

Investigations on the Structural, Optical and Magnetic Properties of RF Magnetron Sputtered Mn Doped BaTiO₃ Thin Films

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Abstract :- Barium titanate (BaTiO₃, BT) is a well known perovskite used in microelectronic industry as high permittivity capacitors, infrared detectors and transducers. The present study investigated the incorporation of manganese on the structural and optical properties of BT thin films deposited on quartz substrates by RF magnetron sputtering. Pure and Mn doped BaTiO₃ (BT:Mn) (0, 1, 3 and 5 wt %) thin films were deposited onto quartz substrates maintained at room temperature by RF magnetron sputtering. All the diffraction peaks correspond to tetragonal crystal structure of BT. It was observed that with increase in Mn concentration, the average crystallite size decreased from 18.00-12.26 nm. An average transmittance of > 80 % in visible region was observed for all the films. Doping with Mn has resulted in a red shift of absorption edge, causing a decrease of optical band gap. The photoluminescence (PL) spectra of each sample showed a sharp peak in the green band centered approximately at 554 nm and a weaker peak in the blue band centered nearly at 453 nm. PL emission intensity was found to increase with Mn concentration, but at higher concentrations (5 wt%) quenching was observed. Pure BT film shows diamagnetism, incorporation of Mn into BT lattice show ferromagnetic behavior.

Key words: Thin films, BaTiO₃, multiferroics, ferromagnetism.

1. INTRODUCTION

BaTiO₃ (BT) has been exceedingly investigated due to its very interesting practical applications in capacitors, thermistors, varistors, energy converting systems etc. Magneto electric multiferroics, such as BaTiO₃, simultaneously exhibit ferroelectricity and ferromagnetism. Such materials continue to attract great fundamental scientific interests in past several years due to their potential application in multifunctional devices, such as the data storage, magnetic filter, and sensors [1].

The perovskite structure of BT has the capability to host different sized ions and the properties of this material could be tailored by doping. Manganese (Mn) acts as an acceptor-type impurity at the grain boundaries. The size of ionic Mn is small when compared to ionic Ba or Ti. Mn also influences the microstructural and optical properties of BT thin films.

RF magnetron sputtering can produce highly uniform films having good adherence to the substrate. The method also offers the advantage of depositing films on a large area and on large scale which makes the method suitable for industrial applications. The present work deals with the preparation and characterization of pure and BT:Mn thin films by r.f. magnetron sputtering. A systematic investigation of structural, optical and photoluminescence properties is carried out. The effects of magnetic properties on BT-Mn thin films are also presented.

2. EXPERIMENTAL DETAILS

Pure BaTiO₃ and MnO₂ (99% Sigma Aldrich) powders were used for target preparation. They were mixed together in the desired proportions and ball milled for 5 h using ball milling apparatus. The sputtering target was prepared by standard ceramic procedure [2]. The target discs with four Mn compositions (0, 1, 3 and 5 wt%) were sintered 1473 K for 4h. The substrate-target distance was 5 cm. Sputtering was carried out at sputtering pressure 0.01 mbar and RF power 100 W for 2 h in pure Ar atmosphere. The films were coated on quartz substrates initially maintained at room temperature. Post deposition thermal annealing of the films at 1073 K was done in air for 1 h.

The X-ray diffraction (XRD) pattern of the films were measured by Philips X'pert Materials Research diffractometer operated at a voltage of 40 kV and a current of 30 mA, using Cu K α radiation ($\lambda=1.54 \text{ \AA}$). Optical transmittance measurements were carried out in the range 200-900 nm with a JASCO V-550 UV-visible spectrophotometer. Photoluminescence (PL) spectra of the samples were recorded using the Horiba Scientific Fluoromax-4 equipped with 150 W xenon lamp. Excitation wavelength used was 400 nm. The magnetic properties of the films were investigated by vibrating sample magnetometer, VSM (Lakeshore VSM 7410). **3.3.**

Results and discussions

3.1 XRD Studies

Fig. 1 shows the XRD patterns of pure BT and BT:Mn thin films post-annealed at 1073 K. The XRD data of the undoped BT and BT:Mn films revealed reflections at 21.88, 31.21, 38.52, 44.87 and 55.85° corresponding to the (100), (101), (111), (200) and (211) reflection planes respectively. All the prominent reflections in the pattern correspond to the tetragonal structure of BT and are indexed on the basis of JCPDS file no.81-2203. No reflections corresponding to either Mn or Mn oxides appear in the diffraction pattern of the films, indicating that no detectable secondary phase exists in BT:Mn films. These results confirm that the doped Mn ions were completely dissolved in the BT host lattice with small shift in peak position and without any significant change in the crystal structure. Intensity of the peak slightly decreased with increase in Mn concentration [3].

