Research Article

Structural and Surface Morphology Studies of $\text{La}_{0.67}\text{Ba}_{0.33}(\text{Mn}_{1-x}\text{Al}_x)\text{O}_3$ Thin Films Prepared by Sol-Gel Method

H. Abdullah and M. S. Zulfakar

Department of Electrical, Electronic & Systems, Faculty of Engineering and Built Environment, Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia

Correspondence should be addressed to H. Abdullah; huda@eng.ukm.my

Received 17 October 2012; Revised 18 January 2013; Accepted 28 February 2013

Academic Editor: Jun Liu

Copyright © 2013 H. Abdullah and M. S. Zulfakar. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Nanocrystalline thin films of $\text{La}_{0.67}\text{Ba}_{0.33}(\text{Mn}_{1-x}\text{Al}_x)\text{O}_3$ ($x = 0.00, 0.05, 0.10$, and 0.15) were prepared by sol-gel method, as a starter material consisting of La_2O_3 , BaNO_3 , $\text{Mn}(\text{NO}_3)_2$, and $\text{Al}(\text{NO}_3)_3$. The molarities of La_2O_3 and BaNO_3 are constant, while molarities of $\text{Mn}(\text{NO}_3)_2$ and $\text{Al}(\text{NO}_3)_3$ were calculated based on stoichiometric theory. Thin films were deposited on quartz glass substrate by using spin coating technique and sintered at 700°C . X-ray diffractometer (XRD) patterns showed that these thin films consist of pure $\text{La}_{0.67}\text{Ba}_{0.33}(\text{Mn}_{1-x}\text{Al}_x)\text{O}_3$ phase where the most prominent peak is observed at (104) . All the samples display a rhombohedral structure. Scanning electron microscopy (SEM) showed that aggregation of small particles occurred more in doped films than in undoped films. The surface morphology has been studied by using AFM, and the roughness of thin films was analyzed.

1. Introduction

LnMnO_3 oxides with the structure of perovskite type, are usually an antiferromagnetic semiconductor or insulator. If the trivalent rare earth element is partially doped with the divalent alkaline earth element, the doped manganese oxides $\text{RE}_{1-x}\text{A}_x\text{MnO}_3$ (Ln: the trivalent rare earth elements, A: Ca, Sr, Ba) are formed with novel and rich physical phenomena since the discovery of colossal magnetoresistance (CMR) [1–3]. $\text{RE}_{1-x}\text{A}_x\text{MnO}_3$ is known as parent compound which is antiferromagnetic. By doping with other divalent ions, it can be changed into a metallic ferromagnetic state due to the conversion of proportional number of Mn^{3+} to Mn^{4+} via the oxidation process [4]. This process was known as double exchange (DE) mechanism that was reported by Zener [5]. The physical properties of these perovskite manganites are mostly investigated in a bulk form, single crystal [6], and thin or thick film [7]. The electrical and magnetic transport of film forms are of special interest than the other forms due to the large magnetoresistance (MR) effect. This finding also has been reported by Zou [8] where the newest patterning technologies of magnetic thin films have a great effect on application of new micron electromagnetism devices. It gives the potential

technological usefulness such as sensor, magnetic recording applications, and also development of spin electronic devices [9, 10]. Among the various La-based perovskite manganites, $\text{La}_{1-x}\text{Ba}_x\text{MnO}_3$, especially the $\text{La}_{0.67}\text{Ba}_{0.33}\text{MnO}_3$ film form, are of great interest because of their Curie temperature which can reach up to 360K [3]. The manganese oxide not only shows a metallic conduction below Curie temperature T_c , but also enhances the ferromagnetic interaction when La^{3+} ions are replaced with alkaline earth elements or known as divalent metal ion (Ca^{2+} , Sr^{2+} , Ba^{2+}) in perovskite oxide structures [11]. By comparing the substitutions of divalent alkaline earth elements, A at the rare earth elements, Ln site will not change the interaction of $\text{Mn}^{3+}\text{-O-Mn}^{4+}$ can produced more complicated interaction between Mn ions with other dopants element [12]. Other than that, the distortion of Jahn-Teller might give an effect to the transport properties where by removing the double-degeneracy of Mn in e_g orbital, that will provide a mechanism for coupling between lattice degrees of freedom, electronic and magnetic [13]. In this work, nanocrystalline thin films of $\text{La}_{0.67}\text{Ba}_{0.33}(\text{Mn}_{1-x}\text{Al}_x)\text{O}_3$ (LBMAO) with concentrations of $x = 0.00, 0.05, 0.10$, and 0.15 were successfully deposited on quartz glass substrate by sol-gel method and were annealed at 700°C . We studied the

effect of nanoparticles size on structural and microstructures of nanocrystalline $\text{La}_{0.67}\text{Ba}_{0.33}(\text{Mn}_{1-x}\text{Al}_x)\text{O}_3$.

