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Synthesis of High Throughput Multiferroic Nanocomposite for using Sol-Gel Process

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ABSTRACT

Multiferroic ceramic thin films are important for their application in electro-optic, computer memories, smart sensors, and high frequency microelectronic devices. Coexistence of magnetism and ferroelectricity in ordered thin films offers additional degree of freedom for the said applications. In the present work we have synthesized $La_{0.65}Sr_{0.35}MnO_3$ (LSMO) / $Pb_{0.85}La_{0.15}TiO_3$ (PLT15) composite thin films by sol-gel technique. The volume content of LSMO was maintained in 3:7 ratio in PLT15 matrix. Scanning electron microscopy and X-ray diffraction reveal the microstructure and phases in the films. Vibrating sample magnetometer, ferroelectric test unit were used to characterize magnetic and dielectric properties of LSMO-PLT composite film.

Keywords-- Multiferroic, thin films, sol-gel, nanocomposite

I. INTRODUCTION

Multiferroic materials are attractive for their potential applications in multiple-state memories, spintronics, and sensors [1, 2]. The most important property of multiferroic materials is the coexistence of at least two primary ferroic states. These ferroic states are ferroelasticity, ferroelectricity and ferromagnetism. However, the most interesting combination is multiferroic materials which present ferroelectricity and ferromagnetism. All the multiferroic materials that have been studied can be classified into two categories: single phase ferroelectromagnets and multiferroic composites. Most of single phase multiferroic can be used only at very low temperature which would further complicate the design of the fabricated devices. As an effective alternative, magnetoelectric effect “product properties” based composites are a model system with large linear magnetoelectric (ME) coefficient at room temperature. For preparing nanocomposite thin films, sol–gel route is a versatile method with several advantages, such as low processing temperature, non-vacuum process, low cost equipment required, and large area deposition [3]. The two phases – ferroemagnetic and ferroelectric prepared by sol-gel processes for multiferroic nanocomposite films were typically deposited from different sources, and the nanocomposite multiferroic films were formed by a spontaneous phase separation process that occurred during the deposition or annealing process [4, 5, 6, and 7]. Depending on phase connectivity [8], the structures of a two-phase composite depict by some notation such as 1-3, 2-2, 0-3, etc., in which each number denotes the connectivity of the phase. Among those, connectivity 0-3-types nanocomposite film structure with the less-resistive CFO phase embedded in PZT matrix is leading to enhance strong magnetoelectric coupling. In this present work, attempt has been made to improve the ferromagnetic and ferroelectric behaviors of 0-3 type composite thin films. We report a hybrid synthesis method for nanocomposite multiferroic thin film with nano-scale mixed strontium-doped lanthanum manganite (LSMO) and $Pb_{0.85}La_{0.15}TiO_3$ (PLT15) phase. The precursors of both the ferromagnetic and ferroelectric phases were mixed before spin coating. The spin coating of the mixed precursor solution of the ferromagnetic and ferroelectric phases on platinized silicon substrates allows for nanoscale mixing of the subsequent multiferroic composite phases. The microstructures of the films were determined using a field emission scanning electron microscope (FESEM). It revealed fine nano-grain size PLT15 film and a deeply buried distribution of LSMO in the PLT15 matrix with a crack-free surface. The nanofilm thickness has been confirmed by Profilometer and by cross-sectional view of FESEM. Room temperature ferroelectric and magnetic properties were characterized by measuring polarization hysteresis (P-E loop) and magnetization hysteresis (M-H loop).