The average crystallite size (D) of BT: Mn films were calculated using Scherrer’s formula

$$D = \frac{k\lambda}{\beta \cos\theta} \quad (1)$$

Where, k = 0.9 is a correction factor, β the full width at half maximum (FWHM) of the most intense diffraction plane, λ the wavelength of X-ray and θ the Bragg angle.

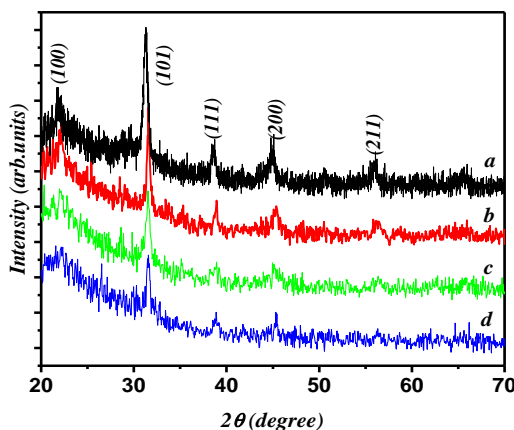


Fig.1 XRD pattern of BT:Mn thin films (a) 0, (b) 1, (c) 3 and (d) 5 wt %

The crystallite size decreased with increase in Mn content. From Table 1 it was observed that, the crystallite size of BT: Mn nanoparticles reduced from 18.0 - 12.26 nm with increase in Mn concentration. This indicates that the presence of Mn ions in BT, prevented the growth of crystallites. This effect is in conjunction with the smaller ionic radius of Mn²⁺ ion (0.82 Å) in comparison with Ba²⁺ (1.61) and Ti⁴⁺ (0.94). This can disturb the long range crystallographic ordering and hence, reducing the crystallite size. It is observed that the lattice parameter (c) decreases from 4.028 Å for pure BT film to 4.008 Å for 5.0 wt% BT:Mn film. This indicates that the Mn²⁺ ions with radius 0.82 Å might have completely incorporated into BT lattice.

Table 1. Full Width Half Maximum (β), Lattice Parameter

Mn concentration (wt%)	β (rad)	c (Å)	D (nm)	E _g (eV)	t (nm)
0	0.0071	4.028	18.00	4.01	448
1	0.0079	4.016	17.77	3.45	387
3	0.0099	4.009	14.54	3.36	354
5	0.0101	4.008	12.26	3.32	306

(c), Crystallite Size (D), Band gap (E_g), and Thickness (t) of BT:Mn Films for Various Mn Concentrations.

3.2 Optical Studies

UV–vis optical transmission spectra of BT:Mn thin films are shown in Fig. 2. An average transmittance >70 % was observed for all the films. It was very clear from the transmittance spectra that the pure BT film had better transparency than BT:Mn films (89% at 537 nm for pure BT film and 57% for 5 wt% Mn:BT films). The transmittance slightly decreases with increase in Mn concentration. The absorption edge shifts towards longer wavelengths (red shift) with increase in Mn dopant concentration.

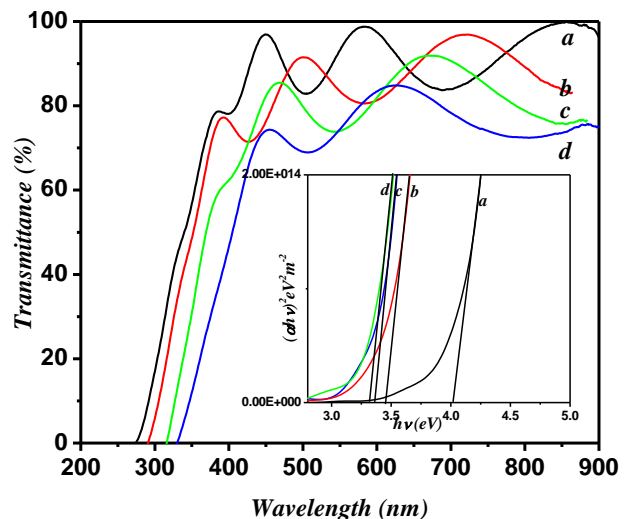


Fig. 2 Transmittance spectra of BT: Mn thin films (a) 0, (b) 1, (c) 3 and (d) 5 wt%. Inset shows (αhν)² versus hν plot.

The optical band gap can be deduced from transmission measurements using Tauc relation $\alpha h\nu = A (h\nu - E_g)^n$ (2)

Where, A is a constant, E_g, the band gap of the film and n = 1/2 for direct transition.

