

BiFeO₃ thin films: Novel effects

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Abstract. In this paper we report synthesis of phase-pure highly resistive magnetoelectric BiFeO₃ thin films on Pt/TiO₂/SiO₂/Si substrate by using pulsed laser deposition technique. For the first time saturated ferroelectric hysteresis loop has been observed. It has confirmed the presence of ferroelectricity in BiFeO₃ compound. The films exhibit dielectric anomaly near Néel temperature. This anomaly is related to the influence of vanishing magnetic order on the electric order. *In situ* domain alignment occurs during observation of the films under transmission electron microscope.

Keywords. Magnetoelectric materials; thin films; ferroelectricity; dielectric anomaly; domains.

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1. Introduction

Progress in modern science and technology depends largely on the development of new advanced materials. Magnetoelectric materials (seignettomagnets) are the new class of materials characterized by the coexistence of interrelated electric and magnetic dipole structures within a certain range of temperatures. This unique feature makes these materials potential candidates for many radically new applications.

BiFeO₃ with perovskite structure is one of the very few known magnetoelectric systems. It is antiferromagnetic with a relatively high Néel temperature ($T_N \sim 380^\circ\text{C}$) and ferroelectric with high T_c ($\sim 810^\circ\text{C}$). However, though its antiferromagnetism was proved beyond doubt, there was no confirmatory evidence of the presence of ferroelectricity. Due to high conductivity of the samples arising from non-stoichiometric oxygen content, it was not possible to observe saturated ferroelectric hysteresis loop. The only confirmation of the ferroelectric nature of BiFeO₃ was the observation of ferroelectric/ferroelastic domain using polarized light microscopy.

2. Experimental

Phase-pure BiFeO₃ thin films on Pt/TiO₂/SiO₂/Si substrate were grown by using pulsed laser deposition (PLD) technique. The process has been described in the patent under process [1]. PM882 GSI-Lumonics Laser is used for the ablation process. Single phase BiFeO₃ powder sample is prepared by oxide mixing technique followed by leaching with

dilute nitric acid to eliminate unreacted impurity phases [2]. Phase-pure BiFeO_3 powder thus obtained is pressed into pellet and sintered at 810°C for 1 h so as to obtain a dense target suitable for ablation. Laser ablation conditions are optimized [1], in order to realize phase pure (X-ray diffraction pattern shown in figure 1), granular, continuous (scanning electron micrograph shown in figure 2) and highly resistive BiFeO_3 thin films. The typical

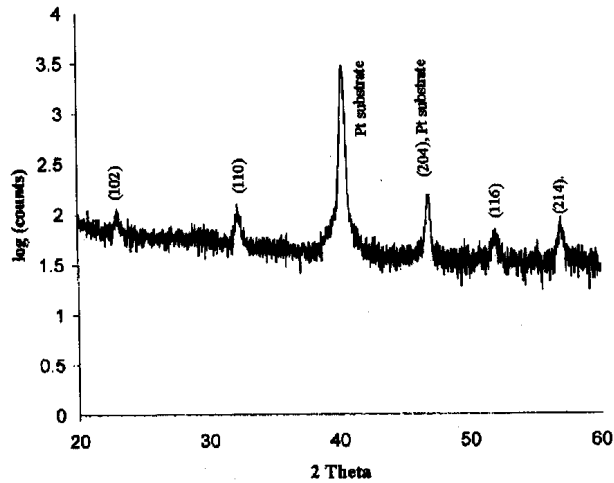


Figure 1. X-ray diffraction pattern for BiFeO_3 thin film grown on $\text{Pt/TiO}_2/\text{SiO}_2/\text{Si}$ substrate by PLD showing the film phase pure.

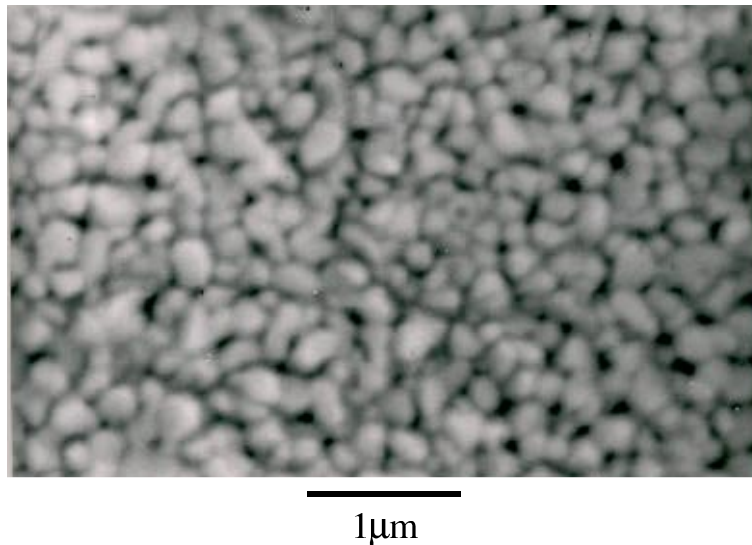


Figure 2. Scanning electron micrograph of BiFeO_3 thin film grown by PLD. The micrograph reveals that the film is granular and continuous.

conditions used during ablation were as follows: laser energy density incident on the target, – fluence $\sim 1.5 \text{ J cm}^{-2}$; target- to- substrate distance – 5 cm; substrate temperature – 625°C ; oxygen pressure – 0.3 torr.

