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Size-controllable gly–nitrate low temperature combustion synthesis (LCS) of nanocrystalline $La_xSr_{1-x}MnO_3$

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Abstract

The rare earth magnetic perovskite structure $La_xSr_{1-x}MnO_3$ has attracted renewed attention due to their novel physical properties. Nanocrystalline CMR material $La_xSr_{1-x}MnO_3$ was prepared by the LCS method, and the normal size $La_xSr_{1-x}MnO_3$ was synthesized by the high sintering method. The crystal structure, property and morphology were studied by XRD spectra, FT-IR and TEM. The results showed great difference between nanocrystalline and normal samples. © 2000 Published by Elsevier Science S.A.

Keywords: Nanocrystalline; $La_{2/3}Sr_{1/3}MnO_3$; LCS

1. Introduction

The recent observation of colossal magnetoresistance (CMR) in manganese oxides with perovskite structure had attracted considerable interest from both fundamental and practical points of view [1,2]. Normally, CMR materials with perovskite structure were synthesized by the high sintering method. The grain size of the product by this method was at the magnitude of micrometres. In this paper, we report, to the best of our knowledge, the first size-controllable low temperature combustion synthesis of nanocrystalline CMR material, which should provide new opportunity for better understanding the CMR phenomenon.

Comparing to self-propagating high temperature synthesis (SHS), low temperature combustion synthesis (LCS) [3], developed in recent years, has many advantages. The combustion temperature of SHS is normally above 2000°C. The size of the production powder by SHS is comparably large. While by LCS, the flame temperature may be only about 1000–1600°C, all of the reaction would finish in several minutes. The LCS provides a clipping and particular method to synthesize the nanocrystal.

2. Sample preparation

To synthesize the nanocrystalline $La_xSr_{1-x}MnO_3$ by the low temperature combustion method, stock aqueous solutions of $La(NO_3)_3$, $Sr(NO_3)_2$ and $Mn(NO_3)_2$ were prepared before use. The solution was mixed according to the formula $La_xSr_{1-x}MnO_3$, the ratio of Gly/NO_3^- could be adjusted when blending the reagents. The solution was heated on a heat board, with raising the temperature the solution would ablate and bubble up. When the water of the reaction style was almost dry, the temperature would rise quickly and enkindle the glycine, the reaction style combusted to combine the nanocrystalline till the glycine and nitrate was over. The surplusage was a black fluey foam. We could set the combustion process at different temperatures and thus produce nanocrystalline $La_xSr_{1-x}MnO_3$ with different particle sizes by controlling the ratio of Gly/NO_3^-. The reaction equation is:

$$x\,La(NO_3)_3\,(l) + (1-x)\,Sr(NO_3)_2\,(l) + Mn(NO_3)_2\,(l) + H_2NCH_2COOH\,(l) \rightarrow La_xSr_{1-x}MnO_3\,(s) + CO_2\,(g) + H_2O\,(g) + N_2\,(g)$$

A normal sample synthesized by the high sintering method was used for comparison. Blending the A.R La_2O_3, $SrCO_3$, MnO_2 with the $La_xSr_{1-x}MnO_3$ ratio, the stock was pre-heated to 1200°C three times, for 24 h, and then the

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stock sintered at 1350°C for 24 h to get the final product. The reaction equation is:

$$x\,La_2O_3\,(s) + (1-x)\,SrCO_3\,(s) + MnO_2\,(s) \rightarrow La_xSr_{1-x}MnO_3\,(s) + CO_2\,(g)$$

From the comparison of the synthesis procedure of the two methods, the LCS technique was better than the high sintering method in the preparation of crystalline materials.

3. Results and discussion

The crystal structure was analyzed by a Japanese D/max-rA X-ray diffraction apparatus. It was shown that the samples made from the LCS and high sintering method were all crystals whose diffraction data are consistent with those of JCDPS No. 35-1353. Dopant Sr^{2+} ions substitute La^{3+} in the lattice of nanocrystalline $LaMnO_3$, the particle sizes were estimated from the half height width of the XRD peaks, by the well known Sherrer equation. The calculated particle sizes were about 20, 40 and 80 nm. These three samples' XRD patterns are shown in Fig. 1. To measure the CMR property, the samples were molt under 15 MPa pressure to meet the experimental requirement. The XRD pattern after the pressing had no difference from that before the pressing. That showed that the nanocrystalline particles did not grow up under high pressure.

