μm. Annealing at 700 °C for one hour gave tetragonal $BaTiO_3$ powder (Fig. 1). Upon pressing and sintering, the particles coalesce to form large well-defined crystallites (Fig. 2a). The as-fired film was also found to be amorphous, which crystallized to tetragonal phase after annealing at 700 °C for one hour in air.

3.2. Ferroelectric properties

3.2.1. Polarization-field (P-E) hysteresis

The room temperature polarization-field hysteresis of the bulk ceramics showed well saturated loops (Fig. 3a). The values of the remnant polarization, spontaneous polarization and coercive field determined from Fig. 3a are reported in Table I. It may be noted that the polarization values of the bulk ceramics are lower than that of the single crystal whereas the coercive field is higher. This may be attributed to the existence of the non-ferroelectric layers at the metal-ferroelectric interfaces and grain boundaries [12]. However, the polarization values of the bulk ceramics are comparable to the best-reported values of $BaTiO_3$ bulk ceramics prepared by solid state reaction method [7]. The thin film also showed a well saturated P-E hysteresis loop at room temperature (Fig. 3b). The loop is slim as compared to that of the bulk ceramic. The values of P_r, P_s and E_c are reported in Table I. It may be pointed out that the spontaneous polarization and remanent polarization of the films are much lower than that of bulk ceramics whereas the coercive field is higher. The lower value of the polarization in the film may be due to the smaller grain size and lower packing density of the films as compared to that of the bulk ceramics. Higher values of the coercive field in ferroelectric films than their bulk ceramic counterparts have reported in the literature several workers [7, 13]. A decrease in the polarization and increase in E_c with decreasing thickness has also been reported in TGS single crystal [14]. This has been attributed to the existence of non-ferroelectric surface layer at the crystal-electrode interface. The existence of non-ferroelectric layers at the metal-film interface and at the grain boundaries may be responsible for the higher value of the coercive field and lower value of the polarization in the films.

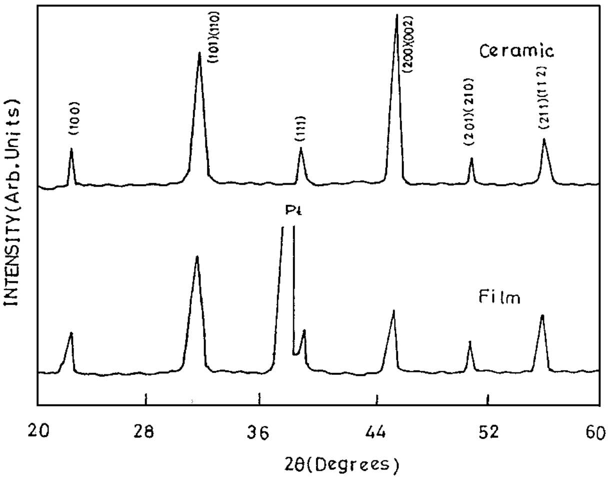

Figure 1 X-ray diffraction pattern of sol-gel processed $BaTiO_3$ bulk ceramic and thin film.

3.2.2. Capacitance-voltage characteristics

The investigation of dc electric field dependence of the dielectric constant (ϵ) and loss tangent ($\tan\delta$) is one of the methods for gaining insight into the behavior of the ferroelectric materials and have been used to characterize ferroelectric thin films [15, 16]. The dc field dependence of ϵ and $\tan\delta$ of the films were investigated by measuring capacitance-voltage (C-V) and conductance-voltage (G-V) characteristics. It was not possible to measure the C-V and G-V characteristics of the bulk ceramic samples due to the requirement of high dc biasing field. Fig. 4 shows the room temperature C-V and G-V characteristics of $BaTiO_3$ film fabricated on PS substrate. Similar to the P-E hysteresis loop

TABLE I Ferroelectric properties of $BaTiO_3$ bulk ceramic and thin film

Sample	Remanent polarization P_r (μC cm^{-2})	Spontaneous polarization P_s (μC cm^{-2})	Coercive field (P-E) E_c (kV cm^{-1})	Coercive field (C-V) E_{cl} (kV cm^{-1})	Reference
Single crystal	20.0	25.0	10	—	[8]
Sol-gel bulk ceramic	12.6	19.0	30	—	Present work
Sol-gel film	3.2	14.0	53	45	Present work

