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STRUCTURAL, DIELECTRIC AND MAGNETIC PROPERTIES OF EPITAXIAL GROWN $YMn_{0.5}Cr_{0.5}O_3$ THIN FILMS

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$YCr_{(1-x)}Mn_xO_3$ is an intriguing member of the perovskite family, attracting significant interest due to its versatile properties and potential applications in various fields. Epitaxial orthorhombic $YMn_{0.5}Cr_{0.5}O_3$ films are grown on STO substrates by pulsed laser deposition method. Well crystalline with (0 ℓ 0) orientation of $YMn_{0.5}Cr_{0.5}O_3$ films are identified by X-ray diffraction. Field emission scanning electron microscopy used to capture the morphological behavior of crystalline $YMn_{0.5}Cr_{0.5}O_3$ films. Temperature dependent dielectric properties are analyzed thoroughly. The magnetic properties of $YMn_{0.5}Cr_{0.5}O_3$ films are characterized using physical property measurement system. There is a clear magnetic transition observed around 60K for three $YMn_{0.5}Cr_{0.5}O_3$ films. Films deposited at 600°C exhibited high dielectric and magnetic properties.
Keywords: *Thin films; Multiferroics; Dielectric properties; Magnetic properties*
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INTRODUCTION

Multiferroics are the materials which exhibits both the ferroelectric and ferromagnetic properties together, have gained much interest due to possibility of significant applications such as sensors, telecommunications, and non-volatile memory devices etc. From past few years, the extensive work has been going on different material compounds ($BiFeO_3$, $YMnO_3$ and $GaFeO_3$) in order to explore the multiferroics properties [1-3]. In addition to these materials, recently, rare-earth chromites ($RCrO_3$, R = Y, Ho, Er, Yb) have found to exhibit the multiferroic properties due to antiferromagnetic nature and local non-centrosymmetric behavior [4-6]. These multiferroic properties are extracted from the interaction between rare-earths (R^{3+}) and chromium (Cr^{3+}) cations. Among the rare-earth orthochromites $YCr_{(1-x)}Mn_xO_3$, have exhibited the temperature dependence of magnetic, ferroelectric and dielectric properties due to spin-phonon coupling. $YCr_{(1-x)}Mn_xO_3$, a derivative of the well-known perovskite $YCrO_3$, has emerged as a fascinating material in the field of materials science due to its diverse and tunable properties [7-8]. The broad spectrum of potential applications and the ability to fine-tune the properties of $YCr_{(1-x)}Mn_xO_3$ by adjusting the Mn concentration underscore its significance. As researchers continue to develop into its complexities, this material stands out as a promising candidate for next-generation technologies. Its adaptability and multifunctionality position of $YCr_{(1-x)}Mn_xO_3$ at the forefront of materials science, promising exciting developments in both fundamental research and practical applications. Studies have been carried out with $YCr_{(1-x)}Mn_xO_3$ in bulk ceramic form, Sinha *et al* studied the electric and optical properties of $YCr_{(1-x)}Mn_xO_3$ nanoparticles [9]. Zhang et.al, explored the effect of Mn content on electric properties and activation energy [10]. Rajeswaran et.al, studied the ferroelectric and ferromagnetic properties [11]. However there haven't been many studies on thin film form of $YCr_{(1-x)}Mn_xO_3$. Properties in thin film form are strongly related to microstructural and thickness. For example, $BiFeO_3$ exhibits the ferroelectric behavior in thin films rather than to bulk form. Hence it important to study $YCr_{(1-x)}Mn_xO_3$ in thin film form in order to explore multiferroic behavior in detail. There are different methods, such as physical vapor deposition methods (RF sputtering, pulsed laser deposition, evaporation etc,), chemical vapor deposition techniques (sol-gel, hydrothermal, combustion synthesis etc.). Pulsed laser deposition is the most suitable technique among all the others for compounds deposition to obtain stoichiometrically balanced thin films. This manuscript discusses the temperature dependence of dielectric and magnetic characteristics, as well as morphological studies, and describes fabrication single phase epitaxial $YCr_{(1-x)}Mn_xO_3$ thin films.

