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LETTER TO THE EDITOR

Hydrothermal synthesis of single-crystal $La_{0.5}Sr_{0.5}MnO_3$ nanowire under mild conditions

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Abstract

Single-crystal $La_{0.5}Sr_{0.5}MnO_3$ nanowires were successfully synthesized by a hydrothermal method at 553 K. This reaction temperature is much lower than that of traditional methods. The nanowires have a cubic perovskite structure without any other secondary or impurity phase. Typical lengths of the nanowires are in the range of 1.5 to 15 micrometers, and typical widths are in the range of 50 to 400 nanometers. They grow along the [110] direction, and their surfaces are clean, very regular, and without any sheathed amorphous phase. The nanowires could be an ideal system for studying dimensionally confined transport phenomena in perovskite manganites and for fabricating functional devices.

The discovery of the magnetoresistive effect [1–5] in Mn-based perovskite oxides $(La, R)_{1-x}A_xMnO_{3-\delta}$, where R is a rare earth element and A=Ca, Sr, or Ba, has attracted considerable attention because of the potential field-sensor and device applications of these materials. A number of studies on the preparation, structure and magnetotransport of polycrystalline, single-crystal and thin film doped manganites have appeared in the literature over the past years [6–12]. Single crystals of the manganites have been grown in several ways. The flux method has been used for the preparation of $(La_{1-x}Pb_x)MnO_3$ with $0.25 < x < 0.45$ [3], $(Nd_{0.5}Pb_{0.5})MnO_3$ [13] and other lead-containing compositions [14]. Another more generally applicable growth method is from a molten zone, produced in an infrared image furnace [15]. Crystals grown in this way include $LaMnO_3$, $(La_{1-x}Ca_x)MnO_3$ with $0 < x < 0.25$ [16], $(La_{1-x}Sr_x)MnO_3$ with $0 < x < 0.6$ [17, 18], $(Pr_{0.5}Sr_{0.5})MnO_3$ [19], $(Pr_{0.7}Ca_{0.3})MnO_3$ [20] and $(La_{0.7}Pb_{0.3})MnO_3$ [21]. In the above methods, single crystals were grown at high temperature (>1273 K) with sizes in the range of several millimeters to several

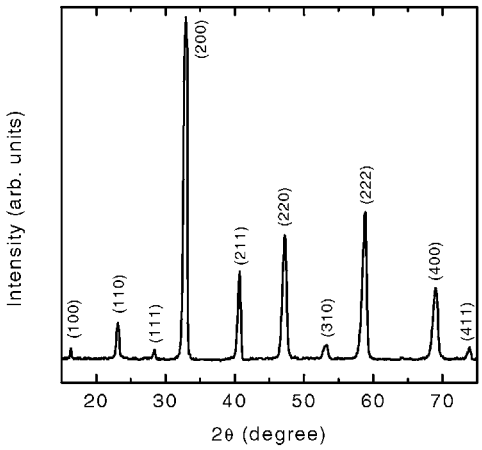

Figure 1. XRD pattern recorded from the $La_{0.5}Sr_{0.5}MnO_3$ nanowires.

centimeters. Other disadvantages of the above methods include large equipment, complex operating procedures etc. Here, using the hydrothermal technique, the authors prepare single-crystal $La_{0.5}Sr_{0.5}MnO_3$ nanowires under mild conditions for the first time. Compared to other methods, the hydrothermal method is preferable due to its low reaction temperature (553 K), simple apparatus and simple operation.

In the synthesis of $La_{0.5}Sr_{0.5}MnO_3$, high-purity $KMnO_4$, $MnCl_2 \cdot 4H_2O$, $La(NO_3)_3 \cdot 6H_2O$ and $Sr(NO_3)_2$ were used as the starting materials, and KOH served as the mineralizer. The typical synthesis procedure is as follows. The reaction reagents selected were dissolved in deionized water to form a solution, to which KOH was added with stirring to adjust the alkalinity of the solution. The initial mole ratios of the input species were 0.6 $KMnO_4$:1.4 $MnCl_2 \cdot 4H_2O$:1.0 $La(NO_3)_3 \cdot 6H_2O$:1.0 $Sr(NO_3)_2$:400H_2O:70 KOH. The reaction mixture was intensively stirred and poured into a teflon vessel till 80% of its volume was filled, then the vessel was placed in a stainless steel tank to undergo hydrothermal treatment. The crystallization reaction was performed at 553 K for 50 hours. After the autoclave was cooled and depressurised, the products were washed with deionized water and dried in an oven at 393 K. A black powder was finally obtained. Chemical analyses of the product indicate that the molar ratio of La:Sr:Mn was 0.5:0.5:1.0. The prepared samples were characterized and analysed by x-ray diffraction (XRD), transmission electron microscopy (TEM) and high-resolution TEM (HRTEM).