In the LCS procedure, the particle size is effected by many factors but the most important reasons are the combustion temperature, the product powder size increase with the rise of the flame temperature. In a LCS style, the sort of fuel and nitrate affect the reaction temperature, temperature is not the same when different fuel [4] or nitrate [5] are used.

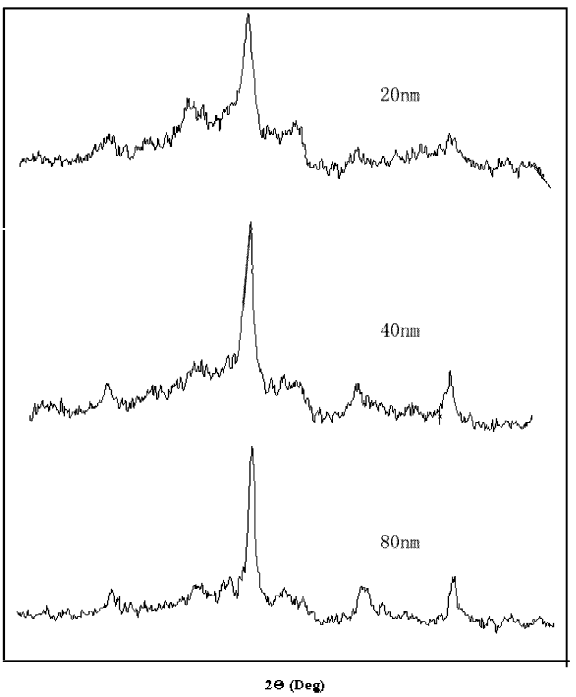

Fig. 1. X-ray diffraction pattern of different size nanocrystalline $La_{2/3}Sr_{1/3}MnO_3$.