The measured optical band gap decreased from 4.01 - 3.31 eV with increase in the Mn concentration (Table 1). The BT:Mn films shows a decrease in the optical band gap values originating from the breaking of structural symmetry. This decreasing in the values is due to the appearing of the localized states into the band gap region [4].

3.3 Photoluminescence Properties

Fig.3 shows the photoluminescence spectra of BT:Mn films at an excitation wavelength of 400 nm. PL spectra of BT:Mn thin films exhibited emission bands in visible region. The emission spectra of BT:Mn films consists of emission peaks at 452 and 553 nm, 453 and 554 nm and 451 and 555 nm, respectively for 1,3 and 5 wt% Mn doping. The incorporation of Mn^{2+} ion into the BT lattice leads to formation of doubly charged oxygen vacancies to compensate the charge imbalance. Douglas et al. attributed the blue luminescence to donor-acceptor pair radiative recombination mode in Mn doped ZnS phosphor [5]. In our case, it is expected that a similar mechanism may be responsible for blue luminescent i.e., radiative recombination from some donor states associated with oxygen vacancies (due to certain defects) to acceptor states of manganese.

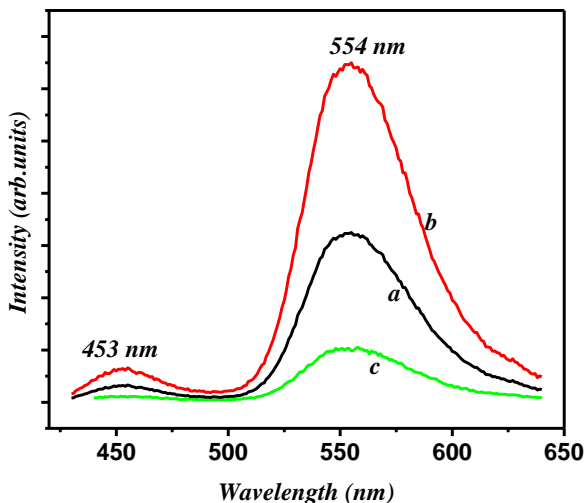


Fig. 3 Photoluminescence spectra of BT: Mn thin films (a) 1, (b) 3 and (c) 5 wt%.

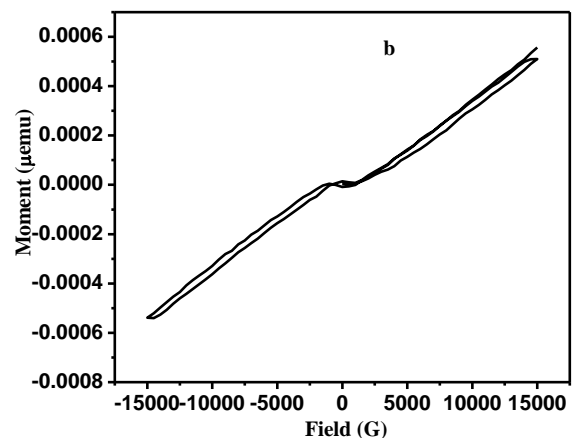
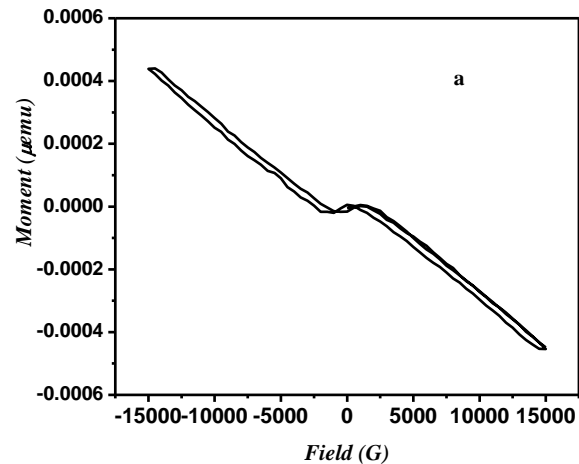
The emission peaks centered in the green band (554 nm) may be attributed to intraband transitions from higher excited states of Ti^{3+} or self trapped excitons. The intensity of luminescent emission increases with the increase in Mn dopant concentration (1-3 wt%), which may be attributed to the increase in oxygen vacancies as a function of dopant concentration. Probably, after incorporating Mn ions into the BT host matrix, the defect still plays a dominant role with respect to the luminescence processes. Generally, oxygen vacancies are known to be the most common defects and usually act as radiative centers in luminescence processes. This may be the reason for the increment in the PL intensity after introducing the Mn ions into the BT matrix.

