JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 8, No. 2, April 2006, p. 470 - 472

Synthesis and magnetic properties of Sr and Cr doped lanthanum manganite

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This paper reports the synthesis and characterization of two new complex precursors of $LaMnO_3$ perovskite oxide doped with Strontium. The complex precursors have been prepared in La $(CH_3COO)_3$ – Mn $(CH_3COO)_2$ – AOH – DMF systems (where AOH = dimethylaminoethanol or 2[(diethylamin) methyl]-6-ethylpheno; DMF - dimethylformamide). Electronic and FT-IR spectra, TG / DTA analysis as well as molar conductivity measurements, have been used. According to the XRD patterns, $LaMnO_3$ obtained by the calcinations of the heterodinuclear complex precursors are single phase with rhombohedral perovskite type structure. The magnetic properties of the powders and thin films of perovskite manganite, obtained by annealing at different temperatures of Sr doped Lanthanum Manganite precursors, have been determined by Vibrating Sample Magnetometry and correlated with microstructural properties of thin films of Sr doped Lanthanum Manganite.

(Received January 18, 2006; accepted March 23, 2006)

Keywords: Heterodinuclear complex precursor, Perovskite, Lanthanum Manganite, Magnetic properties

1. Introduction

Doped perovskite manganites are known to be half metallic oxides that have spin-polarization of conduction carriers in the ground state [1]. During the last decades, the perovskite-type oxides $LaMO_3$ (M=Cr, Mn, Fe, Co, Ni) have been extensively studied not only for their catalytic properties, but in the same time due to their electrical and magnetic properties. The heterodinuclear complexes have been successfully used as precursors in the preparation of doped $LaMnO_3$ perovskite oxide, favoring an intimate mixing of the elements which can enable reactions at lower temperatures than for the traditional preparative routes [2,4].

This paper reports on the synthesis and characterization of a new heterodinuclear complex precursor for $LaMnO_3$ preparation, obtained in La $(CH_3COO)_3$-Mn$(CH_3COO)_2$ – AOH - DMF systems (where AOH = 2- [(diethylamino)- methyl]- 6-ethylphenol).

The choice of an aminophenol as ligand in the complex precursors of oxides systems has been determined by the capacity of such ligands to generate a lot of polynuclear complexes, in which the oxygen atom from the deprotonated phenolic group acts as a bridge, joining the different monomeric entities [2,3].

The complex precursor and the mixed oxide have been characterized by molar electrical conductivity measurements, electronic and FT-IR spectroscopy, TG/DTA, as well as X ray patterns. After annealing at different temperatures of Sr doped Lanthanum Manganite powders and thin films, we have measured magnetic properties by Vibrating Sample Magnetometer method [5]. The microstructural properties of Sr doped Lanthanum Manganite thin films, deposited on Silicon wafer were determined by Atomic Force Microscopy.

2. Experimental

2.1 Synthesis of complex precursor, $[LaMn(AO)_2(OH)(CH_3COO)_3]$

A mixture of 0.17 g (1mmol) Mn $(CH_3COO)_2.2H_2O$, 0.316 g (1mmol) La$(CH_3COO)_3$ and 0.418 g (2 mmol) of 2-[(diethylamino)-methyl]-6-ethylphenol in DMF (15ml) was refluxed for 5 hours at 40 – 50 ^oC. The brown crystals formed have been collected, by suction filtration, washed successively with distilled water, methanol and diethylether and dried on P_4O_{10} in a dessicator.

The reflectance diffuse spectrum of the complex precursor (Fig. 1a) with a large, small intensity band in visible range, confirms the existence of Mn(II)(d^5) in a square planar geometry.

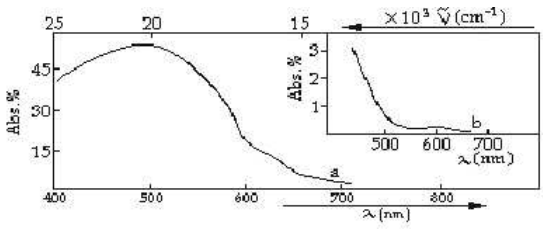

Fig. 1. Electronic spectra of (a) $[LaMn(AO)_2(OH)(CH_3COO)_3]$; (b) $LaMnO_3$ obtained from (a).

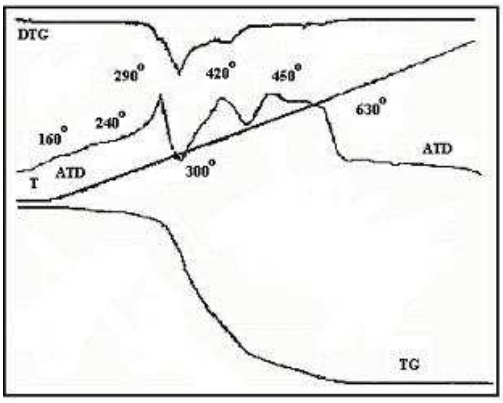

Fig. 2. TG/DTA curves of [LaMn(AO)$_2$(OH)(CH$_3$COO)$_3$] complex.

