Solid-state Reaction for Preparation of Lanthanum Manganite

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(Received December 24, 2004; final form January 12, 2005)

ABSTRACT

The solid-state reaction process of $La_{0.95}MnO_3$ prepared from the reaction between La_2O_3 ($La(OH)_3$) and MnO_2 was investigated using TG/DSC and XRD at high temperature as well as room temperature. The reaction process involved a multi-step decomposition of reactants and a formation of $La_{0.95}MnO_3$. The formation of $La_{0.95}MnO_3$ started around 1273K. No intermediate phase was found in the formation of $La_{0.95}MnO_3$ .The prepared $LaMnO_3$ and $La_{0.95}MnO_3$ were both orthorhombic. The content of Mn^{4+} in two samples was found to be very close.

1. INTRODUCTION

AE-doped (AE: alkali earth metallic ions, such as Ba,Sr,Ca) lanthanum manganites have received significant interest by many researchers /1,2/ in the last decades due to their unique electrical and magnetic properties. More recently, there was increasing interest in La-deficient lanthanum manganites /3,4/.

It is widely accepted that the colossal magnetoresistance (CMR) effect in lanthanum manganite results from the presence of Mn^{4+} caused by doping of AE ions or hole and oxygen nonstoichiometry. However, the content of Mn^{4+} in samples is known to depend upon the preparation. Namely, the conditions of synthesis and thermal treatment have a great affect on the oxygen nonstoichiometry, structure and magnetic properties of lanthanum manganites /5-7/.

Regardless of shortcomings of bringing large particle size and inhomogeneous composition, the solid-state reaction method is still dominant for synthesizing lanthanum manganite. This could be attributed to easy and efficient control of composition and simple operation. However, a solid-state reaction process for synthesizing lanthanum manganite has not yet been reported.

In this work, lanthanum manganites with La/Mn ratio of 1 and 0.95 were synthesized using a solid-state reaction approach. The reaction process for La-deficient lanthanum manganites(La/Mn=0.95) was investigated by TG/DSC and XRD at high temperature and room temperature. The crystal symmetry, lattice parameters and the content of Mn^{4+} for samples were determined.

2. EXPERIMENTAL

La_2O_3(99.9%) and MnO_2(99.99%) were used as starting materials. La_2O_3 was heated at 1223K to remove moisture absorbed before being weighed. Powders with an appropriate molar ratio were mixed thoroughly in an agate mortar using ethanol. The powder mixture was used for high temperature XRD and TG/DSC analysis. Also, the mixture was then pressed into 12mm-diameter pellets under a pressure of 177MPa for isothermal calcinations at 1473K. The isothermal calcination setup used was described in our previous publication /8/. The pellets were calcined for various time at 1473K. After calcination, the pellets were removed from the furnace quickly and quenched in air.

2.1 Powder X-ray diffraction measurements

Powder X-ray diffraction measurements at room temperature (RT) and high temperature were carried out on a M21X-SRA X-ray diffractometer (MAC Science) equipped with graphite crystal monchromator in air. The scanning speed and step size were 8°/min and 0.02°respectively. The XRD patterns were collected with Cu-Kα radiation. High temperature measurements were carried out at 633K, 773K, 883K, 1083K, 1193K and 1273K in air .The XRD patterns were indexed using the Treor90 program. Lattice parameters and unit cell volumes were then calculated.

2.2 TG/DSC analysis

TG/DSC analysis was performed in a NETASCH STA 409C Thermal Analyzer at a heating rate of 30 K/min between RT and 1573K in air with a flow rate of 20ml/min.

2.3 The determination of valency of manganese ions

The valency of manganese ions in samples was determined using an iodometric titration method.This method involves separated processes of the sample dissolution in concentrated HCl and chlorine absorption by KI solution. 1M sodium thiosulfate standard solution was used to titrate the content of iodine in the solution.The error on Mn^{4+} content did not exceed 2%.