Ferroelectric measurements were carried out on capacitors made using parallel-plate geometry. Platinum was used as the bottom electrode while the top surface was coated with silver by thermal evaporation. Circular dots of 50–100 μm diameter were patterned by photolithography followed by etching of the silver film. Saturation and remnant polarization values were determined with the help of RT 66A Radiant technologies ferroelectric loop tracer (figure 3). The dielectric response study with temperature was carried out on BiFeO₃ thin films (figure 4). The measurements were done at 1 MHz frequency with silver as top electrode and platinum as bottom electrode using a capacitance bridge (HP 4277A LCZ Meter). Differential scanning calorimetric (DSC) study was done using Perkin-Elmar DSC7 to determine antiferromagnetic to paramagnetic transition temperature (figure 5). BiFeO₃ thin films were observed under transmission electron microscope (TEM) for domain study (figure 6).

3. Results and discussion

Oxygen pressure required in the growth chamber during ablation process is found to be very critical as it is an important deciding factor for oxygen stoichiometry in the films. The deviation from oxygen stoichiometry leads to valence fluctuation of Fe ions (+3 to +2 state) in BiFeO₃, resulting in films with high conductivity. While measuring ferroelectric properties, if the samples are conducting, the applied electric field instead of inducing electric polarization gives rise to increase in current. As a result, unsaturated lossy loop is obtained. Highly energetic process like laser ablation carried out in controlled oxygen pressure helps to achieve required oxygen stoichiometry in the films. It helps to maintain Fe in +3 state. Films thus obtained are therefore highly resistive ($\rho \sim 10^8\text{--}10^9 \Omega \text{ cm}$) and hence exhibit saturated ferroelectric hysteresis loop (figure 3).

Anomaly in dielectric behavior observed in the vicinity of Néel temperature ($\sim 380^\circ\text{C}$) of BiFeO₃ is shown in figure 4. Ascher *et al* [3] have observed similar dielectric anomaly in ferromagnetolectric material like nickel–iodine boracite ($\text{Ni}_3\text{B}_7\text{O}_{13}\text{I}$) at $\sim 64 \text{ K}$ which is

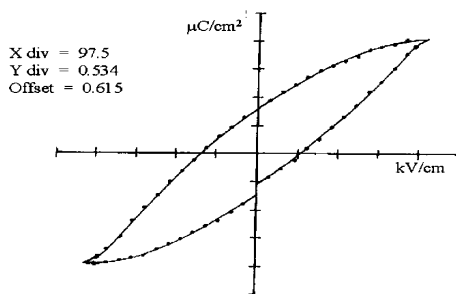


Figure 3. Ferroelectric hysteresis loop obtained for BiFeO₃ thin film grown by PLD. Film thickness 0.2 μm , resistivity $\sim 10^9 \Omega \text{ cm}$, saturation polarization (P_s) 2.2 $\mu\text{C/cm}^2$, remnant polarization (P_r) 0.83 $\mu\text{C/cm}^2$ and applied voltage 7.8 V.

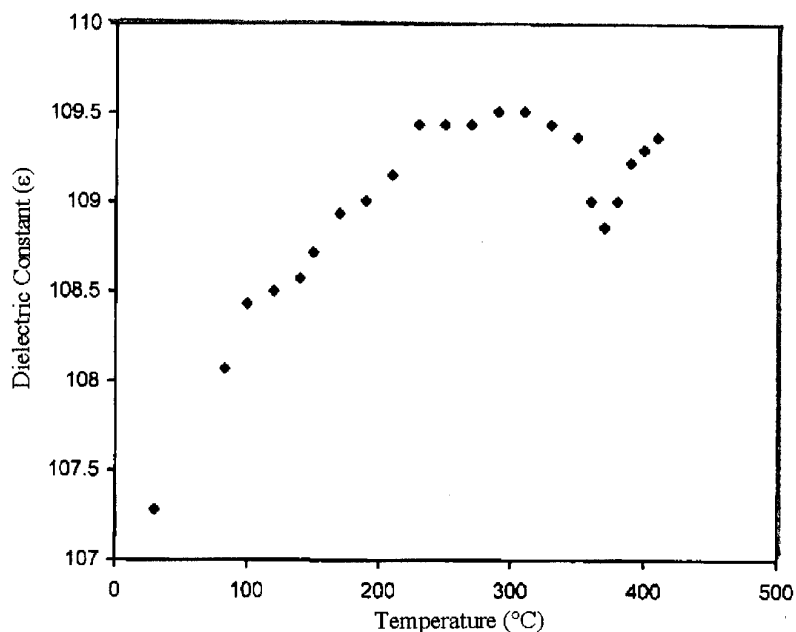


Figure 4. Plot of dielectric constant vs. temperature for BiFeO₃ thin film. Dielectric anomaly has been observed near Néel temperature (measurements frequency – 1 MHz, amplitude – 1 Vrms).