The powder XRD pattern (figure 1) was recorded on an MXPAHF x-ray diffractometer with Cu Kα radiation. The detection range was 15° to 75°. All peaks can be indexed to the cubic perovskite structure with a lattice constant of $a = 5.45$ Å, which shows that the prepared $La_{0.5}Sr_{0.5}MnO_3$ materials are single phase without any other secondary or impurity phase.

The TEM images and electron diffraction (ED) patterns were taken with a Hitachi H-800 transmission electron microscope. Figures 2(a) and (b) show two TEM images of our samples, which reveal that the samples consist of a large quantity of wire-like nanostructures with typical lengths in the range of 1.5 to 15 micrometers. Some particles are also observable in figure 2(a), but it was found in the experiment that their amount is far less than that in nanowires. Each nanowire has a uniform width along its entire length, and the typical widths of the nanowires are in the range of 50 to 400 nanometers. Two different ED patterns are exhibited in figures 2(c) and (d). The diffraction rings are the ED patterns of gold that was evaporated on the copper

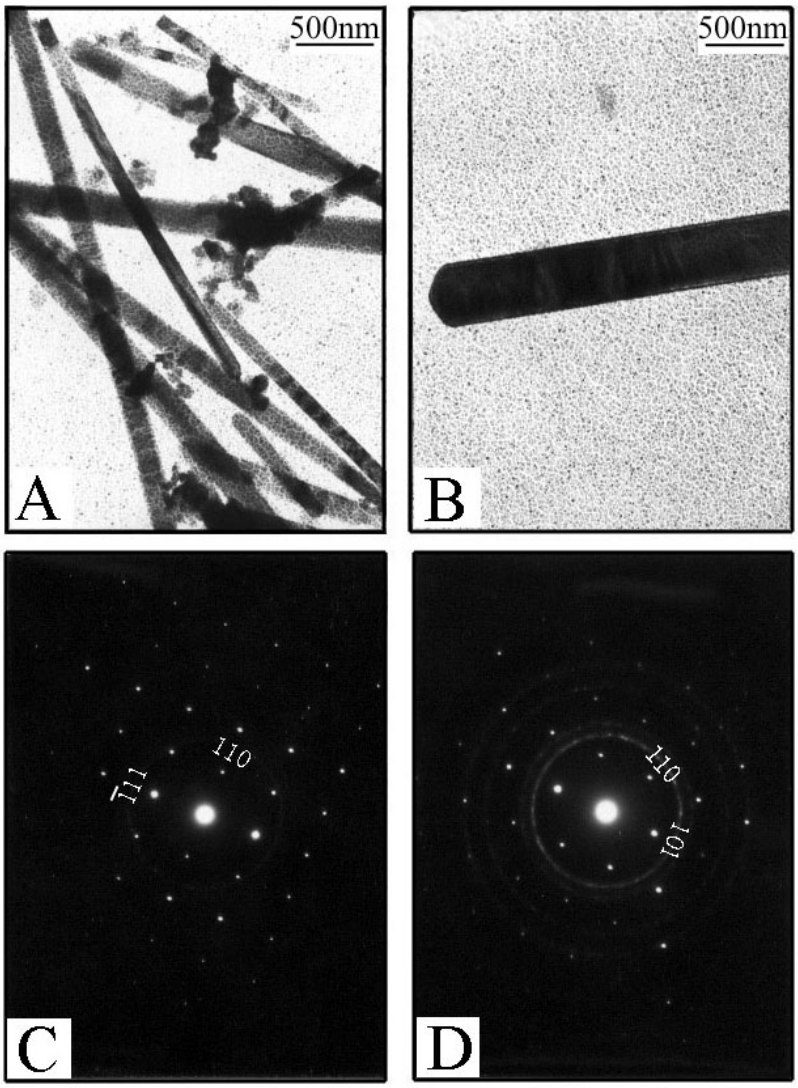

Figure 2. (a)–(b) Two TEM images of the $La_{0.5}Sr_{0.5}MnO_3$ nanowires. (c)–(d) Two different ED patterns of the nanowires.

netting film carrier beforehand, and they act as the reference standard of our calculations. The ED patterns show that the $La_{0.5}Sr_{0.5}MnO_3$ nanowires are single-crystal.

In order to study the lattice structure and judge the growth direction of the nanowires, an HRTEM experiment was carried out on a JEOL-2010 high-resolution transmission electron microscope. During the experiment it was found that the structure was unstable and changed markedly due to the electron beam bombardment, which brought complications to our experiment. When the electron beam bombarded the samples, initially the samples showed good single crystal characteristics, but the single-crystal structure quickly changed into a polycrystalline structure with prolonged bombardment. To avoid the structural change to a certain extent, images were obtained by snapping (taking images immediately after the electron

