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## Determination of oxygen stoichiometry in the mixed-valent manganites

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### Abstract

The possible redox (oxidation reduction) chemical methods for precisely determining the oxygen content in the perovskite manganites including hole-doped  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_y$  and electron-doped  $\text{La}_{1-x}\text{Te}_x\text{MnO}_y$  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.

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### 1. Introduction

Recently, the hole-doped manganese perovskites  $\text{Ln}_{1-x}\text{A}_x\text{MnO}_3$  (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  $\text{Mn}^{3+}/\text{Mn}^{4+}$  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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such as  $\text{La}_{1-x}\text{Ce}_x\text{MnO}_3$  [4–7] and  $\text{La}_{1-x}\text{Te}_x\text{MnO}_3$  [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  $\text{KMnO}_4$ . 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  $\text{KMnO}_4$  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  $\text{Na}_2\text{C}_2\text{O}_4$

solution was obtained by dissolving dried salts (1g) in 1:1 v/v  $\text{H}_2\text{SO}_4$  (200 ml).

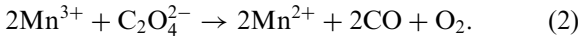
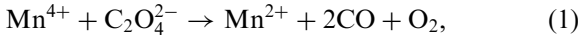
The concentration of  $\text{KMnO}_4$  solution made above was already decided before the solution was used to titrate. Approximately 20 ml  $\text{Na}_2\text{C}_2\text{O}_4$  standard solution was taken out using a graduated flask and placed in a 50 ml beaker. Then the solution was heated up to 60–80 °C. At the same time, the  $\text{KMnO}_4$  solution in the buret was dripped drop by drop into the  $\text{Na}_2\text{C}_2\text{O}_4$  solution containing  $\text{H}_2\text{SO}_4$  until a pink color of the  $\text{KMnO}_4$  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  $\text{KMnO}_4$  solution can be calculated as 0.086 N according to the dosage of the  $\text{Na}_2\text{C}_2\text{O}_4$  standard solution.

The  $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_y$  and  $\text{La}_{0.9}\text{Te}_{0.1}\text{MnO}_y$  reference samples were synthesized through solid-state reaction from a stoichiometric mixture of high-purity powders of  $\text{La}_2\text{O}_3$ ,  $\text{CaCO}_3$ ,  $\text{MnO}_2$  and  $\text{La}_2\text{O}_3$ ,  $\text{TeO}_2$ ,  $\text{MnO}_2$ . 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  $\text{N}_2$  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

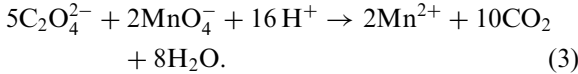
Approximately 0.2 g of the powder samples were weighed and placed in a quartz crucible, then dissolved in (1+1) sulfuric acid containing an excess of sodium oxalate (20 ml). Note that the crucible containing the powder samples was sealed through lidding on and placed in a bigger crucible, which was also 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  $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_y$  reacted with a suitable excess of  $\text{Na}_2\text{C}_2\text{O}_4$  (~0.1 g for 0.2 g of sample), which deoxidize  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  to  $\text{Mn}^{2+}$  according

to the quantitative reaction



For the electron-doped manganites  $\text{La}_{0.9}\text{Te}_{0.1}\text{MnO}_y$ , reaction (2) does not occur due to the mixed-valence state of  $\text{Mn}^{3+}$  and  $\text{Mn}^{2+}$ .

When the time of heat preservation was over, the crucible was taken out and the solution in it was moved into a clean and dry beaker (400 ml), and then distilled water was added till 150 ml. The beaker was placed on the magnetic heating stirrer and stirred for about 10 min. Then the  $\text{KMnO}_4$  solution above prepared in the buret was dripped drop by drop into the beaker until a pink color of the solution remains for 30 sec and the temperature of the solution for the end-point of titration was not less than 60 °C. Note that the titration was carried out in the process of heating and stirring at the same time. The unreacted  $\text{Na}_2\text{C}_2\text{O}_4$  after finishing reactions (1) and (2) oxidized  $\text{Mn}^{7+}$  to  $\text{Mn}^{2+}$  according to the quantitative reaction



So the oxygen content for the samples  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_y$  is then obtained by

$$y = \frac{5-x}{2} + \frac{n_1-n_2}{n_3}, \quad (4)$$

and the oxygen content for the samples  $\text{La}_{1-x}\text{Te}_x\text{MnO}_y$  can be calculated as follows:

$$y = \frac{5+x}{2} + \frac{n_1-n_2}{n_3} \quad (5)$$

where  $n_1$  is the amount of total  $\text{Na}_2\text{C}_2\text{O}_4$ ,  $n_2$  is the amount of  $\text{Na}_2\text{C}_2\text{O}_4$  reacted with  $\text{KMnO}_4$  and  $n_3$  is the amount of the powder samples.

