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The Photoluminescence and Ferromagnetic Behavior of Sprayed $LaMnO_{2.75}$ thin Layers

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Abstract. The study of Sr-doped lanthanum manganites (La1-xSrxMnO2.75, LSMO) with x= 0 and 0.4 are synthesized by spray pyrolysis method onto glass substrate at 460°C. The structural properties of the prepared samples are characterized by X-ray diffraction (XRD) technique and some parameters such as lattice parameters, crystallite size, microstrain and dislocation density have been reported. It is shown that LaMnO2.75: Sr thin films crystallize in orthorhombic structure with a preferred orientation of the crystallites along (040) direction. In addition, atomic force microscopy (AFM) investigation displays the nanosphere aspect. UV-VIS-IR measurements show that the average transmittance of the LaMnO2.75: Sr thin films is greater than 70% and optical band gap (Eg) of 2.85 eV is recoded. The photoluminescence (PL) measurements exhibit emission in the visible region, which is located at 530 nm. Finally, magnetic measurements at room temperature using vibrating sample magnetometer (VSM) technique reveal ferromagnetic behavior.

Keywords. La1-xSrxMnO$_{2.75}$; LSMO; Sr doping; Structural properties; AFM; magnetic properties.

INTRODUCTION

Perovskite-based manganite have been the subject of intense research because of their complex magnetic and electric transport properties, especially in colossal magnetoresistance (CMR) (Hong et al., 2003). The general formula for these types of manganite is $A_{1-x}B_xMnO_3$, where A is a rare earth atom and B is a divalent ion such as Sr, Ca or Ba (Nagaev, 2000). LSMO possesses excellent physical properties, including high spin polarization, half-metallic-like conductivity, and good thermal stability, and spin charge and orbital ordering, which are

suitable for applications in nanospintronic and nanoelectronic devices (Beltran-Huarac et al., 2013). Indeed, this perovskite shows very promising magnetic activity and electromagnetic applications due to oxygen vacancies and cation excess, which are created for $LaMnO_x$ compounds (Dezanneau, 2003). These properties can be related to different oxidation numbers of manganese (Mn^{3+} and Mn^{2+}) which exist in the crystalline structure (Vincent et al., 2002). Many different chemical methods have been developed for the synthesis of LSMO films including pulsed laser deposition (PLD) (Ishii et al., 2014), RF sputtering (Zongfan et al., 2016), sol gel (Danyan, 2015), hydrothermal method (Darko et al., 2013), solid-state reaction (Sakthipandi et al., 2013) and polymerizable complex method (Leandro et al., 2011).
The purpose of this study is to achieve the synthesis of $La_{1-x}Sr_xMnO_{2.75}$ (x=0 and 0.4%) thin films which are prepared onto glass substrate using the spray pyrolysis route at 460°C. Meanwhile, these films have been investigated by using XRD, atomic force microscopy, optical, photoluminescence and magnetic properties. Up to our knowledge no paper on Sr doped LaMnO perovskite thin layers prepared by spray pyrolysis has been previously reported.

EXPERIMENTAL PROCEDURE

$La_{1-x}Sr_xMnO_{2.75}$ thin films with x= 0 and 0.4 are prepared using spray pyrolysis method on glass substrates at 460 °C using 10^{-2} M of both aqueous solution of lanthanum chloride heptahydrate ($LaCl_3$,$7H_2O$) and manganese chloride sexahydrate ($MnCl_2$,$6H_2O$). We have used a high-resolution X-ray diffraction for X-ray patterns in the 2θ configuration with a copper anticathode (CuKα, 1.54 Å) using Philips PW 1729 system. The transmittance spectra of the films are obtained using PerKin Elmer Lambda 950 spectrophotometer in 250-2500 nm wavelength range. The PL spectra are performed at room temperature in 500-600 nm wavelength range. Finally, the morphology of our sample is obtained with the atomic force microscope analyzer using the tapping mode.

RESULTS AND DISCUSSIONS

Structural characterization

The X-ray diffraction analysis of prepared of $LaMnO_{2.75}$: Sr perovskite samples is depicted in figure 1. X-ray diffraction spectra show well-defined peaks of (040), (141), (202) and (002), corresponding to orthorhombic phase according to JCPDS N° 00-035-1354 card. Based upon X-ray analysis, it is obvious that the diffraction intensity has a tendency to decrease with an increase in the strontium doping level, and as-grown LSMO thin layers have preferential orientation along (040) direction.
In the LSMO structure, the d_{hkl} plane spacing is related to the lattice parameters a, b and c are calculated by using the following relation (Boukhachem et al., 2016):

$$\frac{1}{d_{hkl}^2} = \frac{h^2}{a^2} + \frac{l^2}{b^2} + \frac{l^2}{c^2} \quad (1)$$

