



Synthesis of novel perovskite crystal structure phase of strontium doped rare earth manganites using sol gel method



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ARTICLE INFO

Article history:

Received 7 January 2015

Received in revised form

11 May 2015

Accepted 24 May 2015

Available online 27 May 2015

Keywords:

Perovskites

Monoclinic

$R_{0.6}Sr_{0.4}MnO_3$

Sol-gel

IV measurements

Magnetoresistance

ABSTRACT

In the present work, polycrystalline perovskites of $R_{0.6}Sr_{0.4}MnO_3$ nanocomposites ($R=La, Nd, \text{ or } Sm$) were synthesized using the sol-gel method in the presence of citric acid and polyethylene glycol as chelating and structure directing agents respectively. The synthesized gel was calcined at 800 °C for 5 h. The XRD revealed that the obtained nanocrystalline $R_{0.6}Sr_{0.4}MnO_3$ is monoclinic crystal structure of space group (I2/a). TEM images showed that the prepared perovskites are homogeneous and uniform with particle sizes in a range 20–40 nm and the HR-TEM images and lattice fringes displayed the monoclinic structure. IV measurements showed that $Nd_{0.6}Sr_{0.4}MnO_3$ has semiconducting properties at room temperature. With applying low magnetic field, a transition from semiconductor behavior to Ohmic resistivity was observed. The static resistance of $Nd_{0.6}Sr_{0.4}MnO_3$ was calculated to be $\sim 2.985 \text{ T}\Omega$ for semiconductor phase and the resistance increased 1000 times that gives rise to negative magnetoresistance (MR). The value of MR of $Nd_{0.6}Sr_{0.4}MnO_3$ equals to 99.84%, which leads to the use of these materials in fabrication of magnetic devices in the industrial scale.

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1. Introduction

Spin, which has been realized as the “fourth” degree of freedom in the motion of electron, is drawing a large amount of attention since the last century, for its significant meaning in quantum physics study [1], nanomagnetism [2] and spintronics [3]. With the success of giant magnetoresistance [4,5], spintronics has become one of the most highlighted subjects in condensed matter physics and materials science [6]. Its commercial application to read head of hard disk drive strongly excites further desire of spintronics research, which gives rise to magnetic tunnel junction [7], spin-transfer torques [8,9] and non-local spin valves [10]. A hetero-epitaxial perovskite metal-base transistor was synthesized for electronic devices due to their vast array of physical properties [11]. Polycrystalline perovskites $La_{2/3}Ba_{1/3}MnO_{3-\delta}$ with different oxygen deficiencies were prepared by sol-gel method [12]. A lot of efforts have been done to get large magnetic entropy near room temperature. Large magnetic entropy change ($\Delta S_M \sim 2.26 \text{ J/kg K}$) at $T_c = 354 \text{ K}$ was observed by Phan et al. [13], in $La_{0.6}Sr_{0.2}Ba_{0.2}MnO_3$ in

magnetic field range from 0 to 10 kOe. A large magnetocaloric effect in perovskites ($La_{1-x}Nd_x)_{0.7}Sr_{0.3}MnO_3$ and $La_{0.7-x}Nd_xBa_{0.3}MnO_3$ at room temperature was reported [14,15]. The large ΔS_M was determined around 300 K for manganese perovskites with large magnetic entropy changes induced by low magnetic field change [16], which is beneficial for the household application of active magnetic refrigerant materials. Crystal structure of rare earth manganite is not only a cubic perovskites structure but also is orthorhombic [17,18], rhombohedral [19], hexagonal [20] or monoclinic [21] depending on the synthesis procedure and heat treatment. The crystal structure of $Sm_{0.6}Sr_{0.4}MnO_3$ and $Nd_{0.65}Sr_{0.35}MnO_3$ prepared using the conventional solid state method [22,23] showed the orthorhombic crystal structure of space group 62. The Sm–Nd/Sr atoms have $(x, 1/4, z)$ coordinates while the Mn atoms have $(0, 0, 1/2)$ coordinates. The parameters of the crystal and magnetic structures of $Yb_{0.6}Sr_{0.4}MnO_3$, prepared using solid state method have been studied and compared with $YbMnO_3$ [20]. It is shown that the crystal structure of the investigated compound corresponds to a mixture of orthorhombic Pbnm (enclosing Jahn–Teller Mn^{3+} ions) and hexagonal $P6_3cm$ (JT ions free) phases. The Yb/Sr atoms occupy two positions 2a and 4b. Yb1/Sr1 has $(0, 0, 0.2754)$ and $(1/3, 2/3, 0.2274)$ coordinates while Mn atoms are in 6c $(0.3518, 0, 0)$ in the hexagonal crystal structure while Sm/Sr atoms have $(x, 1/4, z)$ coordinates and the Mn atoms have $(0, 0, 1/2)$ coordinates in