EXPERIMENTAL

Polycrystalline $YCr_{0.5}Mn_{0.5}O_3$ bulk powder samples were synthesized by solid state method with help of the stoichiometric compounds such as Y_2O_3, Cr_3O_3 and Mn_2O_3 at 1400 °C about 40 h with grinding at different interval of time. X-ray diffraction technique used to confirm the phase purity of final powder samples. These crystalline $YCr_{0.5}Mn_{0.5}O_3$ powders were pressed and sintered at various temperatures in order to get good densification for the sputtering target compound. Highly densified (95%) target was used to deposit the thin films. The pulsed laser deposition method was used to deposit $YCr_{0.5}Mn_{0.5}O_3$ thin films on STO substrates at different temperatures. Prior to deposition,

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high vacuum ($10x^{-5}$ Torr) was created using turbo molecular pump in order to avoid the impurities in the films. Mixture of oxygen; argon atmosphere was maintained during the thin film deposition. Thin film deposition optimized condition is tabulated in Table 1. Deposited thin films crystalline nature and phase purity was examined by X-ray diffractometer (Bruker D8 advanced diffractometer). Grain size, shape and surface morphology studies were obtained from FE-SEM (Car Zeiss, Ultra 55). QD-PPMS-6600 was used to study the magnetic measurements of $YCr_{0.5}Mn_{0.5}O_3$ thin films. LCR meter and electrometer was used to study the dielectric properties of $YCr_{0.5}Mn_{0.5}O_3$ thin films.

Table 1. Dielectric constant and loss tangent at various deposition temperatures.

S.No	Deposition temperature	Dielectric constant	Loss tangent
1	500 °C	161	1.2
2	600 °C	183	0.8
3	700 °C	165	0.85

RESULTS AND DISCUSSION

Structural properties

Figure 1(a-c) shows the X-ray diffraction pattern of the $YCr_{0.5}Mn_{0.5}O_3$ thin films deposited at various temperatures (500–700°C) on STO (0 ℓ 0) oriented substrates.

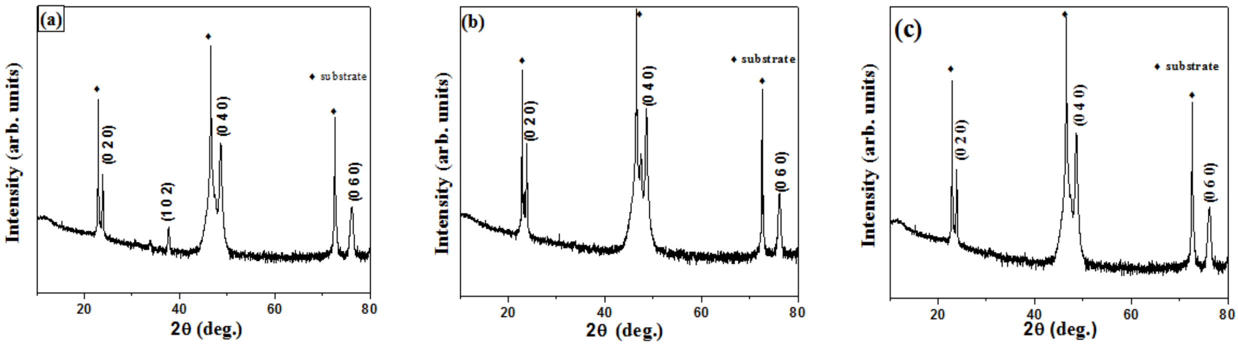

Figure 1. X-ray diffraction pattern of $YCr_{0.5}Mn_{0.5}O_3$ thin films deposited at (a) 500°C (b) 600°C (c) 700°C

As it was observed from Figure 1, all the films were crystallized into orthorhombic structure (*pnma*) with (0 ℓ 0) orientation which indicates that the epitaxial nature of the films. Films deposited at 500°C exhibited crystalline nature and epitaxial grown along with other peaks from (1 0 2) reflections due to low annealing temperature. Films deposited at 600°C and above exhibited good crystalline nature and perfect epitaxial growth without any other peaks. The X-ray diffraction patterns demonstrates that the films exhibited crystalline nature and phase purity without any secondary phases. The lattice parameters of $YCr_{0.5}Mn_{0.5}O_3$ thin films and STO substrates are nearly same which results in films were grown in (0 2 0) (0 4 0) and (0 6 0) orientations.

$$D = \frac{k\,\lambda}{\beta\cos\theta}. \qquad (1)$$

Scherer's equation was used to calculate the crystallite size of the thin films. Formula description was provided by A Rambabu et.al [12]. The crystallite values are estimated for films deposited at 500°C, 600°C and 700°C are 25, 33 and 45 nm respectively.