2. Experimental

Sol-gel method was used in synthesizing $\text{La}_{0.67}\text{Ba}_{0.33}(\text{Mn}_{1-x}\text{Al}_x)\text{O}_3$ ($x = 0.00, 0.05, 0.10$, and 0.15) solution. La_2O_3 , BaNO_3 , and $\text{Mn}(\text{NO}_3)_3$ were used as a starter material which acted as parent compound, and $\text{Al}(\text{NO}_3)_3$ was doped into the parent compound. The molarities for La_2O_3 and BaNO_3 were fixed, while molarities for $\text{Mn}(\text{NO}_3)_3$ and $\text{Al}(\text{NO}_3)_3$ were calculated by following the stoichiometric. The starter material was dissolved with deionized water to produce a clear solution. AlO_2 was added into parent compound by dissolving ammonium (NH_4) and ethylenediaminetetraacetic acid (EDTA). The solutions with concentrations of $x = 0.00, 0.05, 0.10$, and 0.15 were separated in different beakers. Each beaker contained 30 mL of LBMAO solution. Each beaker was heated with 95°C – 105°C for 2 hours. Magnetic bar was used to expedite the process of materials to dissolve. After that, the LBMAO solution was deposited on a clean quartz substrate using spin coating in order to form the film. Each layer was deposited with 1500 rpm for 30 seconds. All the films were dried on the hot plate with 80°C – 90°C . In order to get a good structure, the films were annealed using furnace tube (Carbolite, CTF 12/75/700) at 700°C . Each of the films were annealed for 1 hour with heating rate and cooling rate $1^\circ\text{C}/\text{min}$. The finished film was analyzed using X-ray diffractometer (XRD) at room temperature using Cu-K α radiation, scanning electron microscopy (SEM), and atomic force microscope (AFM).

3. Results and Discussions

The films of X-ray diffraction (XRD) spectrums for selected $\text{La}_{0.67}\text{Ba}_{0.33}(\text{Mn}_{1-x}\text{Al}_x)\text{O}_3$ system are shown in Figure 1. It shows that the peaks have been observed at (104) and (024) peaks, and the most prominent peak is given by the (104) peak. It is observed that samples $x = 0.00$ to $x = 0.05$ have clean phase pattern, while samples $x = 0.15$ exhibit an unknown peak at 41° . Observation of secondary phases in XRD is due to the incorporation of Al in Mn site when its intensity gradually increased with the increasing of Al content. All the samples are in rhombohedral distortion perovskite structure. By increasing Al concentration, the intensity of peak (104) was found to be shifted to the right. This is because the radius of Al^{3+} is smaller as compared to either Mn^{3+} or Mn^{4+} . The difference in size induces a compressive strain in the lattice which might cause a decrease in the lattice parameters. According to Li et al. [14], the orbital degeneracy leads to a Jahn-Teller instability, which caused the oxygen octahedral to distorted and lower its site symmetry to orthorhombic and thus remove an orbital degeneracy.

From the XRD spectra, crystal size can be calculated using the Scherrer formula [15]:

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

FIGURE 1: X-ray diffraction patterns for thin films with $x = 0.00, 0.05, 0.10$, and 0.15 .

TABLE 1: Crystal size d and at 2θ from XRD spectra.

Concentration, x	2θ (degree)	Crystal size, d (nm)
0.00	32.53	18.99
0.05	32.40	17.99
0.10	32.25	16.18
0.15	32.45	14.77

where the constant K depends on the shape of the grain size, $\beta = \text{FWHM}$, λ is the wavelength of the Cu-K α radiation, and θ is the glancing angle. The grain size of the sample is found in Table 1, by considering that the grains are circular in shape. This calculated result is, however, not exactly the same as the value of the obtained grain size from the scanning electron micrograph of the sample (see Figure 2). According to the micrograph, grain size ranges from 22 nm to 36 nm; some are even bigger. The grain growths of different sizes could be because we have not shivered the composition during its synthesis [4].

Morphology of $\text{La}_{0.67}\text{Ba}_{0.33}(\text{Mn}_{1-x}\text{Al}_x)\text{O}_3$ ($x = 0.00, 0.05, 0.10$, and 0.15) films' surface was analyzed using SEM to observe the surface roughness of the thin film. The captured images of the thin film during SEM are shown in Figures 2(a)–2(d). The picture with 20 K times bigger shows the different surface structure with increasing concentration. The addition of Al to the parent compound will increase the magnetic isolation of magnetic films with a small grain size [16]. Figure 2(a) shows the nanoparticle seen rarely on surface of substrate without any doped materials. By increasing the concentration of the doped material, it is seen that the nanoparticle was tight together and the size of particle became smaller. Comparison is shown in Figure 2(a) where it is proven that different types of crystallite can be identified on the composites after doping as shown in Figures 2(b)–2(d) [17].