The thermal decomposition of the complex precursor was studied in order to establish the best conditions for pure $LaMnO_3$ obtaining. Fig. 2 shows the TG/DTA curves for [LaMn(AO)$_2$(OH)(CH$_3$COO)$_3$] complex. An abrupt weight loss observed on TG curve at ~ 300 ^oC was followed by two slower losses that ended at ~ 650 ^oC. These weight losses were partially overlapped corresponding to: [LaMn(AO)$_2$(OH)(CH$_3$COO)$_3$] → $LaMnO_3$ + volatile products.

The DTA curve showed three exothermic peaks due to the decomposition of the complex, the oxidation of the organic ligands and the formation of $LaMnO_3$ crystalline lattice.

The weight loss percentage 65.7 wt % in the last plateau range was in good agreement with the theoretical value of 66.4 % calculating by assuming the formation of $LaMnO_3$ from the complex with [LaMn(AO)$_2$(OH)(CH$_3$COO)$_3$] formulae.

The X-rays diffraction pattern on the solid powders after the calcination of the complex precursors was recorded on a TUR-M-62 diffractometer with CuK_α radiation.

According to the XRD pattern, (Fig. 3), from the decomposition of the precursor at 800 ^oC (3h) was single phase with orthorhombic perovskite type structure (JCPDS file no. 33 – 0711).

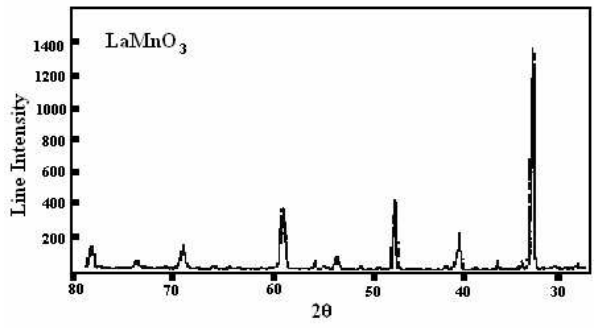

Fig. 3. XRD diffraction pattern of $LaMnO_3$ powder.

The XRD results showed that the mixed oxides were directly formed from the complex precursors after the decomposition of the organic ligands without formation of intermediate crystalline compounds.

2.2 Preparation of Sr doped Lanthanum Manganite

The Sr doped complex precursors have been obtained in the above systems in the presence of measured Sr $(NO_3)_2$ quantities. Stoichiometric amounts of $La(NO_3)_3$ 6 H_2O, $Sr(NO_3)_2$ and $Mn(CH_3COO)_2$.4 H_2O were dissolved in water, to which aminophenol was added during stirring. The molar ratio of metal ions to aminophenol was 1:4. The clear solution obtained was heated in reflux at 70-80 ^oC for 3 hours with continuously stirring and than evaporated in air until gelation occurred.

From this gel, thin films of $La_{0.67}$ $Sr_{0.33}MnO_3$ and $La_{0.67}$ $Sr_{0.33}Mn_{0.85}Cr_{0.15}O_3$ have been deposited by spin coating with 1000 RPM, on alumina substrates, and SiO_2/Si wafer. After deposition, manganite thin films were obtained by drying treatment at 100 ^oC/ 1 hour in oxygen atmosphere, and by heat treatment at 800 ^oC from 1 hour in oxygen atmosphere.

3. Results and disscusion

3.1 Microstructural properties

Figs. 4 and 5 show Atomic Force Microscopy of $La_{0.67}Sr_{0,33}MnO_3$ thin film deposited on silicon wafer.We can observe granular microstructure with the root-mean-square roughness (rms): 10.6853 nm.

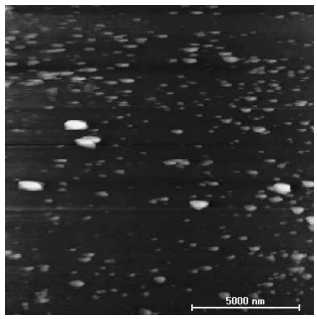

Fig. 4. 2D AFM image of thin film of $La_{0.67}Sr_{0,33}MnO_3$.

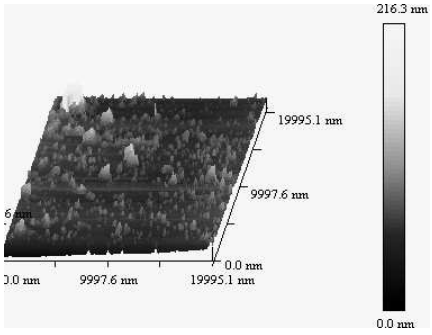

Fig. 5. 3D AFM image of thin film of $La_{0.67}Sr_{0,33}MnO_3$.