II. EXPERIMENTAL

PLT15 and LSMO are adopted as a piezoelectric and magnetostrictive phase respectively for nanocomposite thin films multiferroic property study. PLT15 is prepared by hybrid sol-gel route and LSMO is synthesized using metal salt solution route. To prepare 0.25M PLT15 precursor sol, lead acetate tri-hydrate ($Pb(CH_3COO)_2.3H_2O$), lanthanum nitrate hexahydrate ($LaN_3O_9.6H_2O$) and titanium *butoxide* [$Ti(OC_4H_9)_4$] are used. Lead acetate tri-hydrate and lanthanum nitrate were dissolved in warm acetic acid through continuous stirring. In a separate three-neck flask, stoichiometric titanium butoxide is dissolved in glacial acetic acid (in 1:2 molar ratio) to reduce the moisture sensitivity of the alkoxide precursor. The chelated sol thus prepared is added drop by drop to the mixed solution of lead acetate tri-hydrate and lanthanum nitrate through continuous stirring for 15-20 minutes to prepare PLT15 precursor sol. Simultaneously for preparing $La_{0.65}Sr_{0.35}MnO_3$, lanthanum oxide (La_2O_3),strontium hydroxide ($Sr(OH)_2$. $8H_2O$), manganese chloride($MnCl_2$.4 H_2O) and sodium hydroxide (NaOH) were used as as-received. 1 mol/L aqueous solution of La_2O_3, $Sr(NO_3)_2$, and $Mn(NO_3)_2$ were mixed according to stoichiometric amounts. To this mixture, aqueous sodium hydroxide is added dropwise to adjust the pH to about 6 at 50 ^oC for synthesis 0.25M LSMO precursor sol. These two chemicals are dissolved into acetic acid and mixed together in 1:2 molar ratios. Finally LSMO precursor sol is mixed in 3:7 volume ratios in to PLT15 precursor sol through continuous stirring. This LSMO-PLT15 precursor sol is deposited on the cleaned $Pt/Ti/SiO_2/Si$ substrate by spin coating technique. The coating speed and time is kept at 4000 rpm and 30 s, respectively. The gel films thus prepared are directly inserted into a preheated furnace kept at 400 ^oC and heated for 300s for the removal of organics. The coating and firing steps are repeated 10 times to attain films approximately 450 nm thick. The resultant films are annealed at 700^oC for 1h in the air for crystallization followed by normal furnace cooling. Phase formation behaviors of the calcined films are evaluated using an X-ray diffractometer using CuKα radiation (Ultima III, Rigaku, Japan). Thickness of the films are measured by Surface profilometer (NCS model, Taylor Hobson). Surface morphologies and cross-sectional view of these thin films are investigated using field emission scanning electron microscopy (FESEM) Magnetic behaviors are studied using a 14T Vibration Sample Magnetometer (Quantum design ,Model-6000, physical property measurement system). For the measurement of electrical property a musk with circular diameter ~ 0.3mm is used to deposit gold as top contact on the film surface. Ferroelectric hysteresis loops are measured using a precision pro ferroelectric analyzer (Radiant Technologies Inc., USA).

III. RESULTS AND DISCUSSION

Structural characteristics of LSMO-PLT15 nanocomposite thin films are evaluated by X-ray diffraction (XRD) technique using Cu Kα radiation.

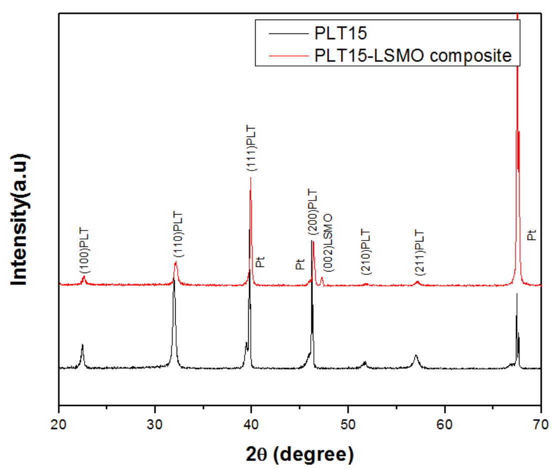

Fig. 1. X-ray diffractograms of annealed PLT15 and PLT15-LSMO composite thin film

Figure 1 shows the typical XRD pattern of PLT15 and PLT15-LSMO nanocomposite thin films. Desired perovskite structure of PLT15 is identified without any preferential crystallographic orientations. In the PLT15-LSMO composite film, only (002) diffraction peaks corresponding to LSMO (LSMO ~ 47.16°)The first three major diffraction peaks of 700^o C annealed PLT15 thin film have been fitted by Gaussian method. From this fitted data, accurate

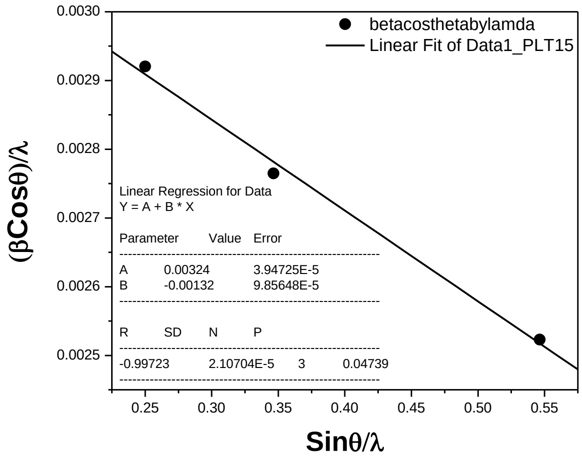

Fig. 2. Liner fit of βCosθ/λ as a function of Sinθ/λ of annealed PLT15 composite thin film.