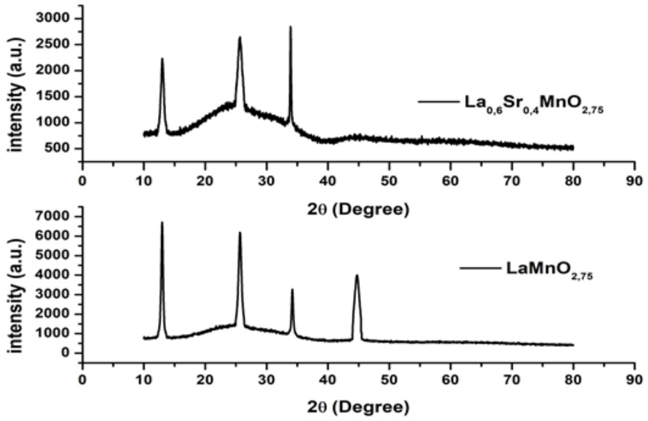

Fig. 1. X-ray diagram of pure and Sr-doped LMnO thin films prepared at 460°C.

Where h, k, l are the Miller indices. Moreover, the texture coefficient (TC) which indicates the maximum preferred orientation of the films along the diffraction plane means $T_{C\,(hkl)}$ values have been calculated from X-ray data, using formula (El-Nahass et al., 2004):

$$TC\ (hkl) = \frac{I_{(hkl)}/I_{0\,(hkl)}}{N^{-1}\sum I_{(hkl)}/I_{0\,(hkl)}} \quad (2)$$

Where $I_{(hkl)}$ is the measured relative intensity of (hkl) plane, $I_{0\,(hkl)}$ is the standard intensity, and N is the reflection number. The calculated values of $T_{C(hkl)}$ of the $LaMnO_{2.75}$:Sr sprayed thin films are gathered in table 1.

Table 1. Lattice parameters and texture coefficient values of pure and Sr-doped $LaMnO_{2.75}$ thin layers.

	A (Å)	B (Å)	C (Å)	$TC\ (040)$
$LaMnO_{2.75}$	6.301	27.296	5.237	1.886
$La_{0.6}Sr_{0.4}MnO_{2.75}$	6.275	27.296	5.268	0.589

The crystallite sizes of LSMO are determined from full-width at half-maximum ($\beta_{1/2}$) and angle of diffraction (2θ) of the XRD peaks using Scherrer equation (Benouis et al., 2010):

$$D = \frac{k\lambda}{\beta_{1/2}\cos\theta} \quad (3)$$

Where λ (=1.54 Å) is the X-ray wavelength, k= 0.90 is the Scherer constant. The grain size D values are estimated from (040) diffraction lines of $LaMnO_{2.75}$: Sr sprayed thin films deposed at 460°C as indicated in table 2. It can be noted that the average crystallite grain size is found to be 47 nm for pure films. The crystalline size has a tendency to decrease with Sr doping.

Table 2. Grain size, dislocation density and microstrain of sprayed La $MnO_{2.75}$: Sr thin layers.

	D (040) (nm)	δ (040) (10^{14}lines/m^2)	ε (040) (10^{-3})
$LaMnO_{2.75}$	47.77	4.382	6.43
$La_{0.6}Sr_{0.4}MnO_{2.75}$	34.12	8.587	9.01

The microstrain (ε), which is an interesting structural parameter of $LaMnO_{2.75}$: Sr sprayed thin films is obtained using the following relation (Junaid et al., 2009):

$$\varepsilon = \frac{\beta}{4\tan\theta} \quad (4)$$

Where $\beta_{1/2}$ is the full-width at half-maximum of (040) peak and 2θ is the Bragg angle.

Finally, the dislocation density, defined as the length of dislocation lines per unit volume, has been estimated via the following equation (Jang et al., 2008):

$\delta = \frac{1}{D^2}$ (5)

The calculated dislocation density and micro strain of the samples are listed in tables 2. Finally, from this rapid calculation of structural constants, it can be seen that thin film based on LSMO perovskites exhibits some defaults such as dislocation and microstrain. This aspect is probably related to the low preparation temperature.

Surface morphology investigation

The surface morphology of deposited $LaMnO_{2.75}$: Sr films is examined by AFM (5µm × 5µm) as shown in figure 2. The tridimensional atomic force microscopy (3D) image reveals that the surface of $LaMnO_{2.75}$ is composed with a nanosphere particle size. The grain size decreases with Sr-doping and surface becomes more homogenous. Such results corroborate with those reported in reference (Liu et al., 2016). As we can see, such decrease is corresponding to a decrease in crystallization, which is firstly confirmed by XRD analysis as shown in figure 1.