As it is seen in the spectra, at 5 wt% Mn, the intensity gets decreased. This is due to concentration

quenching. At higher amount of Mn doping, mutual activator quenching seems to be dominating which means that when the Mn^{2+} ion concentration goes beyond an optimum value within a given radius, suppression of each ions effect dominates, resulting in reduction of luminescence efficiency in the blue/green band. Hence, the presence of Mn in BT films probably induces a high density of defects, which act as nonradiative centers and affects the intensity of emitted light.

3.4 Magnetic properties

The magnetic properties of BT:Mn films were investigated by using vibration sample magnetometer (VSM). Fig.4 (a)-(d) shows the magnetization-field (M-H) hysteresis loops of pure and BT:Mn thin films. The M-H curve of pure BT shows the diamagnetic behavior. The magnetization measurement of pure BT sample exhibited diamagnetic nature (Fig. (4 a)) confirming that there is no positive susceptibility contribution from defects and oxygen vacancies of BT, which has been cautioned to be a universal feature of nonmagnetic oxide nanoparticles. The diamagnetic behavior of pure BT film suggests that the ferromagnetic signal in BT: Mn films are solely due to the presence of Mn ions in BT host matrix. The M-H curves of BT:Mn films with higher Mn-doping concentrations exhibit room temperature ferromagnetism (RTFM).



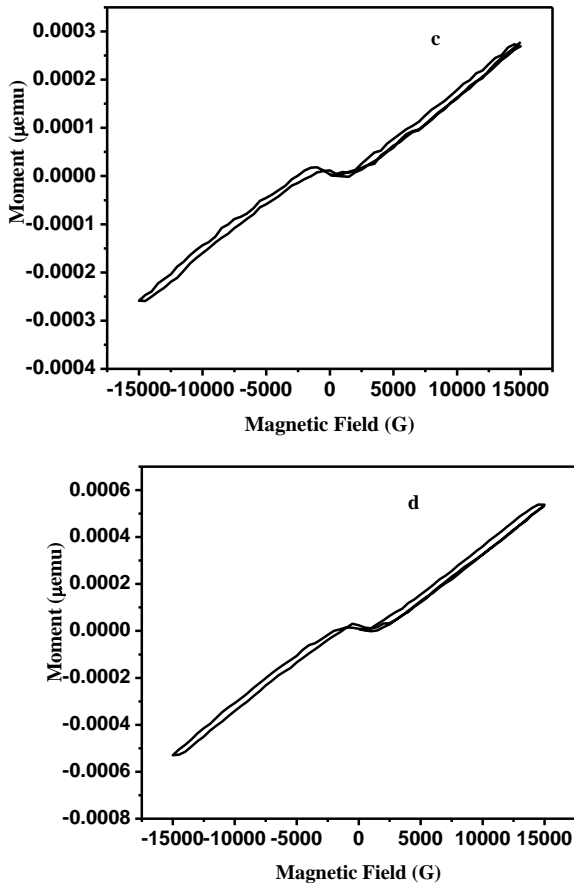


Fig. 4. (a) M-H curve of (a) pure BT (b) 1 (c) 3 and (d) 5 wt% of Mn doped BT: Mn films

In 1 - 5 wt% BT: Mn films, ferromagnetic behaviour was observed. This magnetic behavior may be due to the substitution of Mn into BT lattice. The room-temperature ferromagnetism of BT:Mn films was attributed to bound magnetic polarons (BMPs) formed by localized electrons and Mn^{2+} [6]. With the increase in Mn^{2+} ions, the reduced value of magnetization might be attributed to the direct Mn-Mn paramagnetic or anti ferromagnetic exchange coupling between the neighboring Mn^{2+} ions through O^{2-} ions ($Mn^{2+}-O^{2-}-Mn^{2+}$) that reduce the ferromagnetic signal. With the increase of Mn concentration in BT films, crystallization of the films decreased as observed from the XRD patterns. This can cause decrease in the magnetic moment in the films and affect the magnetic order. Therefore, the total magnetization of the BT: Mn (1-5 wt%) films are due to the sum total of a ferromagnetic and a paramagnetic part.

CONCLUSIONS

This study systematically discussed the influence of Mn^{2+} doping concentration on BT films prepared using rf magnetron sputtering. Undoped and BT: Mn films were deposited by rf magnetron sputtering onto quartz substrates. Effect of the Mn content on the structural, morphological, optical and magnetic properties of the BT films were investigated. The incorporation of Mn into the BT film caused a decrease in crystallite size. The optical band gap values decreased from 4.01 - 3.32 eV with increasing Mn doping. The intensity of the PL emission peaks increased with increase in Mn doping concentration.

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