Roles of Te and Mn in the two phases of manganite with nominal composition La_{0.6}Sr_{0.1}Te_{x}MnO_{3}

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Received 9 July 2010; received in revised form 10 October 2010; accepted 11 October 2010
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Abstract
Powder samples with nominal composition La_{0.6}Sr_{0.1}Te_{x}MnO_{3} (x = 0.00, 0.05, 0.10, 0.15, 0.20) were prepared using the sol-gel method with thermal treatment up to 1473 K. On the basis of powder X-ray diffraction (XRD), thermogravimetric and magnetic measurements, it was found that almost all of the Te and a few of the Mn ions were lost from the samples when they were calcined at 1473 K. The reason for the Te loss and a quantitative phase analysis for the samples calcined at 1473 K are discussed in detail.

Keywords: condensed matter physics; crystal defects; X-ray diffraction; perovskite manganite; magnetic properties

1. Introduction
Over the last ten years or more, much effort has been devoted for understanding the magnetic and transport properties of doped perovskite manganites with the composition La_{1-x}D_{x}MnO_{3} (where D represents divalent cations, such as Ca, Sr, etc.)[1-5]. However, there are still some unresolved problems concerning manganites doped with tetravalent cations[6-11]. For example, Yang et al.[12] observed that there exists an anomaly in the M-T curve for the La_{1-x}Te_{x}MnO_{3} (x ≥ 0.1) system at about 40 K, and thought that this phenomenon resulted from a Mn$_3$O$_4$ second phase. In fact, in the studies by Tan et al.[13-14] and Zheng et al.[15], a similar phenomenon was also presented in the M-T curve, but was not commented upon by the authors. Chou et al.[16] showed experimentally that Te cannot be doped into the perovskite structure of manganite with the nominal composition La_{0.6}Sr_{0.1}Te_{x}MnO_{3}. However, as in all the previous studies, the authors failed to note reasons why only a few Te ions can enter the perovskite structure or why a Mn$_3$O$_4$ second phase forms.

According to our previous studies[17-18], the manganite with nominal composition La_{0.6}Sr_{0.1}MnO_{3} should possess two phases with a perovskite main phase and a Mn$_3$O$_4$ second phase. As we know, if Te ions can be doped into A sites of the ABO$_3$ perovskite phase, similarly to La or Sr ions, the content of the Mn$_3$O$_4$ second phase in the samples should decrease or even disappear with increasing x in our samples La_{0.6}Sr_{0.1}Te_{x}MnO_{3}. Therefore, the content ratio of the two phases can act as an indication as to whether Te can be doped into the perovskite structure. In this paper, we confirm that almost all of the Te and a few of the Mn ions have been lost in the sintering process at 1473 K for our samples with nominal composition La_{0.6}Sr_{0.1}Te_{x}MnO_{3}.

2. Experiments
Polycrystalline samples with nominal composition La_{0.6}Sr_{0.1}Te_{x}MnO_{3} (x = 0.00, 0.05, 0.10, 0.15, 0.20) were prepared by the sol-gel method[19-20]. Stoichiometric quantities of La$_2$O$_3$, Sr(NO$_3$)$_2$, Mn(NO$_3$)$_2$, and TeO$_2$ were dissolved in dilute HNO$_3$ solution. Suitable amounts of citric acid and ethylene glycol were added as complexing agents until a completely homogeneous transparent solution was achieved. This solution was subjected to slow evaporation at 360 K until a highly viscous gel was formed. The gel was then dried at 473 K. After grinding, the gel was thermally treated at 873 K for 5 h in order to decompose the organic precursor. Finally, five powder samples were obtained, after calcination at 1073 K (for 10 h), 1273 K (for 10 h) and 1473 K.
K (for 10 h), successively, with intermediate grinding, and with a final cooling of the furnace down to room temperature. The heat treatment and the calcination were all performed in air. At every calcination step in the sample preparation process, the weight of the samples was obtained using an electronic balance with an accuracy of 0.0001 g. Phase identification of the samples was performed using X-ray diffraction (XRD) on an X’Pert Pro diffractometer with Cu Kα radiation. The dependence of the specific magnetization \( \sigma \) on temperature and applied field were measured with a Lake Shore vibrating sample magnetometer. The Curie temperature measurements were performed at an applied field of 0.05 T. In order to make the following discussion more convenient, we label the samples with nominal compositions \( \text{La}_{0.6}\text{Sr}_{0.1}\text{Te}_{x}\text{MnO}_3 \) (\( x = 0.00, 0.05, 0.10, 0.15, 0.20 \)) as N1, N2, N3, N4 and N5, respectively.

3. Results and discussion

3.1. X-ray diffraction analysis (XRD)

Fig. 1 shows the XRD patterns for the samples with nominal composition \( \text{La}_{0.6}\text{Sr}_{0.1}\text{Te}_{x}\text{MnO}_3 \) calcined at 1073 K (a), 1273 K (b) and 1473 K (c). It can be seen that there is a perovskite phase, a \( \text{Mn}_3\text{O}_4 \) phase and a third phase in the samples with \( x \geq 0.05 \), calcined at 1073 and 1273 K, and that there is no third phase in the samples \( x = 0.00 \). The perovskite phase is the main phase. The three main peak positions of the third phase are located at \( 2\theta = 26.03^\circ, 26.50^\circ \) and \( 34.76^\circ \), respectively. The main diffraction peak of the \( \text{Mn}_3\text{O}_4 \) and third phase are indicated by “∇” and “↓”, respectively. However, it can also be seen that there are only two phases in the samples sintered at 1473 K: perovskite phase and \( \text{Mn}_3\text{O}_4 \) phase. The diffraction peak intensities in Fig. 1 have been obtained by peak profile fitting using the X’Pert HighScore Plus software. Fig. 2 shows the intensity ratios of the highest peak of the third phase (\( I_3 \)) and the \( \text{Mn}_3\text{O}_4 \) phase (\( I_\text{M} \)) to the perovskite phase (\( I_\text{P} \)) in the samples calcined at 1073, 1273 and 1473 K. From Fig.1 and Fig.2, it can be seen that the value of \( I_3/I_\text{P} \) remains approximately constant. In comparison, the value of \( I_\text{M}/I_\text{P} \) increases rapidly with increasing \( x \) after calcination at 1073 and 1273 K. However, after calcination at 1473 K, the value of \( I_3/I_\text{P} \) falls to zero, while the value of \( I_\text{M}/I_\text{P} \) still remained approximately constant.

3.2. X-ray energy dispersive spectrum

The Te content for the sample \( \text{La}_{0.6}\text{Sr}_{0.1}\text{Te}_{0.2}\text{MnO}_3 \) was detected using INCA-350 X-ray energy dispersive spectroscopy (EDS). The EDS patterns of the samples calcined at 1273 and 1473 K are shown in Figs. 3 (a) and (b), respectively. Fig. 3 (a) clearly show s the presence of Te in the sample calcined at 1273 K. In Fig. 3(b), however, the spec-