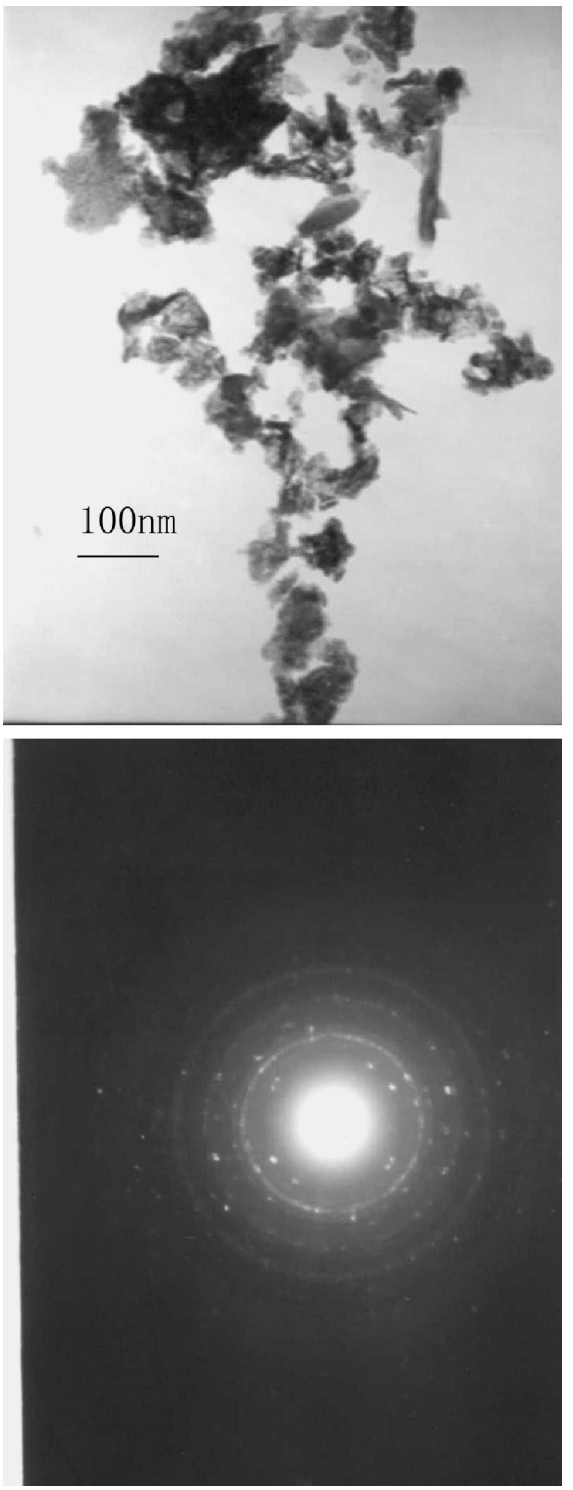

Fig. 2. TEM and electron diffraction patterns of 40 nm $La_{2/3}Sr_{1/3}MnO_3$.

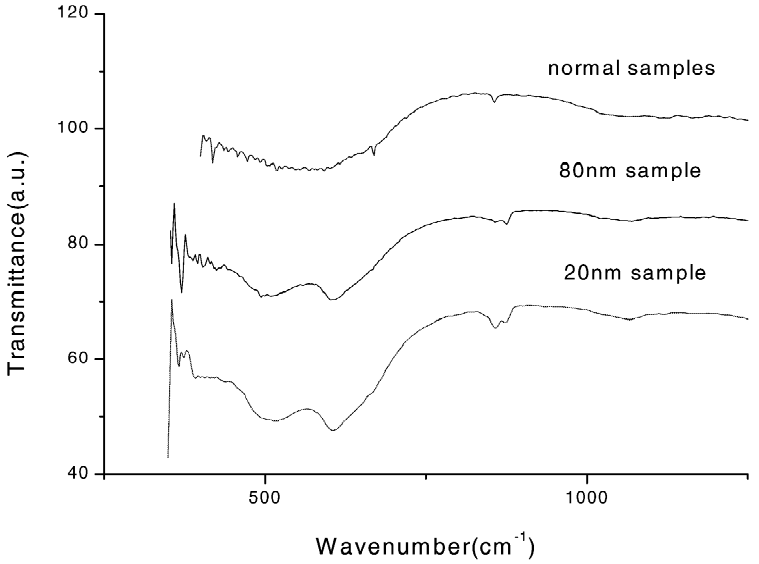

Fig. 3. FT-IR of nanocrystalline and normal samples of $La_{2/3}Sr_{1/3}MnO_3$.

In the preparation of $La_xSr_{1-x}MnO_3$, to gain the best performance of colossal magnetic-resistance, the ratio La^{3+}/Sr^{2+} is 2/1, in the synthesis we used only one sort of fuel, glycine. The basic conditions in the combustion were the same, the combustion temperature was only affected by the ratio of Gly/NO_3^-, in other words, nanocrystalline size was only decided by the ratio of Gly/NO_3^-. Regular in the rich fuel style, the combustion temperature is higher than that in the poor fuel style, but in fact the rich fuel style of $La_xSr_{1-x}MnO_3$ gave out much more gas than the poor fuel style [6] and the rich fuel style filled out its product with more space. Because the gas took out a great deal of caloric when it transgressed out of the combustion style, the temperature in the rich fuel style was lower than that in the poor fuel style. Based on this viewpoint, the particle size can be controlled by adjusting the ratio of Gly/NO_3^-. In the high ratio of Gly/NO_3^- style the particle was smaller than that in the low ratio style. In this report, the 20, 40 and 80 nm nanocrystalline were, respectively, made from the style in which the ratio of Gly/NO_3^- was 1.1, 1.0 and 0.8.

The morphology and particle-size were studied by a Hitachi H-800 transmission electron microscope. The sample synthesized by the LCS technique, and the XRD pattern shows that the particle size is 40 nm, which is verified by the TEM direct observation. The TEM of the 40 nm sample and its electron diffraction patterns are shown in Fig. 2.

While showing no organic residues in the nanocrystalline samples, FT-IR spectra show great difference between nanocrystalline and normal samples. The FT-IR spectra are shown in Fig. 3. There are two FT-IR absorption peaks of normal samples, the one at 590 cm^{-1} is broad the other at 856 cm^{-1} is weaker and sharper. Each of them is divided into two in the nano-samples as shown in the figure. These could be due to the nanocrystalline surface effect.

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