Morphological studies

Figure 2(a-c) showed the surface morphology images of the $YCr_{0.5}Mn_{0.5}O_3$ thin films deposited at different temperature (500–700°C) obtained from field emission scanning electron microscopy. Films deposited at 500°C shows relatively uniform distribution of grains with smooth spherical morphology and closely packed. However, grain size is around 80 nm due low annealing temperature. Films deposited at 600°C exhibits the grain size is around 110 nm with good packing density. On other hand, films deposited at 700°C morphology has less dense and separation between the grains is more due to high temperature treatment during thin film deposition.

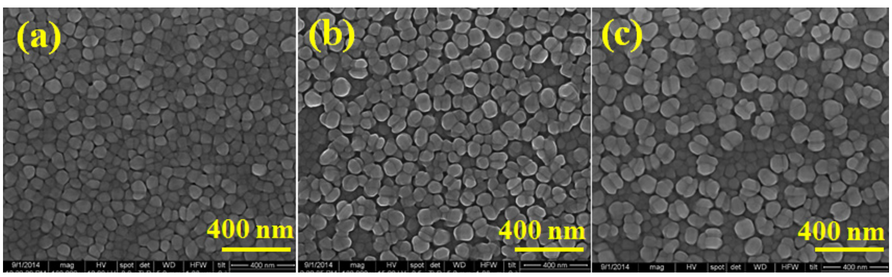

Figure 2(a-c). Surface morphology images of $YCr_{0.5}Mn_{0.5}O_3$ thin films deposited at (a) 500°C (b) 600°C and (c) 700°C

Dielectric properties

Temperature dependent dielectric properties of $YCr_{0.5}Mn_{0.5}O_3$ thin films deposited at various temperatures are shown in Figure 3(a-f). These dielectric measurements were carried out at different frequencies (50 KHz, 100 KHz, 500 KHz and 1 MHz) for all three $YCr_{0.5}Mn_{0.5}O_3$ films. Dielectric properties revealed that the $YCr_{0.5}Mn_{0.5}O_3$ thin films are invariable dependent on temperature as well as frequency. The dielectric constant increases with temperature, peaking at around 300K temperature and then slowly decreases. On other hand, as the frequency increases, dielectric constant decreases as it noticeable significance in multiferroic/dielectric materials. This behavior was consistent across all the frequencies and for all the thin films. There is clear temperature dependent relaxation was observed around 300K for all $YCr_{0.5}Mn_{0.5}O_3$ thin films due to a Maxwell-Wagner like effect with dielectric anomaly at 300K. The relaxation (peak broadening) in dielectric constant behavior at 300K is the noteworthy characteristic of typical relaxor behavior of the bulk ceramic samples, which have reported by many authors [13-15]. Similar effect was observed in case of dielectric losses as well. The presence of dielectric anomaly at T_N, indicates that the magneto dielectric effect. It is surprising to see this magneto dielectric effect in $YCr_{0.5}Mn_{0.5}O_3$ thin films, which was not observed even in $YFeO_3$ and $YCrO_3$ compounds. Films deposited at 600ºC exhibited the highest dielectric properties compared to films deposited at 500 and 700ºC. These results are well supporting to structural and morphological studies. The dielectric constant and loss tangent values for three $YCr_{0.5}Mn_{0.5}O_3$ thin films are tabulated in table 1 for the frequency at 50 KHz. Films deposited at 500ºC exhibited the less dielectric properties due to less crystallization nature. Similarly, films deposited at 700ºC showed the less dielectric properties to due to poor densification and oxygen losses at high temperatures. Overall, films deposited at 600ºC showed good dielectric properties which are favorable to device applications.

