



Synthesis, electronic and magnetic properties of the double B mixed perovskite series $\text{La}_{0.5}\text{Sr}_{0.5}\text{Mn}_{1-x}\text{Fe}_x\text{O}_3$

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ABSTRACT

The perovskite-type oxides $\text{La}_{0.5}\text{Sr}_{0.5}\text{Mn}_{1-x}\text{Fe}_x\text{O}_3$ ($x=0.2-0.5$) were synthesized under mild hydrothermal conditions. Crystal growths of the samples were sensitive to the Mn-containing precursor, alkalinity and the reaction temperature. All the compounds corresponded to orthorhombic structure of space group *Pnma*. The curves M vs. T for the compositions with $x=0.2, 0.3$ and 0.4 indicated the coexistence of ferro- and anti-ferromagnetic contribution. The temperature dependence $\rho(T)$ is semiconducting for all the compounds and explained well by the variable range hopping rather than the adiabatic small polaron hopping.

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1. Introduction

The colossal magnetoresistance (CMR) manganites $\text{La}_{1-x}\text{A}_x\text{MnO}_3$ ($\text{A}^{2+} = \text{Ca}^{2+}, \text{Sr}^{2+}, \text{Ba}^{2+}, \text{Pb}^{2+}$) have attracted worldwide attention because of their extraordinary electrical and magnetic properties and their future potential in technological applications [1,2]. The substitution of the Mn ions by other transition metal ion, such as Cr, Fe, Co and Ni, can give rise to important modifications in the magnetic and transport properties [3–8]. Among others, Fe is particularly interesting, because it does not cause considerable lattice distortion [9] due to close ionic radii of Fe^{3+} and Mn^{3+} [10], which is a special model to study the unique properties of manganites. As the Mn atoms are substituted by Fe the magnetic structure dramatically changes: the charge order (CO) phenomenon is disrupted for low Fe concentration and the larger the Fe content, the lower the Curie temperature and the magnetic moment per Mn/Fe atom, because the ferromagnetic double-exchange chain is broken [11–13].

The conventional syntheses for the Fe-doped manganites are through high-temperature solid-state reactions between oxides, nitrates and/or carbonate precursors [9–14]. But it needs much higher temperature, and the inhomogeneous chemical components and the multiphase of the sample usually cannot be avoided. However, for the advantages of the lower reaction temperature and simple apparatus, hydrothermal process has been employed to synthesize the oxide powders of high purity, narrow particle-size

distribution, high phase homogeneity, controlled particle morphology and a high degree of crystallinity. The partial substitution in A-site of perovskite manganates has been achieved under hydrothermal conditions [15]. To the best of our knowledge, there are no reports on the hydrothermal synthesis of the manganites with other transition metal elements doping on Mn site. Moreover, although there are already some reports on the Fe-doped $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ systems by solid-state reactions [7,16], the effect of Fe doping on the $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ has not been reported on a systematic study. Therefore we explored the applicability of hydrothermal synthesis of the partial substitution in B-site of $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ by Fe. In this paper, we reported a series of the perovskite-type oxides of the formula $\text{La}_{0.5}\text{Sr}_{0.5}\text{Mn}_{1-x}\text{Fe}_x\text{O}_3$ ($x=0.2-0.5$) synthesized under mild hydrothermal conditions. We also investigated the effect of Fe substitution on magnetic and electrical properties.