3 RESULTS AND DISCUSSION

3.1 The preparation process of $La_{0.95}MnO_3$

Fig. 1 shows the XRD pattern of La_2O_3 and MnO_2 powder mixture with a La/Mn ratio of 0.95. It can be seen that parts of lanthanum oxide have absorbed moisture forming lanthanum hydroxide. Fig. 2 shows the TG/DSC curves of La_2O_3 and MnO_2 powder mixture with a La/Mn ratio of 0.95. The first weight loss accompanied by a sharp endothermic peak around 629K corresponds to the decomposition of $La(OH)_3$ into LaOOH and H_2O. The second weight loss with a sharp endothermic peak around 795K corresponds to the decomposition of LaOOH into La_2O_3 and H_2O. This variation is similar to the previous case /8/ on La_2O_3 ($La(OH)_3$) and Co_3O_4 mixture. The third weight loss with a sharp endothermic peak at 894K is caused by the decomposition of MnO_2 into Mn_2O_3 and O_2, The fourth weight loss with a sharp endothermic peak at 1206K could be interpreted by the decomposition of Mn_2O_3 into Mn_3O_4 and O_2. The last part of TG curve shows a weight gain which is caused by the oxygen absorption in the reaction between La_2O_3 and Mn_3O_4 to form $La_{0.}95MnO_3$. The last endothermic peak at 1478K is likely to correspond to the phase transformation of Mn_3O_4 from tetragonal to cubic.

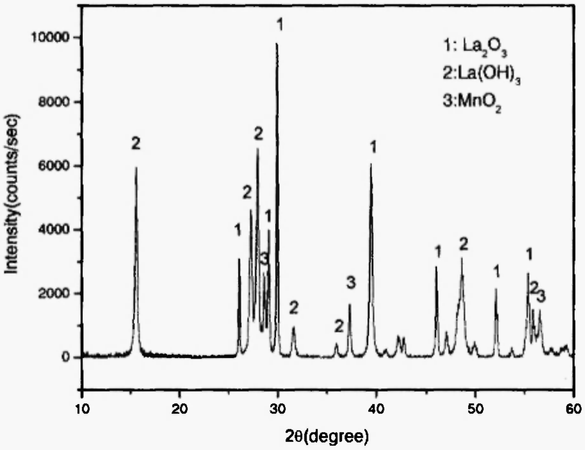


Fig. 1: XRD pattern for La_2O_3 and MnO_2 powder mixture (La/Mn=0.95)

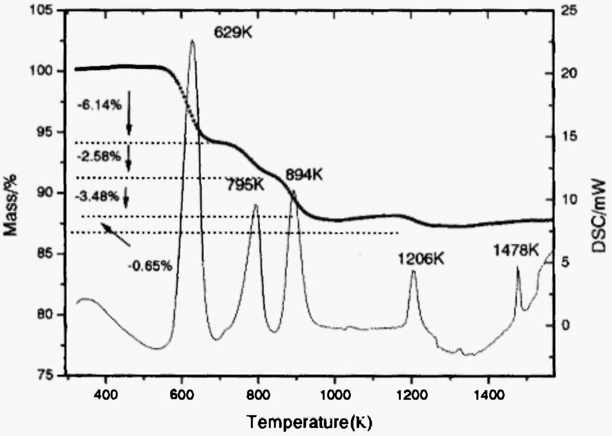
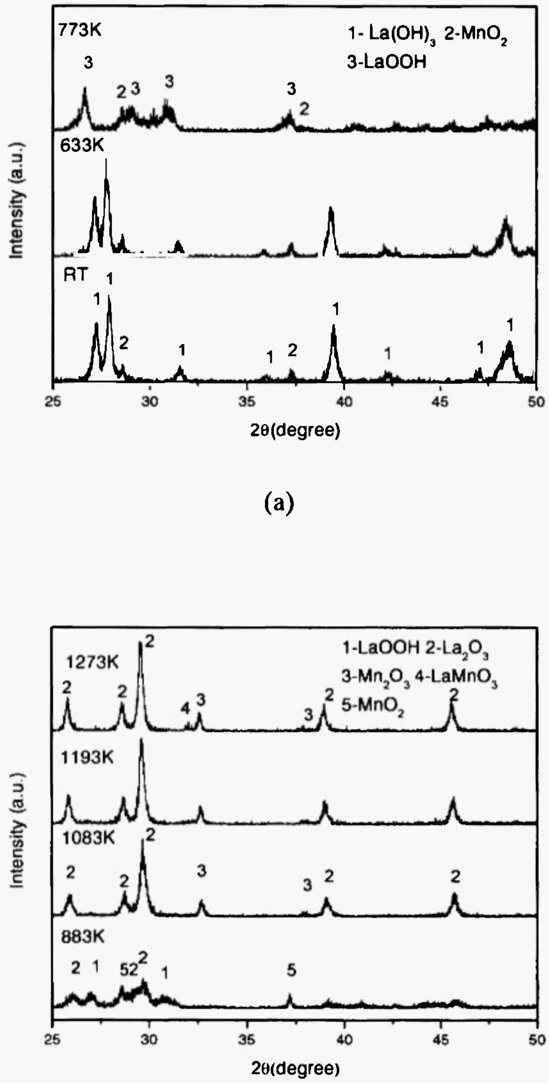