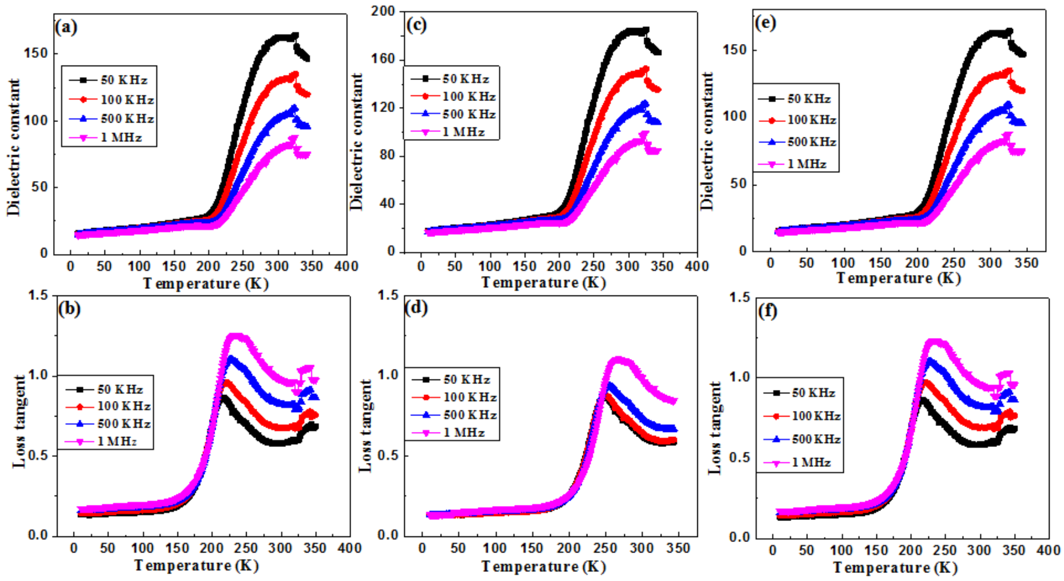

Figure 3 (a-b). Dielectric constant and loss tangent of $YCr_{0.5}Mn_{0.5}O_3$ thin films deposited at 500ºC (c-d) Dielectric constant and loss tangent of $YCr_{0.5}Mn_{0.5}O_3$ thin films deposited at 600ºC (e-f) Dielectric constant and loss tangent of $YCr_{0.5}Mn_{0.5}O_3$ thin films deposited at 700ºC

Magnetic properties

Magnetic properties of $YCr_{0.5}Mn_{0.5}O_3$ thin films are shown in Figure 4 (a-f). Figure 4(a) indicates the magnetization of hysteresis curve in the range of ±5T magnetic field. The hysteresis curve showed inferred loop with well symmetric along the field axis and exhibited no proper saturation. This indicates that films deposited at 500ºC exhibits the weak ferromagnetism. Figure 4(c) shows the hysteresis curve for the films deposited at 600ºC. It's clear from the curve that the magnetization properties of $YCr_{0.5}Mn_{0.5}O_3$ thin films are enhanced with well saturation. This indicates that anti-ferromagnetism behavior decreases and exhibits the strong ferromagnetic behavior [16-17]. However, films deposited at 700 ºC exhibited weak anti-ferromagnetism and ferromagnetism due to pores created at high fabrication temperature, which supports the structural and morphological studies. Overall, films deposited at 600ºC, exhibited superior magnetic properties compared with films deposited at 500ºC and 700ºC. Figure 4 (b, d, f) displays the temperature dependent field cooled magnetization of $YCr_{0.5}Mn_{0.5}O_3$ thin films at an applied field of 100 Oe in a temperature range from 0 – 400ºK. The clear magnetization transition was observed for the $YCr_{0.5}Mn_{0.5}O_3$ thin films deposited at different temperatures. The transition exhibited at 67,55 and 59 K for films deposited at 500ºC, 600ºC and 700ºC respectively. It's surprising to observe the transition temperature decreased compared to pristine $YCrO_3$. This is attributed due to double exchange interaction between Mn^{4+}/Cr^{3+} and Mn^{3+} ions [18-19]. This kind of mechanism reveals that the weakening of antiferromagnetic interaction among Cr^{3+} ions and develops the ferromagnetic behavior which results in decrease in Neel temperature [20]. Properties of the films deposited at 600ºC exhibited the favorable ferromagnetic behavior with low Neel temperature.

