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Journal of Magnetism and Magnetic Materials 285 (2005) 417–421

Journal of magnetism and magnetic materials

www.elsevier.com/locate/jmmm

Determination of oxygen stoichiometry in the mixed-valent manganites

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Received 20 February 2004; received in revised form 19 July 2004
Available online 15 September 2004

Abstract

The possible redox (oxidation reduction) chemical methods for precisely determining the oxygen content in the perovskite manganites including hole-doped $La_{1-x}Ca_xMnO_y$ and electron-doped $La_{1-x}Te_xMnO_y$ compounds are described. For manganites annealed at different temperatures, the oxygen content of the samples was determined by a redox back titration in which the powder samples taken in a quartz crucible were dissolved in (1 + 1) sulfuric acid containing an excess of sodium oxalate, and the excess sodium oxalate was titrated with permanganate standard solution. The results indicate that the method is effective and highly reproducible. Moreover, the variation of oxygen content is also reflected in significant change in the electrical transport property of the samples, which is mainly considered to be closely related to the introduction of oxygen vacancies in the Mn–O–Mn network.

PACS: 72.20.My; 75.50.Cc; 82.33.Pt

Keywords: Oxygen stoichiometry; Mixed-valent manganites; Redox titration

1. Introduction

Recently, the hole-doped manganese perovskites $Ln_{1-x}A_xMnO_3$ (Ln = La-Tb, and A = Ca, Sr, Ba, Pb, etc.) have attracted much renewed attention because of their importance in both fundamental issues in condensed-matter physics and the potential for applications [1–3]. Many studies indeed suggest that the ratio of Mn^{3+}/Mn^{4+} is a key component for understanding the colossal magnetoresistance (CMR) effect and the transition from the ferromagnetic (FM) metal to the paramagnetic (PM) semiconductor. Recently, many researches have placed emphasis on electron-doped compounds

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doi:10.1016/j.jmmm.2004.08.012

such as $La_{1-x}Ce_xMnO_3$ [4–7] and $La_{1-x}Te_xMnO_3$ [8–10] because both electron as well as hole-doped FM manganites may open up very interesting applications in the field of spintronics. It is well established that the electric transport and magnetic properties of manganites are closely related to the Mn oxidation state, which is determined by the oxygen content of the sample. Unfortunately, many of these 3d transition metal oxides possess a strong tendency for oxygen nonstoichiometry in the limit of the preparation method [11]. Therefore, it is crucially important to determine the exact oxygen content of the sample, not only for an accurate characterization of the nonstoichiometric oxide materials but also for a reasonable understanding of the physical properties as a result of the variation in the oxygen content. So far, a brief description of a method for determining the ratio of Mn(III) and Mn(IV) has been given in Refs. [12,13]. However, no quantitative data have been reported. Bloom et al. [14] described a quantitative method determining the amount of Mn(III) and Mn(IV). The solid sample is reacted directly with a reducing medium, ferrous ammonium sulfate. The equivalent of Fe(II) oxidized by Mn(III) and Mn(IV) is then determined by back titration with $KMnO_4$. In addition, Licci et al. mentioned a method determining manganese valence in complex La–Mn perovskites, which is based on two independent iodometric titrations, with amperometric dead-stop end-point detection [15]. The methods described above are quite complex. In this paper, we describe in detail a convenient and effective redox titration method for determining the oxygen content of perovskite CMR manganites including hole-doped and electron-doped manganites.

2. Experimental details

2.1. Reagents and apparatus

Approximately 0.05 N $KMnO_4$ solution was obtained by dissolving 0.8 g AR-grade commercial salts in distilled water (500 ml) and then boiling the solution for 1–2 h by gently heating. The solution was deposited in a shady place for a whole night and preserved in dark containers after filtering the impurities in the solution. About 0.075 N $Na_2C_2O_4$ solution was obtained by dissolving dried salts (1g) in 1:1 v/v H_2SO_4 (200 ml).

The concentration of $KMnO_4$ solution made above was already decided before the solution was used to titrate. Approximately 20 ml $Na_2C_2O_4$ standard solution was taken out using a graduated flask and placed in a 50 ml beaker. Then the solution was heated up to 60–80 °C. At the same time, the $KMnO_4$ solution in the buret was dripped drop by drop into the $Na_2C_2O_4$ solution containing H_2SO_4 until a pink color of the $KMnO_4$ solution remains for 30 sec and the temperature of the solution for the end-point of titration is not less than 60 °C. Thus the concentration of $KMnO_4$ solution can be calculated as 0.086 N according to the dosage of the $Na_2C_2O_4$ standard solution.

The $La_{0.7}Ca_{0.3}MnO_y$ and $La_{0.9}Te_{0.1}MnO_y$ reference samples were synthesized through solid-state reaction from a stoichiometric mixture of high-purity powders of La_2O_3, $CaCO_3$, MnO_2 and La_2O_3, TeO_2, MnO_2. The powders obtained were ground, palletized, and sintered at 1400 and 1030 °C, respectively, for 24 h with several intermediate grindings. In order to vary the oxygen content of the samples, we annealed the samples at 750, 800 and 850 °C, respectively, in N_2 atmosphere under 2 MPa pressure for 4 h with graphite powder placed near the samples. The powder X-ray diffraction at room temperature shows that all the samples are single phase with no detectable secondary phases.

2.2. Analytical procedure

Approximately 0.2 g of the powder samples were weighed and placed in a quartz crucible, then dissolved in (1 + 1) sulfuric acid containing an excess of sodium oxalate (20 ml). Note that the crucible containing the powder samples was sealed through lidding on and placed in a bigger crucible, which was also covered with a crucible lid. The sealed crucible was laid in an oven under the temperature of 50 °C for 10 h. So the powder samples for the hole-doped manganites $La_{0.7}Ca_{0.3}MnO_y$ reacted with a suitable excess of $Na_2C_2O_4$ (~0.1 g for 0.2 g of sample), which deoxidize Mn^{3+} and Mn^{4+} to Mn^{2+} according