Fig. 2: TG-DSC curves of La_2O_3 and MnO_2 powder mixture (La/Mn=0.95)

Fig. 3 shows the result of high temperature XRD analysis. The phases at different temperatures demonstrated by XRD patterns are listed at Table 1. The results are consistent with the TG/DSC case. However, The decomposition of Mn_2O_3 into Mn_3O_4 was not found in the XRD pattern of 1273K. This could be explained by the more compact sample in high temperature XRD experiment. The XRD patterns also show that the formation of $La_{0.95}MnO_3$ will take place at the relativly higher temperature. No $La_{0.95}MnO_3$ was found in the XRD pattern until 1273K.



(a)

(b)

Fig. 3: The high temperature XRD patterns of La_2O_3 and MnO_2 powder mixture (La/Mn=0.95) at different temperatures

Table 1

The phases at different temperatures corresponding to the high temperature XRD patterns

Temperature/K	Phases
RT, 633	$La(OH)_3$, MnO_2
773	LaOOH, MnO_2
883	LaOOH, La_2O_3, MnO_2
1083, 1193	La_2O_3, Mn_2O_3
1273	La_2O_3, Mn_2O_3, $LaMnO_3$

The XRD patterns for samples which have been undergone isothermal calcinations at 1473K are shown in Fig. 4. The lanthanum hydroxide detected for the samples calcined for 1 and 3 hours was caused by the moisture absorption. It can be seen in Fig. 4 that all patterns show the existence of La_2O_3, Mn_3O_4 and $La_{0.95}MnO_3$. The amount of $La_{0.95}MnO_3$ increases with longer calcination time. No intermediate phase was found in all the pellets calcined.