full width half maxima(β) and the brag diffraction angles(θ in radian) were obtained for each peaks. These data were used in Figure 2 to plot βCosθ/λ as a function of Sinθ/λ, and from linear fit of the plot, the crystallite size (t) is calculated from the intercept which is nearly 29 nm. Figure 3 shows the surface morphologies of annealed PLT15-LSMO films which

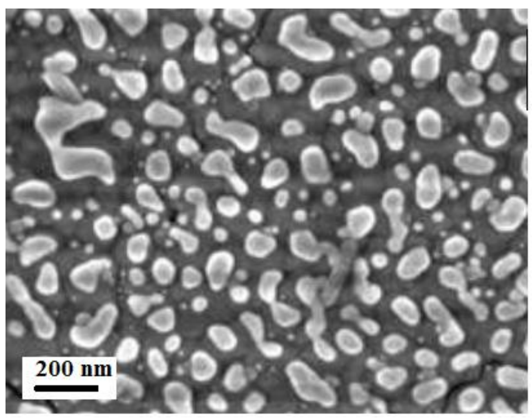

Fig. 3. Surface morphologies of PLT15-LSMO composite thin films.

exhibit uniform nano-size grain microstructure. Both the PLT phase and LSMO phase can be identified together as shown in Figure 3 nanocomposite thin film. The PLT15 and LSMO phases show well-defined grains with their grain sizes in the range of 30–50 nm of PLT15 with LSMO nanograins (bright spots) 10-15 nm nearly surrounded by PLT nanograins, which indicates

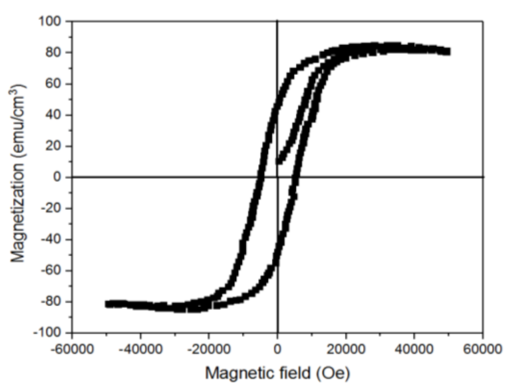

Fig. 4. The magnetic hysteresis characteristics of PLT15 and LSMO-PLT15 composite thin films.

nanoscale mixture of the LSMO phase and PLT phase. In order to verify the multiferroicity of PLT15-LSMO films nanocomposites, we examined the ferromagnetic properties where magnetic hysteresis loops measured along in-plane direction at room temperature. Figure 4 shows hysteresis loops of LSMO-PLT composite film at 300 k. It is also noted that saturated magnetization (M_s) and remanent magnetization (M_r) are proportional with the magnetic content.

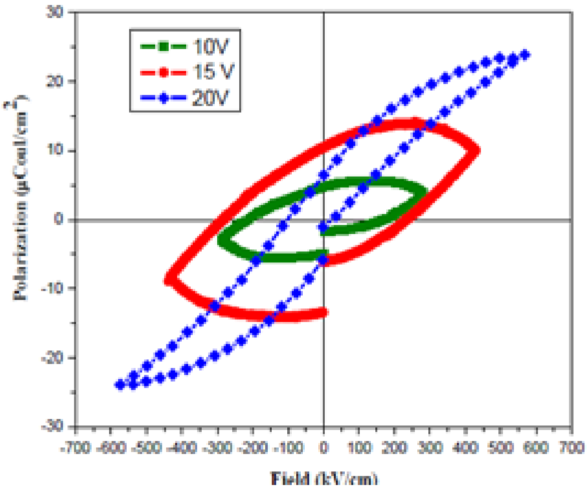

Fig. 5. The polarization hysteresis characteristics of PLT15 and LSMO-PLT15 composite thin films

The (P–E) hysteresis loops of composite PLT15-LSMO thin films at room temperature are shown in Figure 5. All the films show a normal hysteresis behavior. Saturated polarization (P_s) and remanent polarization (P_r) are decreased due to the dilute influence of LSMO on PLT15 thin films.The P-E loop shown sharp at 20V applied bias field with less leakage.

IV. CONCLUSION

We have synthesized 0-3 type LSMO-PLT15 nanocomposite thin film by a hybrid sol-gel process in which a mixed precursor solution of the LSMO phase and the PLT phase was used. The microstructure shows well defined nano-magnetic particle dispersion in nano-fine grain of PLT15 matrix. Room temperature ferroelectric and ferromagnetic properties are simultaneously achieved in nano-composites thin films which evidence of multiferroic property. Further experimental work in the future will be focused on the temperature and magnetic field dependence of the ME voltage coefficient measurement, which is expected to be a good parameter for applications of data storage, magnetic field measurement, smart sensor, transformer, etc.

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