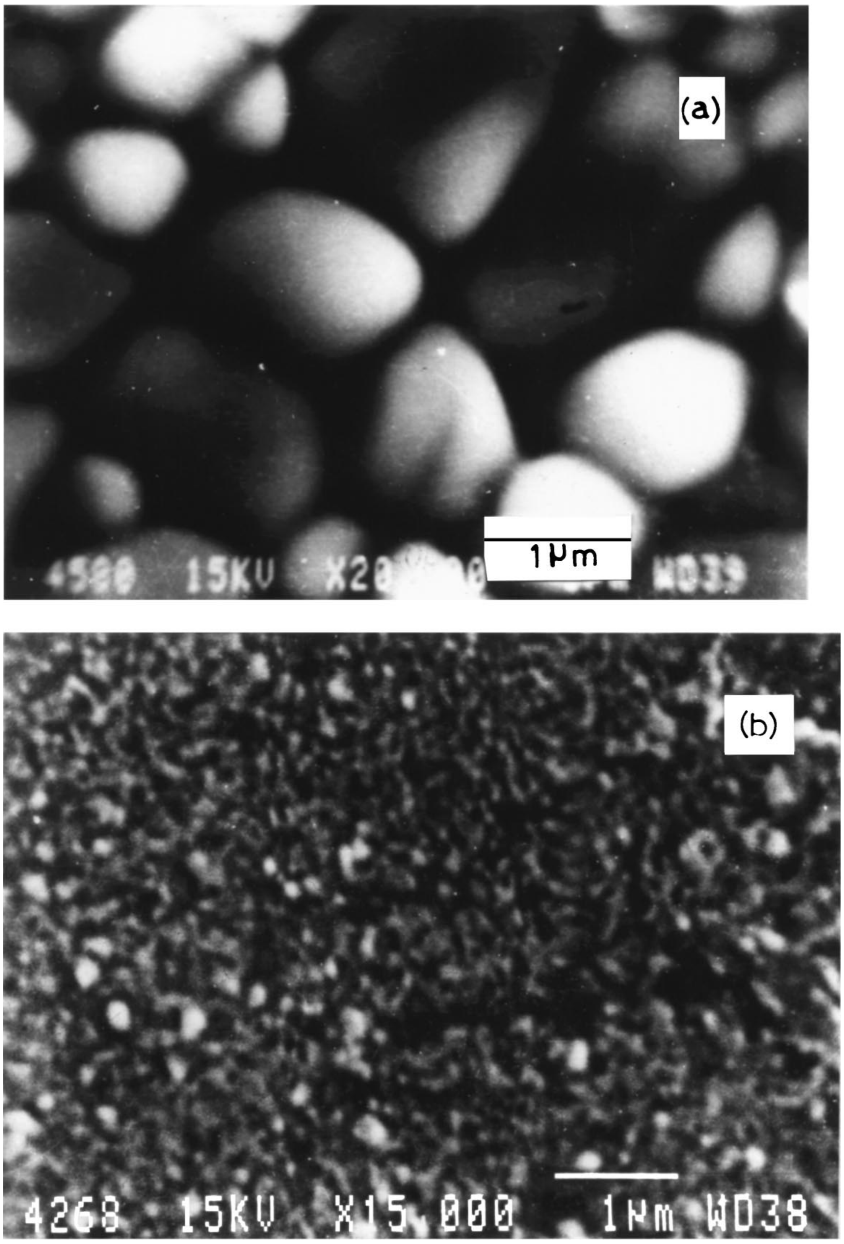

Figure 2 Scanning electron micrographs of $BaTiO_3$: (a) bulk ceramic and (b) thin film deposited on PS substrate.

(Fig. 3b), the C-V plot also showed hysteresis effect. In either of the two (i.e. left and right) branches, both C and G display a bell-like curve and have much reduced values at high biasing fields of positive and negative polarity. They also exhibit a maximum at a dc bias, which can be regarded as the coercive field in the corresponding P-E hysteresis loop. The calculated value of coercive field (E_{cl}) was found to be 45 kV cm^{-1}, which is slightly lower than that determined from P-E hysteresis measurements. This may be attributed to the frequency and field dependency of the ferroelectric properties of the film. The existence of the C-V and G-V hysteresis confirmed the ferroelectricity in our films.