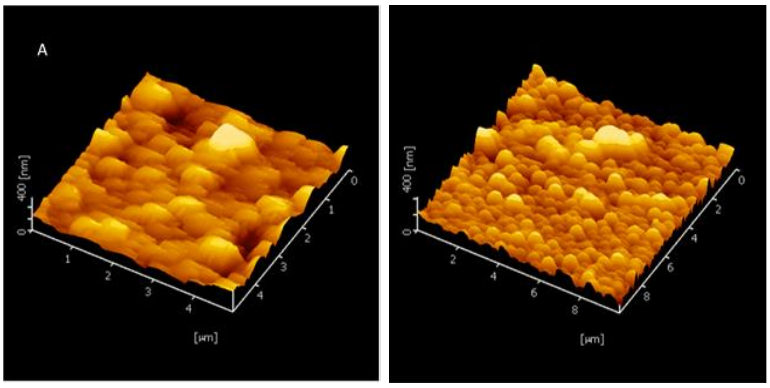

Fig. 2. 3D scanned AFM micrographs of (A) $LaMnO_{2.75}$ and (B) $La_{0.6}Sr_{0.4}MnO_{2.75}$

Optical characterization

The transmittance spectra of $LaMnO_{2.75}$ pure and Sr-doped is depicted in figure 3.a. The transmittance shows a good transparency in the near infrared range (>70%) which is important for transparent electronic applications.

The optical band gap can be extracted from the fundamental absorption edge of the films, which corresponds to electron transitions from valence band to conduction band. In the direct transition materials, the absorption coefficient (α) is expressed as follows (Keskenler et al., 2012):

$\alpha h\nu = A\left(h\nu - E_g\right)^{1/2}$ (6)

Where A is a dimensional constant, E_g the optical band gap. The extrapolation intercepting the photon energy axis gives the optical band gap E_g as shown in figure 3.b. It is found to be 2.85 eV and 2.84 eV for pure and 0.4 % Sr-doped films respectively as listed in table 3.

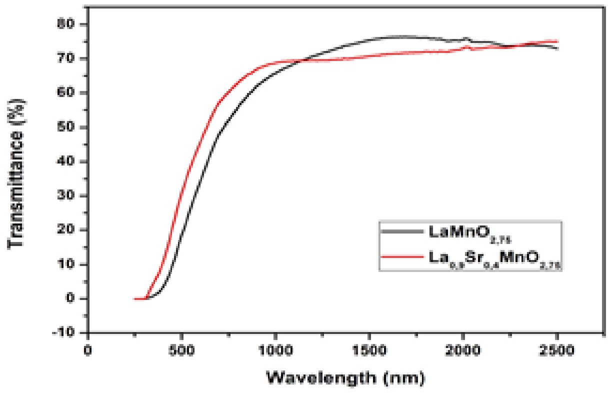

Fig. 3.a. Profile of transmittance spectra of La $MnO_{2.75}$: Sr thin films.

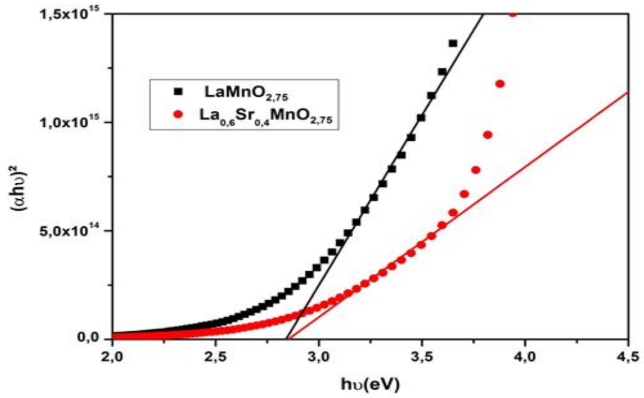

Fig. 3.b. Sketch of $(\alpha h\nu)^2$ vs. hν for sprayed pure and Sr-doped LMnO thin films.

Table 3. Calculated values of optical band gap E_g of sprayed $LaMnO_{2.75}$:Sr thin layers.