Figure 3 shows the graph of sample grain size in diameter against the concentration of Al. The grain size decreases exponentially as the concentration increases. The increment of $x = 0.00$ to 0.25 shows that changes in grain size are not significant. The radii size plays the main role, where Al^{3+} ions are smaller than Mn^{3+} . This indicates that more Al^{3+} will take the place of Mn^{3+} . In $\text{La}_{0.67}\text{Ba}_{0.33}(\text{Mn}_{1-x}\text{Al}_x)\text{O}_3$

FIGURE 2: SEM micrograph of $\text{La}_{0.67}\text{Ba}_{0.33}(\text{Mn}_{1-x}\text{Al}_x)\text{O}_3$ thin film with different concentrations (a) $x = 0.00$, (b) $x = 0.05$, (c) $x = 0.10$, and (d) $x = 0.15$.

FIGURE 3: Sample grain size of $\text{La}_{0.67}\text{Ba}_{0.33}(\text{Mn}_{1-x}\text{Al}_x)\text{O}_3$ system.

system, substitution of Al^{3+} ions for Mn^{3+} site led to grain growth inhibition, Lanthanum segregation, and second phase formation. Similar observations have been reported [18], for compound of Pr_6O_{11} substituted $(\text{La}_{1-x}\text{Pr}_x)_{1/2}\text{Ba}_{1/2}\text{MnO}_3$. The reduction of size and connectivity between the particles are clearly seen, as the samples are doped for several concentrations. This can be seen from the SEM micrographs, where the grains size decreases as the level of porosity increases.

TABLE 2: Average roughness values of $\text{La}_{0.67}\text{Ba}_{0.33}(\text{Mn}_{1-x}\text{Al}_x)\text{O}_3$ ($x = 0.00, 0.05, 0.10$, and 0.15) thin films.

Concentration, x	Surface roughness, R_a (nm)
0.00	17.982
0.05	54.263
0.10	92.504
0.15	138.034

FIGURE 4: Surface morphology for $\text{La}_{0.67}\text{Ba}_{0.33}(\text{Mn}_{1-x}\text{Al}_x)\text{O}_3$ thin film with (a) $x = 0.00$, (b) $x = 0.05$, (c) $x = 0.10$, and (d) $x = 0.15$.

The film texture of as deposited films, as observed by AFM (Figure 4), shows that with increasing dopant concentration, texture of sample becomes rougher. The AFM results reveal that pure LBMAO film has an R_a value of only 17.982 nm, and increasing dopant concentration will result in a slight increment in R_a value. It also reveals that the R_a value will increase drastically after calcination process as observed in Figure 4, especially at heavy doped LBMAO films. The R_a values of as deposited films are listed in Table 2. The R_a value of undoped LBMAO does not undergo any change and has R_a value of 17.982 nm. From Table 2, it is observed that the surface roughness increased as we increase the concentration of the doping [19], while the grain sizes decreased.

4. Conclusion

Nanocrystalline $\text{La}_{0.67}\text{Ba}_{0.33}(\text{Mn}_{1-x}\text{Al}_x)\text{O}_3$ ($x = 0.00, 0.05, 0.10$, and 0.15) thin films were successfully prepared by sol-gel method, and their structural and magnetic properties have been investigated. X-ray diffractometer (XRD) patterns exhibit the most prominent peaks observed at (104) and (024). All samples display the rhombohedral structure. The surface becomes more compact, and the particles size becomes smaller as the doping concentration is increased as viewed through SEM images. The structures of nanoparticle became more tight and smaller by increasing the x concentration. High average roughness of surface texture had been obtained by Al light doped into LBMAO structure. Average roughness (R_a) of ~ 138 nm had been obtained for LBMAO for sample $x = 0.15$.

Acknowledgments

The authors wish to thank the Ministry of High Education of Malaysia for the Grant under Fundamental Research Grant Scheme (FRGS) UKM-KK-07-FRGS0026-2009 (Growth of Nanostructured Colossal Magnetoresistive Material for Low-Field Magnetic Sensing Device).