3.3. Dielectric properties

The room temperature dielectric constant (ϵ) and loss tangent ($\tan\delta$) of the bulk ceramics at 1 kHz were found to be about 1235 and 0.012 respectively. There is small frequency dispersion on the dielectric constant, as shown in Fig. 5. Similar behavior has been observed in majority of ferroelectric bulk ceramics [7]. The value of ϵ of the bulk ceramics is lower than that reported for $BaTiO_3$ single crystal [14]. The lower value of ϵ of the bulk ceramics may be either due to porosity or the existence of low dielectric constant non-ferroelectric layers at the metal-ferroelectric interfaces and grain boundaries [12]. The lower values of in ferroelectric bulk ceramics as compared to their single crystal counterparts have been widely documented in the literature [1, 7]. The room temperature dielectric constant and loss tangent of the film at 1 kHz was found to be 370 and 0.015. Similar to the bulk ceramics, ϵ of the films also shows weak frequency dispersion (Fig. 6). It may be noted that the value of ϵ of the film is much lower than that of the bulk ceramics whereas the value of $\tan\delta$ is higher. Similar results have been reported by earlier workers [17–21]. The further lowering in the dielectric constant of the films from the bulk

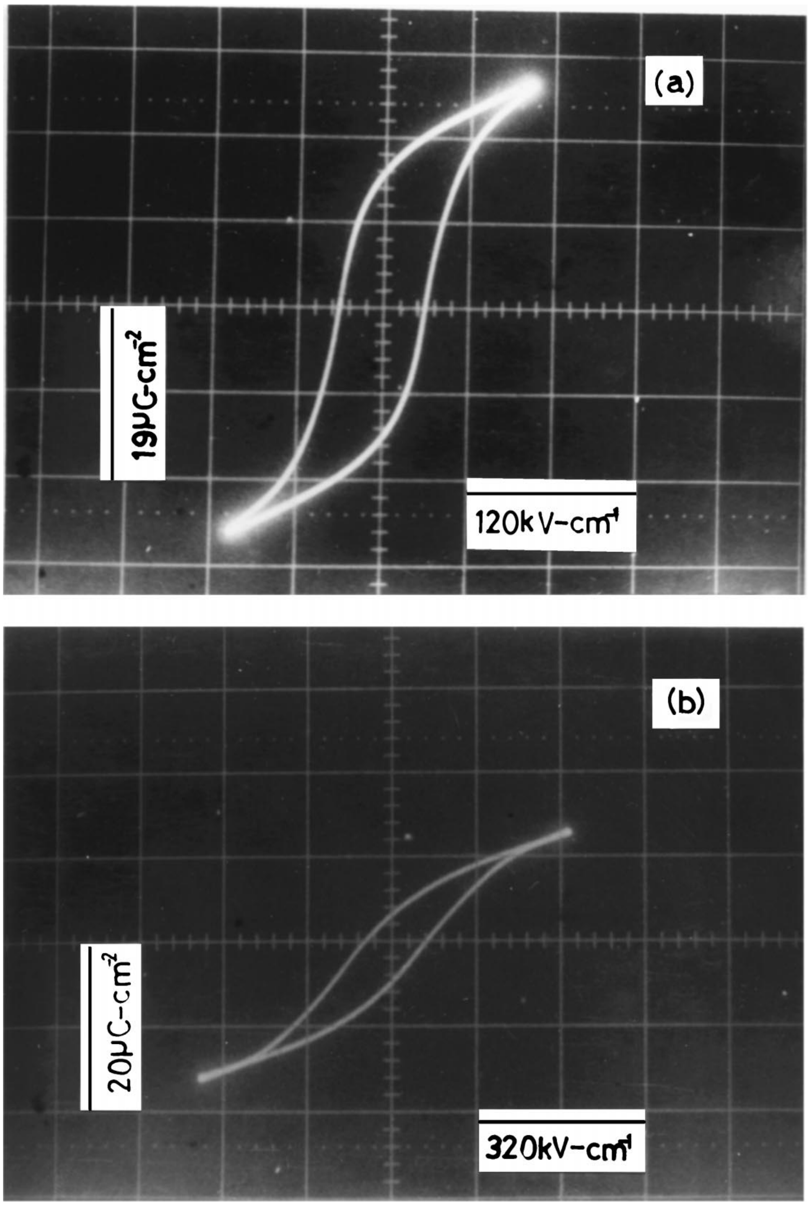

Figure 3 Polarization-field hysteresis loops of $BaTiO_3$: (a) bulk ceramic and (b) thin film.