### 3. Results and discussion

The reliability of the procedure for determining the oxygen content of the sample was examined by analyzing comparison samples of reagent grade  $\text{MnO}_2$  and  $\text{KMnO}_4$ . The results are shown in Table 1. When the measurement is repeated three

Table 1  
Analysis of known compounds

Compound	Mn(III) (%)	Mn(IV) (%)	Mn(VII) (%)	Mn(%) (theoretical)
$\text{MnO}_2$	4.21	58.98	—	63.19(IV)
$\text{KMnO}_4$	—	—	34.51	34.77(VII)

times on the same material, reproducibility of results is better than 1%. As one can see, the reagent grade  $\text{MnO}_2$  contained 4.21% Mn(III) and the determination of Mn(VII) in  $\text{KMnO}_4$  is in good agreement with the theory. The oxygen content and average Mn valence of the samples  $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_y$  and  $\text{La}_{0.9}\text{Te}_{0.1}\text{MnO}_y$  under different annealing temperatures are measured by the method described above and the results are summarized in Table 2. As we can see, the oxygen stoichiometry decreases with increase in annealed temperature, which is consistent with the results reported in Refs. [16,17]. Besides, we find the temperature of end point for titration is a main factor affecting the oxygen content of the samples. The results show that the oxygen content of the samples systematically decreases with increase in the temperature of end point for titration and the maximum difference of the oxygen content according to two extreme temperatures, i.e., 60 and 80 °C, is below 1%. Here we adopt the average value for the results. Other errors are negligible.

In order to confirm the validity of the analytical procedure, the resistance of the sample  $\text{La}_{0.9}\text{Te}_{0.1}\text{MnO}_y$  as a function of temperature was measured by the standard four-probe method from 25 to 300 K. Fig. 1 shows the temperature dependence of resistivity for the sample of as-prepared  $\text{La}_{0.9}\text{Te}_{0.1}\text{MnO}_y$  (curve A), the sample annealed at 750 °C (curve B), annealed at 800 °C (curve C), and annealed at 850 °C (curve D), for 4 h in  $\text{N}_2$  with graphite powders nearby. For sample A, it shows that there exists an insulator–metal (I–M) transition at  $T_{P1}$  (= 246 K). In addition, there exists a bump shoulder at  $T_{P2}$  (= 223 K) below  $T_{P1}$ , which is similar to the double peak behavior observed usually in alkaline–earth–metaldoped and alkali–metal-doped samples of  $\text{LaMnO}_3$  [18–22]. As to the origin of double peak

Table 2  
The oxygen content in the synthetic samples

Sample	Material	Treatment temperature (°C)	Calculated oxygen content	Average Mn valence
1	La <sub>0.7</sub> Ca <sub>0.3</sub> MnO <sub>y</sub>	As-prepared	3.02	3.34
2	La <sub>0.7</sub> Ca <sub>0.3</sub> MnO <sub>y</sub>	750	2.98	3.26
3	La <sub>0.7</sub> Ca <sub>0.3</sub> MnO <sub>y</sub>	800	2.88	3.06
4	La <sub>0.7</sub> Ca <sub>0.3</sub> MnO <sub>y</sub>	850	2.85	3.00
5	La <sub>0.9</sub> Te <sub>0.1</sub> MnO <sub>y</sub>	As-prepared	3.01	2.92
6	La <sub>0.9</sub> Te <sub>0.1</sub> MnO <sub>y</sub>	750	2.97	2.84
7	La <sub>0.9</sub> Te <sub>0.1</sub> MnO <sub>y</sub>	800	2.86	2.62
8	La <sub>0.9</sub> Te <sub>0.1</sub> MnO <sub>y</sub>	850	2.83	2.56