2. Experimental section

In a typical synthesis procedure for $\text{La}_{0.5}\text{Sr}_{0.5}\text{Mn}_{0.5}\text{Fe}_{0.5}\text{O}_3$, 5.75 ml KMnO_4 (0.1 M) and 10 g KOH were mixed by stirring to form a solution. To this solution, we added 9.63 ml MnCl_2 (0.2 M) dropwise on stirring and cooled in an ice bath to form k-birnessite gel precursor. This was followed by an addition of 12.5 ml $\text{Sr}(\text{NO}_3)_2$ (0.2 M), 12.5 ml $\text{La}(\text{NO}_3)_3$ (0.2 M), 12.5 ml $\text{Fe}(\text{NO}_3)_3$ (0.2 M) and 60 g KOH. The reaction mixture was then transferred into an 80-ml Teflon-lined stainless steel autoclave with a filling capacity of 80%. The crystallization was carried out under autogenous pressure at 260 °C for 3 days. After the autoclave was cooled and depressurized, the products were washed with distilled water and sonicated by a direct immersion of a titanium horn (Vibracell, 20 kHz, 200 W/cm²). And then, single-phase $\text{La}_{0.5}\text{Sr}_{0.5}\text{Mn}_{0.5}\text{Fe}_{0.5}\text{O}_3$ was obtained as a fine dark crystalline powder at the bottom of the beaker. The reaction conditions employed for the synthesis of other compositions are listed in Table 1. The reaction equation for the synthesis of $\text{La}_{0.5}\text{Sr}_{0.5}\text{Mn}_{0.5}\text{Fe}_{0.5}\text{O}_3$ can be proposed as below:

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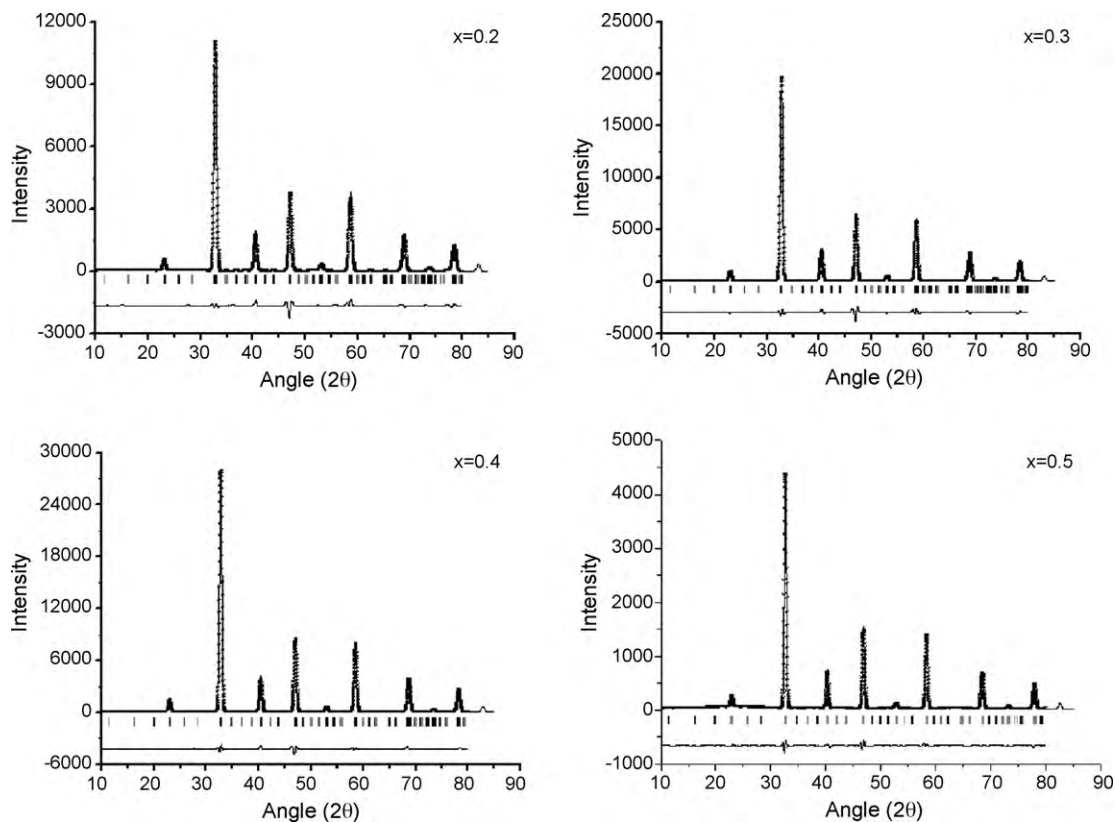


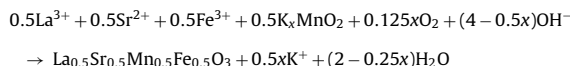
Fig. 1. The experimental, calculated and difference X-ray diffraction profiles for $\text{La}_{0.5}\text{Sr}_{0.5}\text{Mn}_{1-x}\text{Fe}_x\text{O}_3$ ($x = 0.2, 0.3, 0.4$ and 0.5).