ceramics suggests that the grain size and non-ferroelectric layers at metal-ferroelectric interfaces play a major role in determining the dielectric constant of the material.

The effect of temperature on the dielectric constant of the bulk ceramics and films were also investigated. Figs 7 and 8 respectively showed the variation ϵ and $\tan\delta$ at 1 kHz of the bulk ceramic and thin film with

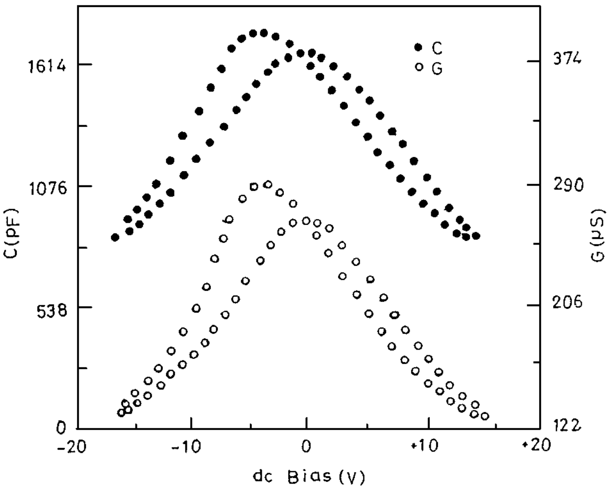

Figure 4 Capacitance-voltage (C-V) and conductance-voltage (G-V) characteristics of $BaTiO_3$ thin film at room temperature.

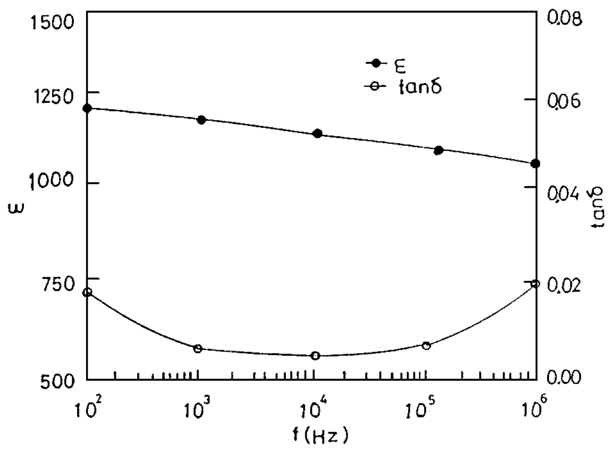

Figure 5 Variation of dielectric constant (ϵ) and loss tangent ($\tan\delta$) of $BaTiO_3$ ceramic with frequency.

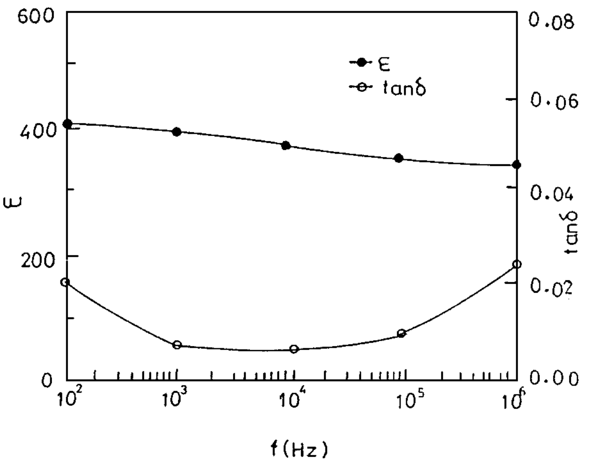

Figure 6 Variation of dielectric constant (ϵ) and loss tangent ($\tan\delta$) of $BaTiO_3$ film with frequency.