3.2 Magnetic properties

The microstructural properties of Sr doped Lanthanum Manganite thin films have been correlated with magnetic properties. Vibrating sample magnetometer (VSM) and magneto-optical magnetometer have been used to study sol-gel thin films from a static and dynamic point of view. We perform the magnetic measurements with a LakeShore Magnetometer (VSM). Measurements were performed in normal conditions, at room temperature, 24°-25 °C.

To VSM the perpendicular position of samples is when the EFGH plane (plane of sample) is perpendicular to applied field, parallel position when the EFGH plane (plane of sample) is in the same direction with applied field, like in the picture. For 45 grade and 135 grade positions, the plane of sample is rotate with 45° and 135°.

Fig. 6 shows the magnetic hysteresis loops of $La_{0.67}Sr_{0.33}MnO_3$ thin films prepared by sol-gel method.

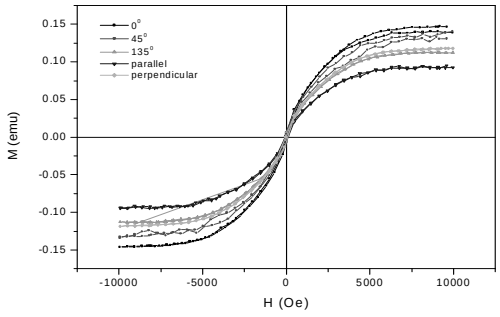

Fig. 6. VSM hysteresis loops of $La_{0.67}Sr_{0.33}MnO_3$ thin films deposited on ceramic substrate.

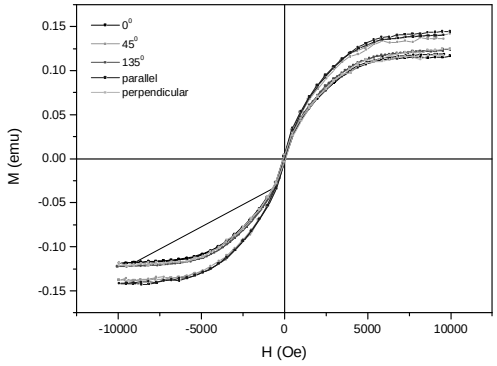

Fig. 7. VSM hysteresis loops of thin films $La_{0.67}Sr_{0.33}Mn_{0.85}Cr_{0.15}O_3$ deposited on ceramic substrate.

From the curves plotted in the Fig. 6 we can observe a magnetic anisotropy, this anisotropy is not depended from orientation of sample.

Fig. 7 shows the magnetic hysteresis loops of $La_{0.67}Sr_{0.33}Mn_{0.85}Cr_{0.15}O_3$ thin films prepared by sol-gel method.

From the curves plotted in the picture 7 we see that the sample have an anisotropy at 90°, this magnetic anisotropy is observed if is compared the perpendicular and parallel measurements and 45° and 135° measurements.

4. Conclusions

Perovskite-type manganite $La_{1-x}Sr_xMnO_3$ and $La_{1-x}Sr_xMn_{1-y}Cr_yO_3$ thin films were prepared by sol-gel method from heterodinuclear complex precursors: La $(CH_3COO)_3$ – Mn $(CH_3COO)_2$ – AOH – DMF systems.

Electronic, FT-IR spectra, TG / DTA analysis as well as molar conductivity measurements, have been used for the characterization of heterocomplex precursors. According to the XRD patterns, $LaMnO_3$ obtained by the calcinations of the heterodinuclear complex precursors are single phase with rhombohedral perovskite type structure.

We have investigated microstructural properties of Sr doped Lanthanum Manganite thin films in correlation with their magnetic properties.

The $La_{0.67}Sr_{0.33}MnO_3$ (Fig. 6) and $La_{0.67}Sr_{0.33}Mn_{0.85}Cr_{0.15}O_3$ (Fig. 7) thin films are ferromagnetic at the room temperature. This feature is very important for the applications of perovskite thin films prepared by sol-gel method. We can observe the shape anisotropy of perovskite thin films, from the VSM measurements at different degrees.

References

[1] M. R. Ibarra, J. M. De Teresa, Journal of Magnetism and Magnetic Materials **177-181**, 846 (1998).
[2] Z. Peng, M. Liu, J. Am. Ceram. Soc, **84**(2), 283 (2001).
[3] I. Jitaru, D. Berger, V. Fruth, A. Novac, N. Stanica, F. Rusus, "Lanthanum chromites doped with divalent transition metals"Ceramics International **26**, 193 (2000).
[4] J. H. Kuo, H. U. Anderson, Journal of Solid State Chemistry **87**, 55 (1990).
[5] V. E. Arkhipov, V. S. Gaviko, A. V. Korolyov, A. A. Arsenov, Journal of Magnetism and Magnetic Materials **196-197**, 539 (1999).

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