	Eg (eV)
$LaMnO_{2.75}$	2.84
$La_{0.6}Sr_{0.4}MnO_{2.75}$	2.85

Photoluminescence characterization

Photoluminescence spectra of $LaMnO_{2.75}$: Sr thin films are shown in figure 4. It is observed that the La $MnO_{2.75}$: Sr exhibit a green emission band centered at 543 nm in range 500-600nm. From such measurement, it can see that 0.4% doping level seems good for luminescence in VIS range. This green emission in $LaMnO_{2.75}$: Sr sprayed thin films can be related to the transitions from the conduction band to the defect levels of O_{La}, O_{Mn} and O_i. Such as (O_i, $O_{Ln/Mn}$) is interstitial oxygen states.

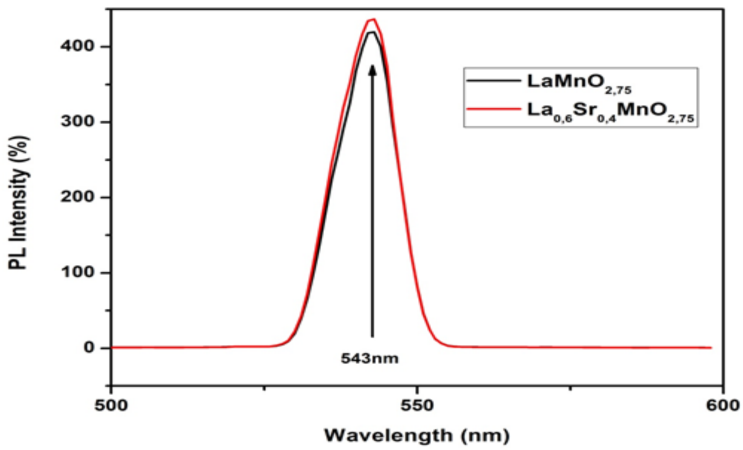

Fig. 4. PL spectra of sprayed $LaMnO_{2.75}$:Sr thin films.

Magnetic characterization

In order to study the magnetic properties of the $LaMnO_{2.75}$: Sr thin films the applied magnetic field (H) of 15 KOe, depending on the magnetization M (H), the magnetic hysteresis loop is measured and plotted as sketched in figure 5. The obtained result of $LaMnO_{2.75}$: Sr sample is shown in figure 5. It is recorded that LSMO sample shows a sharp ferromagnetic to paramagnetic transition, which also further confirms the nature of single-phase of LSMO sample (Zi et al., 2009). It is clea,r after doping, that the sample shows a good ferromagnetic behavior at room temperature and the value of saturation magnetization (Ms) comes out to be 39 emu/g, which is similar to the previous results by the pyrophoric reaction process (Dutta et al., 2007).

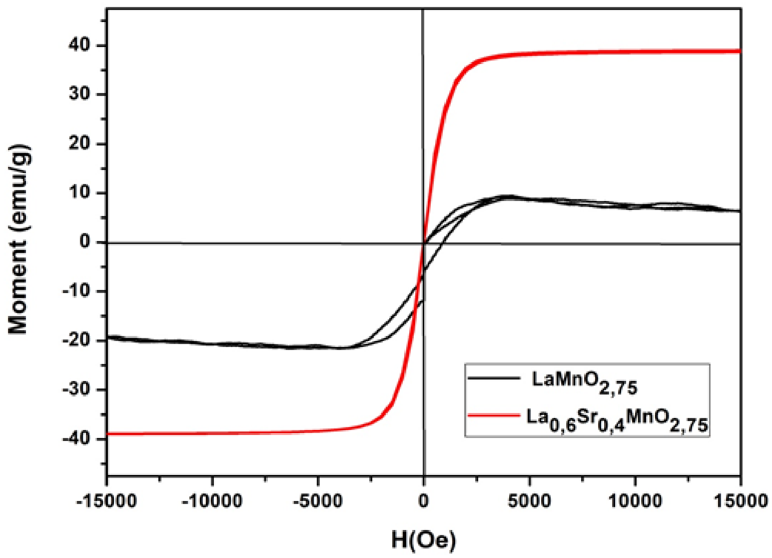

Fig. 5. Plot of magnetization vs. magnetic field of sprayed $LaMnO_{2.75}$:Sr thin films.

CONCLUSION

In this work**,** La $MnO_{2.75}$: Sr thin films are prepared by the spray pyrolysis technique on glass substrates at 460°C. X-ray diffraction analysis shows that prepared films have orthorhombic phase and the crystallites are preferentially oriented along (040). The AFM observation reveals a nanospherical profile of particles. The optical study reveals a good transmittance in VIS-IR range with wide band gap equal to 2.85 eV. PL spectroscopy exhibits emission in VIS range. Finally, magnetic measurements show hysteresis loops leading to a ferromagnetic behavior of sprayed $LaMnO_{2.75}$: Sr thin films.

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