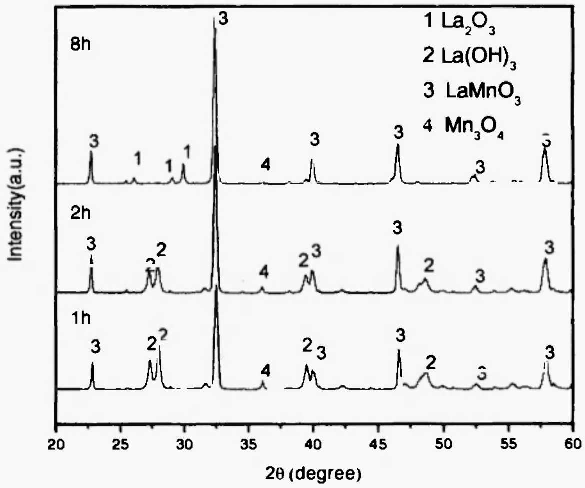


Fig. 4: XRD patterns of samples calcined for different time at 1473K

3.2 Characterizations of prepared $La_{0.95}MnO_3$ and $LaMnO_3$

In order to obtain the single phase of $La_{0.95}MnO_3$, the pellets calcined for 8 hours at 1473K were grinded and remixed in an agate mortar with ethanol as media, then pressed into pellets. These pellets were isothermally calcined again at 1473K for 8 hours, then quenched in air. The XRD pattern shows a $La_{0.95}MnO_3$ single phase (Fig.5). The $LaMnO_3$ single phase was also synthesized using the same procedure as mentioned. The XRD pattern of prepared $LaMnO_3$ is given in Fig. 6.

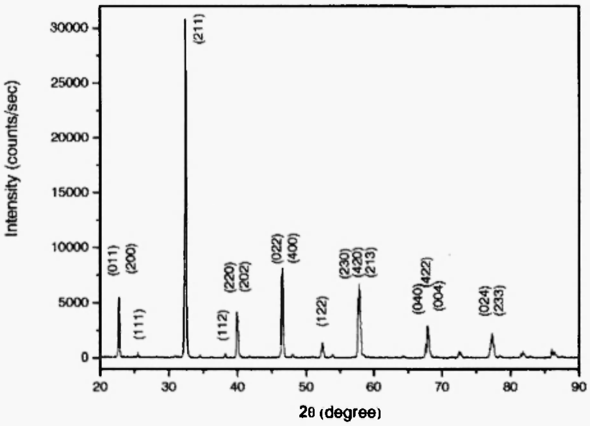


Fig. 5: XRD pattern of prepared $La_{0.95}MnO_3$

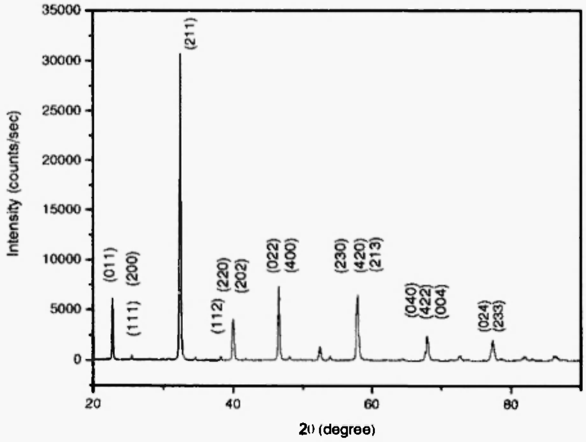


Fig. 6: XRD pattern of prepared $LaMnO_3$

The XRD patterns of prepared $La_{0.95}MnO_3$ and $LaMnO_3$ can be indexed as follows

For $La_{0.95}MnO_3$,
Symmetry: Orthorhombic, spacegroup: Pnma
Lattice parameters a=0.77961nm, b=0.55401nm, c=0.55081nm, $\alpha=\beta=\gamma=90°$
Cell volume V=0.23788nm^3

For $LaMnO_3$,
Symmetry: Orthorhombic, spacegroup: Pnma
Lattice parameters a= 0.77982nm, b= 0.55409nm, c= 0.54945nm, $\alpha=\beta=\gamma=90°$
Cell volume V=0.23741nm^3

For $LaMnO_3$ quenched from 1473K in air, Horyn *et al.* /9/ reported an orthorhombic form with a=0.772nm b=0.565nm c= 0.554nm (extrapolated from Figs. 2 and 3 in Ref. 9). This is different from the present result. The short annealing time in the present study may be the reason for the discrepancy.

The valency of manganese ions in $La_{0.95}MnO_3$ and $LaMnO_3$ prepared was determined. For $La_{0.95}MnO_3$, the valency of manganese ion is 3.11, the content of Mn^{4+} is 11%, For $LaMnO_3$, the valency of manganese ion is 3.12, the content of Mn^{4+} is 12%.