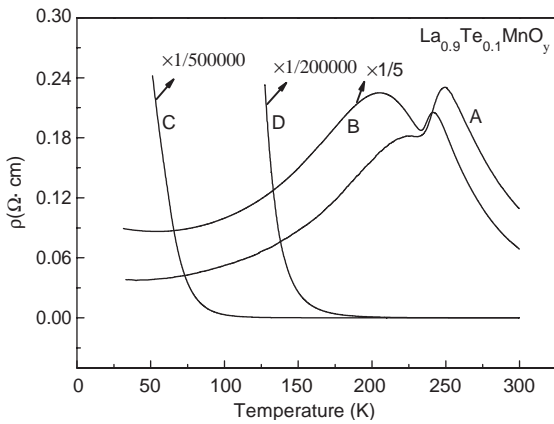


Fig. 1. Temperature dependence of resistivity for the as-prepared (sample A), 750 °C annealed (sample B), 800 °C annealed (sample C) and 850 °C (sample D) samples.

behavior in  $\rho(T)$  observed in hole-doped manganites, several models including the spin-dependent interfacial tunneling due to the difference in magnetic order between surface and core [20], which is intimately related to the size of grains, magnetic inhomogeneity [21], etc. have been proposed. However, its real origin is not very clear at present. More interesting phenomenon is that double I–M transitions occur with significant variation in the annealed temperature. For the sample annealed at 750 °C (sample B), the double I–M transitions shift to low temperatures, which has  $T_{P1} = 240$  K and  $T_{P2} = 205$  K. Additionally, I–M transition at  $T_{P1}$  becomes weak and I–M transition at  $T_{P2}$  becomes more obvious behaving as the noticeable character of peak compared with the character of the bump shoulder of the as-

prepared sample. For the sample C and D,  $\rho(T)$  curves display the semiconducting behavior ( $d\rho/dT < 0$ ) in the whole measurement temperature range and the resistivity maximum is of about 6 orders of magnitude larger than that of the as-prepared sample. It should be mentioned that for La<sub>0.9</sub>Te<sub>0.1</sub>MnO<sub>2.97</sub> (sample B), the ratio of Mn<sup>2+</sup> / (Mn<sup>2+</sup> + Mn<sup>3+</sup>) is close to 16%, comparable to that of La<sub>0.84</sub>Te<sub>0.16</sub>MnO<sub>3</sub>. From the known experimental data [8], such a system should show higher I–M transition temperature and lower resistivity. For La<sub>0.9</sub>Te<sub>0.1</sub>MnO<sub>2.86</sub> (sample C) and La<sub>0.9</sub>Te<sub>0.1</sub>MnO<sub>2.83</sub> (sample D), the ratio of Mn<sup>2+</sup> / (Mn<sup>2+</sup> + Mn<sup>3+</sup>) is close to 38% and 44%, comparable to that of La<sub>0.62</sub>Te<sub>0.38</sub>MnO<sub>3</sub> and La<sub>0.56</sub>Te<sub>0.44</sub>MnO<sub>3</sub>, respectively. In our previous work [23], such two systems showed an insulator–metal transition. However, the case is clearly not observed in sample C and D. So oxygen content reduction in La<sub>0.9</sub>Te<sub>0.1</sub>MnO<sub>y</sub> is expected to cause two effects. One is the increase in the Mn<sup>2+</sup> / Mn<sup>3+</sup> ratio, driving the carrier density increase, and causing the decrease of the resistivity. Another effect is the occurrence of the local lattice distortion due to the introduction of oxygen vacancies in the Mn–O–Mn network, which is important for electrical conduction. The local lattice distortion caused by oxygen vacancies in samples is confirmed by the structural parameter fitting through the Reitveld technique. The local lattice distortion is also expected to increase the resistivity due to the reduced  $e_g$  electron bandwidth [16–17]. As a result, the competition of the two effects suggested above decides the behavior of resistivity and the second factor gets the upper

hand over the first one. Therefore, the increase of resistivity of the samples can be attributed to the reduction of oxygen content in  $\text{La}_{0.9}\text{Te}_{0.1}\text{MnO}_y$ . In addition, the variation of oxygen content of the samples is also reflected in the effect on the magnetic properties of the samples (not shown here).

In conclusion, we develop a reliable and effective redox chemical method, which can be used to determine conveniently and effectively the oxygen content of manganites including the hole-doped and electron-doped CMR materials. The variation of oxygen content is also reflected in the effect on the electrical transport and magnetic properties of the samples

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