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orthorhombic crystal structure form. MR measurements of $\text{Sm}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ reported by Dunaevsky et al. [24] are compared with that reported by Abdel-Latif et al. [22] taking into consideration that $\text{Sm}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ in both works were prepared using similar method but at different calcination temperatures. In spite of both $\text{Sm}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ samples having the same structure, they have different MR values. The thermal treatment during preparation are varied which may lead to the difference in the tilt of MnO_6 octahedra and hence in the MR values. It is also well known that, the exchange interaction between Mn_{eg} and O_{2p} orbital is governed by the $\text{Mn-O}_1\text{-Mn}$ and $\text{Mn-O}_2\text{-Mn}$ angles which are the basic parameters in determining the magnetic and the electronic behavior of this compound. According to Segal et al., the propagation of lattice vibrational modes (phonons) associated with the dynamic octahedral rotations causes drastic changes in the resistivity of a $\text{La}_{0.53}\text{Sr}_{0.47}\text{MnO}_3$ film (LSMO). In other words, enhanced electron-lattice coupling was mediated through the correlated oxygen octahedral motions [25]. Evolution in Raman modes associated with breathing-type octahedral distortions can shed light on the origin and onset of charge ordering metal-insulator transitions in bulk perovskites or super lattices formed by interleaving such materials [26]. The Jahn-Teller activated modes are compatible with the crystal structure, i.e., there is no symmetry change, due to two different types of Mn-O bond lengths induced by the mode in some orthorhombic structures. In contrast, the identical Mn-O bonds in rhombohedral structures would require that the Jahn-Teller activated modes reduce the crystal symmetry and the appearance of these modes in a Raman spectrum would reveal a symmetry-breaking phase transition [27]. It is still of great interest and it is devoted to studying these materials to develop magnetic devices. In this contribution, our strategy focused on the preparation of polycrystalline perovskites $\text{R}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ (R=La, Nd, or Sm) with monoclinic crystal structure through sol-gel reactions in the presence of citric acid and polyethylene glycol as structure direct agent. The newly synthesized perovskite $\text{Nd}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ has been evaluated by the determination IV measurements.

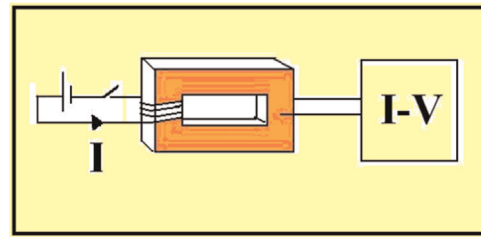
2. Experimental details

2.1. Materials

$\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Sr}(\text{NO}_3)_2$, and $\text{Mn}(\text{NO}_3)_2$, polyethylene glycol (average M.W.=1900–2200), citric acid and ammonium hydroxide (NH_4OH) 28–30% NH_3 basis were purchased from Sigma-Aldrich Chemical Company. All the chemicals were of analytical grade and used without further purification.