These results show the contents of Mn^{4+} in $La_{0.95}MnO_3$ and $LaMnO_3$ prepared are very close. It has been demonstrated by many researchers /3,4/ that the content of Mn^{4+} in lanthanum manganite decreases with lower La/Mn ratio. However, Horyn *et al.* /9/ recently reported that the effect of La/Mn on valency of manganese ion for lanthanum-deficient lanthanum manganite might be negligible at higher annealing temperature. The present result is consistent with theirs, although some further studies are required to obtain a definite conclusion.

4. CONCLUSIONS

From the present experimental results, the synthesis process of $La_{0.95}MnO_3$ with La_2O_3 (with some $La(OH)_3$) and MnO_2 powder mixture could be described in the following several steps: (a) The decomposition of $La(OH)_3$ into LaOOH around 629K; (b) The decomposition of LaOOH into La_2O_3 around 795K; (c) The decomposition of MnO_2 into Mn_2O_3 around 894K; (d) The decomposition of Mn_2O_3 into Mn_3O_4 around 1206K. Meanwhile, La_2O_3 reacted with manganese oxide to form $La_{0.95}MnO_3$; (e) La_2O_3 reacted with Mn_3O_4 to form $La_{0.95}MnO_3$. No intermediate phase was found in the formation of $La_{0.95}MnO_3$ from La_2O_3 and Mn_3O_4.

$La_{0.95}MnO_3$ and $LaMnO_3$ can be synthesized through an approach of isothermal calcinations at 1473K with intermediate grinding. The XRD patterns of prepared $La_{0.95}MnO_3$ and $LaMnO_3$ can both be indexed using orthorhombic symmetric and Pnma spacegroup. The lattice parameters are as follows, a=0.77961nm, b=0.55401nm, c=0.55081nm, $\alpha=\beta=\gamma=90°$ for $La_{0.95}MnO_3$; and a= 0.7798nm, b= 0.55409nm, c= 0.54945nm, $\alpha=\beta=\gamma=90°$ for $LaMnO_3$. The contents of Mn^{4+} for prepared $La_{0.95}MnO_3$ and $LaMnO_3$ quenched are 11% and 12% respectively, which are very close.

ACKNOWLEDGEMENT

The financial support from National Science Foundation of China (50374008) is gratefully acknowledged.

REFERENCES

1. R. Von Helmolt, B. Holzapfel, L. Schultz and K. Samwer. *Phys. Rev. Lett.* , **71**, 2331 (1993)
2. S. Jin, T. H. Tiefel, M. McCormack, R. A. Fastnacht, R. Ramesh and L.H. Chen, *Science*, **264**, 413-415 (1994).
3. Anthony Arulraj, R. Mahesh, G. N. Subbanna, R. Mahendiran, A. K. Raychaudhuri and C. N. R. Rao, *J. Solid State Chem.*, **127**, 87-91 (1996).
4. G. Dezanneau, A. Sin, H. Roussel, M. Audier and H.Vincent, *J. Solid State Chem.*, **173**:216-226 (2003)
5. N. Abdelmoula, K. Guidara, A. Cheikh-Rouhou, and E. Dhahri, *J. Solid State Chem.*, **151**, 139-144 (2000).
6. S.V. Trukhanov, N.V. Kasper, I.O. Troyanchuk , M. Tovar, H. Szymczak and K. Barner, *J. Solid State Chem.*, **169**, 85-95 (2002).
7. P.N. Lisboa-Filho, A.W. Mombru, H. Prado, W.A. Ortiz and E.R. Leite, *J. Phys. Chem. Solids*, **64**, 583-591(2003).
8. B.J. Yan, J.Y. Zhang and J.H Liu, *High Temp. Mat. Proc.*, **23**, 163-175 (2004).
9. R. Horyn, A. Sikora and E. Bukowska. *J. Alloys Compds.*, **353**, 153–169 (2003).