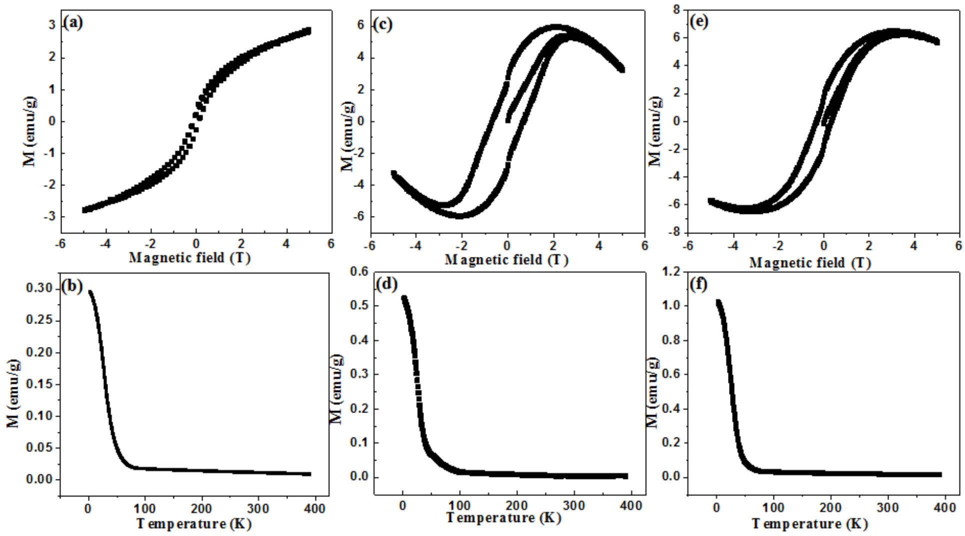

Figure 4 (a-f). Magnetic moment of $YCr_{0.5}Mn_{0.5}O_3$ thin films deposited at 500ºC with respect to: (a) magnetic field (b) temperature; magnetic moment of $YCr_{0.5}Mn_{0.5}O_3$ thin films deposited at 600ºC with respect to (c) magnetic field (d) temperature; magnetic moment of $YCr_{0.5}Mn_{0.5}O_3$ thin films deposited at 700ºC with respect to (e) magnetic field (f) temperature (measured temperature 2K)

CONCLUSIONS

In summary, we have successfully fabricated the epitaxial grown$YCr_{0.5}Mn_{0.5}O_3$ thin films on STO substrates using pulsed laser deposition. Dielectric and magnetic properties of $YCr_{0.5}Mn_{0.5}O_3$ thin films at low temperatures were studied. Films deposited at 600ºC exhibited superior dielectric properties with relaxer behavior. Substitution of $Mn^{4+/3+}$ ions result in weakening of antiferromagnetic nature and strengthening of ferromagnetic behavior. These results indicates that the careful optimized $YCr_{0.5}Mn_{0.5}O_3$ thin film are favorable for fabrication of multistate memory and spintronic devices.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper

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СТРУКТУРНІ, ДІЕЛЕКТРИЧНІ ТА МАГНІТНІ ВЛАСТИВОСТІ ЕПІТАКСІАЛЬНОГО НАРОЩЕННЯ ТОНКИХ ПЛІВОК $YMn_{0,5}Cr_{0,5}O_3$

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$YCr_{(1-x)}Mn_xO_3$ є інтригуючим членом сімейства перовскітів, який привертає значний інтерес завдяки своїм універсальним властивостям і потенційним застосуванням у різних областях. Епітаксіальні орторомбічні плівки $YMn_{0.5}Cr_{0.5}O_3$ вирощені на підкладках STO методом імпульсного лазерного осадження. Добре кристалічні з орієнтацією (0 ℓ 0) плівки $YMn_{0.5}Cr_{0.5}O_3$ ідентифіковані за допомогою рентгенівської дифракції. Полеемісійна скануюча електронна мікроскопія використовується для фіксації морфологічної поведінки кристалічних плівок $YMn_{0.5}Cr_{0.5}O_3$. Температурно залежні діелектричні властивості ретельно аналізуються. Магнітні властивості плівок $YMn_{0.5}Cr_{0.5}O_3$ охарактеризовано за допомогою системи вимірювання фізичних властивостей. Існує чіткий магнітний перехід, який спостерігається близько 60 K для трьох плівок $YMn_{0.5}Cr_{0.5}O_3$. Плівки, нанесені при 600°C, показали високі діелектричні та магнітні властивості.
Ключові слова: *тонкі плівки; мультифероїки; діелектричні властивості; магнітні властивості*