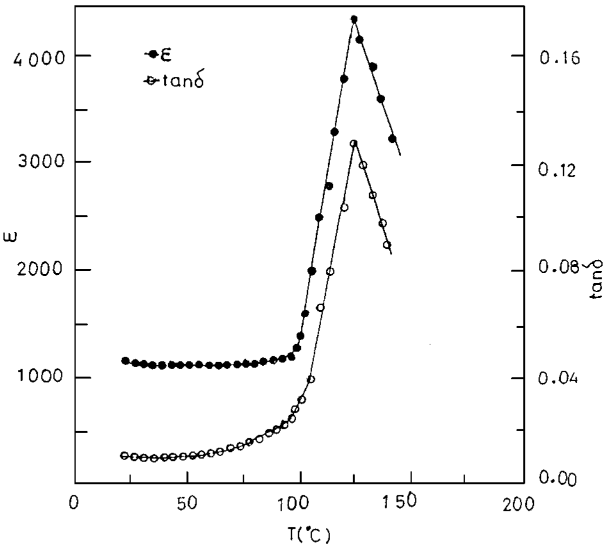

Figure 7 Variation of dielectric constant (ϵ) and loss tangent ($\tan\delta$) of $BaTiO_3$ ceramic with temperature.

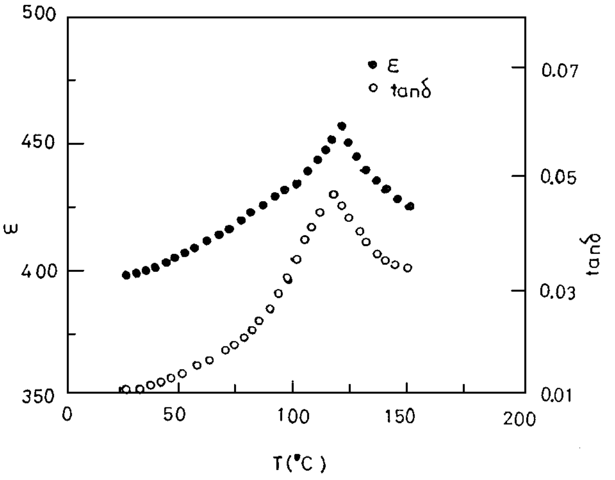

Figure 8 Variation of dielectric constant (ϵ) and loss tangent ($\tan\delta$) of $BaTiO_3$ thin film with temperature.

temperature. It may be pointed out from Fig. 7 that both ϵ and $\tan\delta$ of the bulk ceramic showed a peak at 125 °C, showing a phase transition from ferroelectric to paraelectric. The peak is broad and low in magnitude as compared to that of $BaTiO_3$ single crystal. The peak is more diffuse and lower in magnitude in the case of the film. Similar results have been observed in majority of ferroelectric films [21, 22]. The lowering and broadening of the dielectric anomaly peak in the bulk ceramic and thin film may be attributed to lower density or the existence of space charge layers at the film-electrode interface and grain boundaries. However, the above argument is purely speculative and more studies on the bulk ceramics and thin films having grain sizes are needed to get a conclusive picture.

4. Conclusions

Ferroelectric $BaTiO_3$ bulk ceramics and thin films have been prepared by sol-gel technique. The as-grown powder and thin film were found to be amorphous, which crystallized to tetragonal phase after annealing at 700 °C for one hour. Both the bulk ceramics and thin films showed well-saturated P-E hysteresis loops at room temperature. The values of room temperature spontaneous polarization, remanant polarization and coercive field of the bulk ceramics and thin films determined from the P-E hysteresis loop were found to be 19.0, 12.6; 14.0, 3.2 $\mu\mathrm{C\,cm^{-2}}$ and 30, 53 $\mathrm{kV\,cm^{-1}}$ respectively. The coercive field of the film determined from the C-V characteristics is slightly lower than that determined from the P-E hysteresis loop. The room temperature dielectric constant of the bulk ceramic and the film were found to be 1235 and 370 respectively. Both the films and bulk ceramics showed dielectric anomaly peaks at 125 °C showing ferroelectric to paraelectric phase transition.

Acknowledgements

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