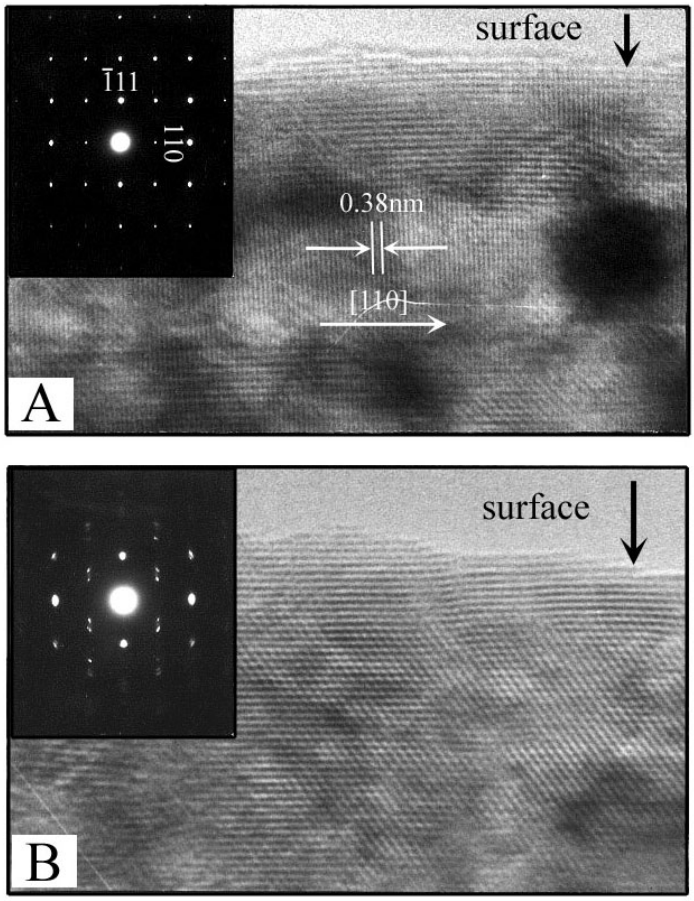

Figure 3. (a) HRTEM image of an $La_{0.5}Sr_{0.5}MnO_3$ nanowire obtained by snapping, showing the single-crystal structure of the nanowire. The inset shows the corresponding ED pattern. (b) HRTEM image of a nanowire showing the polycrystalline structure due to electron beam bombardment. The inset shows the corresponding ED pattern.

beam bombarded the samples). Figure 3(a) exhibits a typical HRTEM image of the nanowires, and the inset shows the corresponding ED pattern. On the basis of calculation and analysis, we reach the conclusion that the nanowires grow along the [110] direction. The HRTEM images reveal that the surfaces of the nanowires are clean, very regular, and without any sheathed amorphous phase. The structural change due to the electron beam bombardment can be observed from figure 3(b) (HRTEM image) and the inset (the corresponding ED pattern). Figure 3(b) and its inset show an obvious polycrystalline structure.

After the synthesis of the nanowires the zero-field cooled (ZFC) and field cooled (FC) magnetization were measured with a vibrating sample magnetometer from 380 K down to 5 K. The ZFC and FC magnetization curves are shown in figure 4 for $H = 0.01$ T. The Curie temperature T_C, defined as the inflection point in the M–T curve, is about 325 K for our sample. The difference between the ZFC and FC magnetization increases with decrease of the temperature. Moreover, the ZFC magnetization shows a peak, below which the magnetization decreases with decrease of the temperature, which suggests a spin freezing behaviour [22].

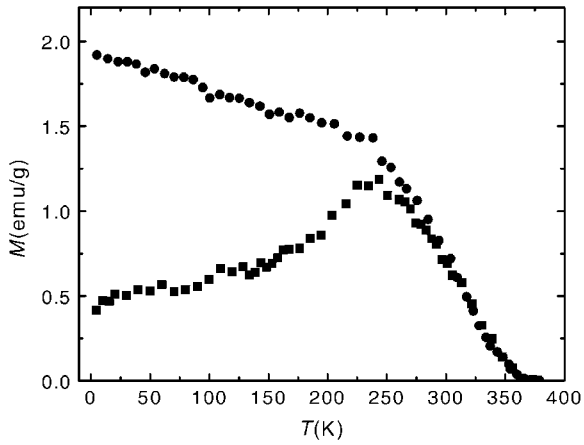

Figure 4. Temperature dependence of the magnetization for $La_{0.5}Sr_{0.5}MnO_3$ nanowires in ZFC (square) and FC (circle) under a 0.01 T field.

To summarize, we have synthesized single-crystal $La_{0.5}Sr_{0.5}MnO_3$ nanowires by a hydrothermal method. The advantages of this method include low reaction temperature (553 K), simple synthesis apparatus and ease of operation in comparison with other traditional preparation methods. Powder XRD and ED patterns show that this material has the cubic perovskite structure without any other secondary or impurity phase. High resolution TEM experiments indicate that the nanowires grow along the [110] direction; their surfaces are clean, very regular, and without any sheathed amorphous phase. Typical lengths of the nanowires are in the range of 1.5 to 15 micrometers, and typical widths are in the range of 50 to 400 nanometers. The nanowires could be an ideal system for studying dimensionally confined transport phenomena in perovskite manganites and for fabricating functional devices.

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