References

- [1] R. von Helmolt, J. Wecker, B. Holzapfel, L. Schultz, and K. Samwer, "Giant negative magnetoresistance in perovskitelike $\text{La}_{2/3}\text{Ba}_{1/3}\text{MnO}_x$ ferromagnetic films," *Physical Review Letters*, vol. 71, no. 14, pp. 2331–2333, 1993.
- [2] Q. Song, N. Liu, G. Yan, W. Tong, and Y. Sun, "Extraordinary transport behaviors of $\text{La}_{0.67}\text{Sr}_{0.33}\text{Mn}_{1-x}\text{Cr}_x\text{O}_3$ ($0.00 \leq x \leq 0.30$)," *Journal of Rare Earths*, vol. 24, no. 3, pp. 332–336, 2006.
- [3] S. Jin, T. H. Tiefel, M. McCormack, R. A. Fastnacht, R. Ramesh, and L. H. Chen, "Thousandfold change in resistivity in magnetoresistive La-Ca-Mn-O films," *Science*, vol. 264, pp. 413–415, 1994.
- [4] S. Keshri and V. Dayal, "Structural and electrical transport properties of nanosized LCMO sample synthesized by a simple low-cost novel route," in *Pramana*, vol. 70, pp. 697–704, Springer, New York, NY, USA, 2008.
- [5] C. Zener, "Interaction between the d-shells in the transition metals. II. Ferromagnetic compounds of manganese with Perovskite structure," *Physical Review*, vol. 82, no. 3, pp. 403–405, 1951.
- [6] H. Guo, N. Liu, G. Yan, and W. Tong, "Transport Property of $\text{La}_{0.67-x}\text{Sm}_x\text{Sr}_{0.33}\text{MnO}_3$ at Heavy Samarium Doping

- ($0.40 \leq x \leq 0.60$),” *Journal of Rare Earths*, vol. 24, no. 2, pp. 206–213, 2006.
- [7] H. Gencer, V. S. Kolat, and S. Atalay, “Microstructure and magnetoresistance in $\text{La}_{0.67}\text{Ba}_{0.33}(\text{Mn}_{1-x}\text{V}_x)\text{O}_3$ ($x = 0, 0.03, 0.06, 0.1, 0.15$ and 0.25) compound,” *Journal of Alloys and Compounds*, vol. 422, no. 1-2, pp. 40–45, 2006.
- [8] G. Zou, X. You, and P. He, “Patterning of nanocrystalline $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ thin films prepared by sol-gel process combined with soft lithography,” *Materials Letters*, vol. 62, no. 12-13, pp. 1785–1788, 2008.
- [9] C. Kloc, S. W. Cheong, and P. Matl, “Floating-zone crystal growth of perovskite manganites with colossal magnetoresistance,” *Journal of Crystal Growth*, vol. 191, no. 1-2, pp. 294–297, 1998.
- [10] M. Gunes, H. Gencer, V. S. Kolat et al., “Microstructure and magnetoresistance of a $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ film produced using the dip-coating method,” *Materials Science and Engineering B*, vol. 136, no. 1, pp. 41–45, 2007.
- [11] R. Müller, W. Schüppel, T. Eick, H. Steinmetz, and E. Steinbeiß, “LaSr-manganate powders by crystallization of a borate glass,” *Journal of Magnetism and Magnetic Materials*, vol. 217, no. 1-3, pp. 155–158, 2000.
- [12] N. Kallel, K. Fröhlich, S. Pignard, M. Oumezzine, and H. Vincent, “Structure, magnetic and magnetoresistive properties of $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Sn}_x\text{O}_3$ samples ($0 \leq x \leq 0.20$),” *Journal of Alloys and Compounds*, vol. 399, no. 1-2, pp. 20–26, 2005.
- [13] K. S. Syed Ali, R. Saravanan, A. V. Pashchenko, and V. P. Pashchenko, “Local distortion in Co-doped LSMO from entropy-maximized charge density distribution,” *Journal of Alloys and Compounds*, vol. 501, no. 2, pp. 307–312, 2010.
- [14] Y. M. Li, N. d’Ambrumenil, and P. Fulde, “Thermodynamic properties of a band Jahn-Teller system,” *Physical Review B*, vol. 57, no. 22, pp. R14016–R14019, 1998.
- [15] A. Taylor, *X-Ray Metallography*, Wiley, New York, NY, USA, 1961.
- [16] D. H. Shin, H. J. Kim, L. Ranno, and G. Suran, “Magnetic properties and Hall effect of CoZrGd films,” *Physica Status Solidi B*, vol. 241, no. 7, pp. 1514–1517, 2004.
- [17] Z. Tian, S. Yuan, Y. Wang et al., “Electrical transport and magnetic properties in $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ and CuFe_2O_4 composites,” *Materials Science & Engineering B*, vol. 150, no. 1, pp. 50–54, 2008.
- [18] S. Halim, “Electrical and microstructural properties of $(\text{La}_{1-x}\text{Pr}_x)\text{1/2Ba1/2MnO}_3$ compounds,” *Sains Malaysiana*, vol. 38, no. 2, pp. 209–213, 2009.
- [19] N. Ariyanto, H. Abdullah, and N. Ghani, “Surface morphology characterisation of Sn-doped ZnO films for antireflective coating,” *Materials Research Innovations*, vol. 13, no. 3, pp. 157–160, 2009.