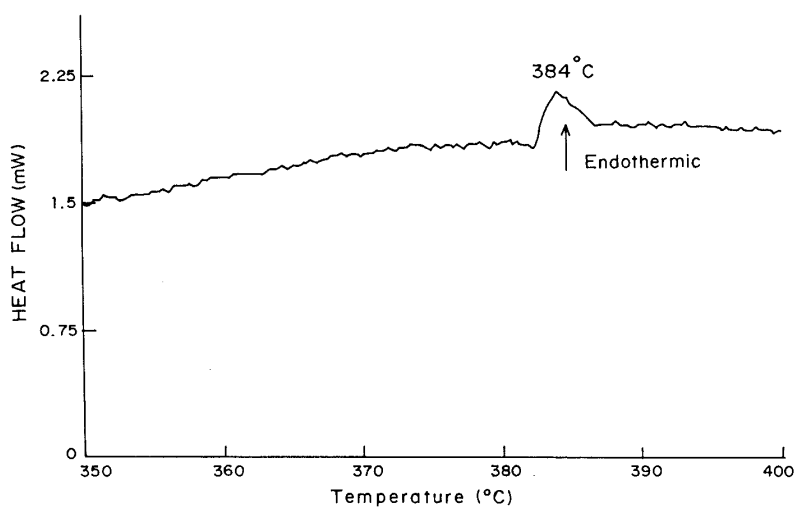


Figure 5. Endothermic peak observed near Néel temperature (384°C) in DSC curve for BiFeO₃ thin film (ambient – nitrogen, heating rate – 10°/min).

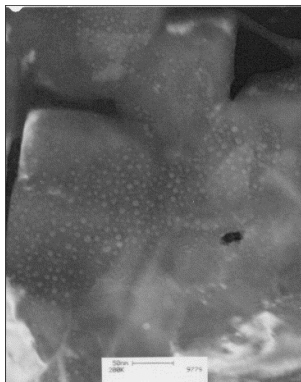


Figure 6. Transmission electron micrograph of BiFeO₃ thin film indicating *in situ* alignment of domains during sample observation.

the reported Néel temperature for the compound. The anomaly in $\varepsilon(T)$ could be related to the influence of the vanishing magnetic order on the electric order. There is an existence of structural change in BiFeO₃ occurring near antiferromagnetic to paramagnetic phase transition (Néel temperature). High temperature X-ray diffraction (XRD) study carried out on BiFeO₃ bulk sample by Rogniskaya *et al* [4] had indicated abrupt change in lattice parameters within the same rhombohedral modification occurring near Néel temperature. Figure 5 indicates the endothermic peak at $\sim 383^\circ\text{C}$ detected in differential scanning calorimetric (DSC) study of BiFeO₃ thin films. The peak in DSC curve also supports a phase transition occurring in BiFeO₃ thin films. At the structural boundary there is a coexistence of antiferromagnetic and paramagnetic ordering. Since the two neighboring structural modifications differ slightly as to their physical properties some anomaly can be expected to occur near the boundary. This is predicted by Landau–Devonshire theory of transition [5]. Generally, a transition from one crystalline structure to another is characterized by the following features:

- The electric susceptibility χ_e tends to infinity .
- It is accompanied by high fluctuations of polarization.
- A very weak field suffices to bring about a reversal in the direction of polarization.

Consequently, anomalies of the measured electric properties could be expected to occur near the boundaries separating one modification from another. Theoretically it is expected to have maxima in dielectric value. However, we have observed dielectric peaking in opposite direction. Further efforts are therefore required to explain this strange behavior.

While studying BiFeO₃ thin films under transmission electron microscope (TEM), interesting new features were observed. As seen in figure 6, when electron beam was focused on the sample, the bright spots appeared. The bright spots were disappearing when the beam was shifted from one area to the other. The spots could be an indication of the domain switching. Spot diameter matches with the width of the domain as could be seen when the domain orientation is perpendicular to the plane. It is speculated that local heating caused due to highly energetic electron beam in the presence of electric and magnetic field can cause domain switching. The domains could be either ferroelectric or magnetic since

BiFeO_3 is magnetoelectric in nature. There are no reports on such kind of *in situ* domain alignment during TEM study in simple ferroelectric or magnetic systems.

4. Summary

In summary, we have reported synthesis of highly resistive thin films of phase-pure BiFeO_3 using pulsed laser deposition technique for the first time. It has been observed that oxygen pressure in the chamber during ablation is very critical in order to maintain oxygen stoichiometry in the films. The phase-pure, stoichiometric films of BiFeO_3 thus obtained exhibit saturated ferroelectric hysteresis loop. It confirms the ferroelectric nature of BiFeO_3 for the first time. The films also show dielectric anomaly near Néel temperature. The anomalous behavior could be related to the influence of vanishing magnetic order on the electric order. *In situ* domain alignment during TEM observation has been reported for the first time.

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