Table 1

The optimal synthetic conditions for preparing $\text{La}_{0.5}\text{Sr}_{0.5}\text{Mn}_{1-x}\text{Fe}_x\text{O}_3$ ($x = 0.2, 0.3, 0.4$ and 0.5).

x	Molar ratio of initial reagents $n(\text{La}^{3+}):n(\text{Sr}^{2+}):n(\text{M})^a:n(\text{Fe}^{3+})$	Calculated value from ICP $(n_{\text{La}}:n_{\text{Sr}}:n_{\text{Mn}}:n_{\text{Fe}})$	Alkalinity (M)	Reaction temperature ($^{\circ}\text{C}$)
0.5	0.50:0.50:0.50:0.50	0.52:0.48:0.51:0.49	19	260
0.4	0.50:0.50:0.60:0.40	0.51:0.49:0.62:0.38	18	260
0.3	0.50:0.50:0.70:0.30	0.50:0.50:0.72:0.28	15	260
0.2	0.50:0.50:0.80:0.20	0.51:0.49:0.81:0.19	15	260

^a $n(\text{M}) = n(\text{MnO}_4^-) + n(\text{Mn}^{2+})$; $n(\text{MnO}_4^-)/n(\text{Mn}^{2+}) = 0.3$.



Powder X-ray diffraction (XRD) data were collected by a Rigaku D/Max 2500V/PC X-ray diffractometer using $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) at 50 kV and 250 mA.

Scanning electron microscopy (SEM) was performed on a Rigaku JSM-6700F microscope operating at 10 kV. Inductively couple plasma (ICP) analysis was carried out on a Perkin-Elmer Optima 3300DV ICP instrument. The average B-site oxidation state of the powders was determined by iodometric titrations. The ^{57}Fe Mössbauer spectra were recorded by a constant acceleration Mössbauer spectrometer with a $^{57}\text{Co(Pd)}$ source at room temperatures.

Table 2

Unit cell, positional and reliability factors for the Rietveld refinements of $\text{La}_{0.5}\text{Sr}_{0.5}\text{Mn}_{1-x}\text{Fe}_x\text{O}_3$ ($x = 0.2, 0.3, 0.4$ and 0.5), in the orthorhombic $Pnma$ space group from XRD data.

x		0.5	0.4	0.3	0.2
a (\AA)		5.478 (8)	5.482 (1)	5.441 (1)	5.428 (1)
b (\AA)		7.762 (2)	7.717 (1)	7.692 (1)	7.672 (1)
c (\AA)		5.479 (7)	5.461 (1)	5.479 (1)	5.465 (1)
v (\AA^3)		232.9 (7)	231.0 (3)	229.3 (1)	227.5 (8)
R/Sr 4c ($x, y, 1/4$)	x	0.00049 (7)	-0.00005 (2)	0.00127 (3)	-0.00088 (6)
	y	-0.00064 (1)	-0.00241 (7)	0.00131 (5)	-0.00420 (5)
Mn/Fe 4b (0, 0, 1/2)					
O1 4c ($x, y, 1/4$)	x	0.5191 (3)	0.5013 (1)	0.5426 (8)	0.5505 (4)
	y	-0.0022 (6)	-0.0055 (6)	0.0317 (1)	0.0097 (1)
O2 8d (x, y, z)	x	0.2191 (2)	0.2593 (6)	0.2331 (7)	0.2359 (3)
	y	0.0177 (5)	0.0006 (8)	0.0004 (2)	0.0059 (5)
	z	0.7785 (5)	0.7608 (8)	0.7649 (9)	0.7610 (8)
R_{wp} (%)		10.45	8.80	11.94	11.59
R_p (%)		6.44	4.58	6.73	6.56
χ^2		1.57	1.15	1.17	1.14

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