2.2. Preparation of perovskites $\text{R}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ (R=La, Nd, or Sm)

In a typical experiment, for preparing perovskites $\text{R}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ (R=La, Nd, or Sm), an appropriate amount of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, or $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Sr}(\text{NO}_3)_2$ and $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in 100 ml H_2O , and then citric acid (the molar ratio of citric acid to nitrate salts is 2:1) was added with continuous stirring at 80 °C for 60 min. Afterward, 1 g of polyethylene glycol was added to the mixture with stirring at 80 °C for two hours. Few drops of ammonium hydroxide (NH_4OH) was added in the mixture solution to maintain the pH=8 to get a clear solution. The produced sol was aged at 80 °C for 24 h until the gels formed. The produced gel was calcined at 800 °C for 5 h to obtain $\text{R}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ (R=La, Sm and Nd).



Scheme 1. Experimental arrangement for IV characteristic measurements.

2.3. Characterizations

X-ray diffraction (XRD) data were acquired on a computer controlled X'Pert Explorer, PANalytical diffractometer. TEM was conducted at 200 kV with a JEOL JEM-2100F-UHR field-emission instrument equipped with a Gatan GIF 2001 energy filter and a 1k-CCD camera in order to obtain EEL spectra. Raman spectroscopy was carried out using a Perkin Elmer Raman Station 400. Fourier transform infrared spectrometer (FT-IR) spectra were recorded in KBr dispersion in the range of 400–4000 cm^{-1} on Perkin Elmer (spectrum 100) FT-IR spectrometer. The IV characteristic measurements were carried out using Keithley Electrometer 6517A. The powder sample was pressed in the rectangular toroid form allowing flow of current in a coil to induce magnetic field and measure the IV curve in the presence of magnetic field. The details of the experimental arrangement (for the IV characteristics measurements) are shown in Scheme 1.

3. Results and discussions

Polycrystalline perovskites $\text{R}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ (R=La, Nd, or Sm) were prepared through sol-gel reactions of $\text{R}(\text{NO}_3)_3$ and $\text{Sr}(\text{NO}_3)_2$ with $\text{Mn}(\text{NO}_3)_2$ in the presence of citric acid and polyethylene glycol as chelating and structure direct agents respectively. The expected mechanism in this reaction was that Sr^{2+} , Mn^{2+} , La^{3+} , or Nd^{3+} , or Sm^{3+} ions were hydrolyzed and formed hydroxides, which were chelated by citric acid at pH=8 [28]. Polyethylene glycol is an essential surfactant as it could be adsorbed onto the surface of a metal hydroxides-citrate complex and thus enhances the growth kinetics of colloids which eventually produces an anisotropic growth of the polycrystalline perovskites $\text{R}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ nanocomposites. Finally, polycrystalline perovskites $\text{R}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ were formed by combination of ions at 800 °C in air and organic compounds PEG and citric acid were completely decomposed. The use of both citric acid and polyethylene glycol enabled the controlled synthesis of uniform $\text{R}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ nanocomposites with small particle size. The XRD analysis based on Rietveld method (using Fullprof program [29]) showed that the crystal structure of the prepared samples corresponds to two mixed phases of crystal systems; monoclinic and hexagonal. The XRD of the rhombohedral crystal phase of $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ perovskites (with space group R-3c) was reported [30]. It was synthesized using the sol-gel conditions but the firing at 500 °C and its lattice parameters were $a=b=5.5032$ Å, $c=13.3675$ Å and $\gamma=120^\circ$ [30]. Here, in the present work, the prepared perovskites $\text{La}_{0.4}\text{Sr}_{0.6}\text{MnO}_3$, $\text{Sm}_{0.4}\text{Sr}_{0.6}\text{MnO}_3$ and $\text{Nd}_{0.4}\text{Sr}_{0.6}\text{MnO}_3$ nanocomposites were tested to satisfy the observed XRD patterns and Rietveld refinement according to the orthorhombic, the rhombohedral, or the hexagonal crystal system. The obtained data confirmed that none of these symmetries is identical to our measured XRD patterns unlike the expected. XRD patterns were refined according to space group number 15 (I2/a) which represent the point group 2/m. The monoclinic phase satisfies double perovskites [31] and $\text{Pr}_{0.6}\text{Sr}_{0.4}$

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