An Effective Preparation Route to A Giant Magnetoresistance Material: Hydrothermal Synthesis and Characterization of $La_{0.5}Sr_{0.5}MnO_3$

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Giant magnetoresistance material $La_{0.5}Sr_{0.5}MnO_3$ has been synthesized under mild hydrothermal condition at 240 °C and characterized by means of powder X-ray diffraction, thermal analysis, scanning electron microscopy, ICP elemental analysis, and iodometry. The alkalinity and molar ratio of Mn(VII)/Mn(II) in initial reaction mixture, associated with hydrothermal reaction temperature, dominated the crystallization of the product, $La_{0.5}Sr_{0.5}MnO_3$.

Perovskite-type manganese oxides with a formula $La_{1-x}A_xMnO_3$ (A = Ba, Sr, Ca or Pb) have been extensively investigated during the past forty years owing to their particular electrical and magnetic properties.[1] According to their different properties, some of them have already been used as electrolytes in solid-oxide fuel cells, high temperature oxygen sensors, and catalysts.[2] Followed by the discovery of giant magnetoresistance (GMR),[3] research in this field renewed. The recent development of GMR has led to extensive investigation of the preparation, structure, magnetic and electron transport properties on such rare-earth manganates. Traditionally, The preparations of the manganese oxide perovskites were realized by using solid-state reactions at high temperatures[4] or sol-gel processes.[5] Recently, mild hydrothermal method was proposed for solid-state material preparation because of its relatively low reaction temperature and autogenous pressure. Hydrothermal method has been an open route to microporous crystals and metastable phases,[6] and recently has been a great extension to the preparation of complex oxides and complex fluoride.[7] In some recent literatures, hydrothermal synthesis of manganese oxides was reported.[8] However, hydrothermal synthesis of manganese oxide perovskites containing rare earth elements has not been clarified so far. With an aim towards developing a mild synthesis route to complex oxides with particular properties, we systematically studied the hydrothermal synthesis of $La_{0.5}A_{0.5}MnO_3$ (A = Ba, Sr, Ca). Herein, the hydrothermal synthesis and characterization of $La_{0.5}Sr_{0.5}MnO_3$ will be described.

In our previous study, $La_{0.5}Ba_{0.5}MnO_3$ single phase has been successfully synthesized by using hydrothermal method.[9] For further exploration of $La_{0.5}A_{0.5}MnO_3$ (A = Sr, Ca), it was observed that the synthesis work was much more difficult than that for $La_{0.5}Ba_{0.5}MnO_3$, since the relatively small ionic sizes of Sr^{2+} and Ca^{2+} easily result in the formation of lattice defects and impurities. By further adjusting the hydrothermal synthesis conditions, in this work, the crystallization of $La_{0.5}Sr_{0.5}MnO_3$ with perovskite structure was realized. An initial reaction mixture with a molar composition range of x $KMnO_4$: y $MnCl_2{\cdot}4H_2O$: 1.0 $La(NO_3)_3{\cdot}4H_2O$: 1.0 $Sr(OH)_2{\cdot}8H_2O$: z KOH: 750 H_2O ($x = 0.8$–0.4, $y = 1.2$–1.6, $z = 200$–240) was employed in the synthesis. In a typical synthesis procedure, 56 mg of $KMnO_4$ (A.R.) and 110 mg of $MnCl_2$ (A.R.) were dissolved in 7 ml of deionized water to form a solution, to which 134 mg of $Sr(OH)_2{\cdot}8H_2O$ (A.R.), and 212 mg of $La(NO_3)_3{\cdot}6H_2O$ (A.R.) and 6 g of KOH (A.R.) were added, respectively. The reaction mixture was stirred with a magnetic stirrer for 40 min and then was transferred into a teflon-lined stainless steel autoclave. The crystallization was carried out under autogenous pressure at 240 °C for 1–3 days. After the completion of crystallization, black crystalline products were obtained. The products were filtered and washed with deionized water until pH = 7, and then dried in air at ambient temperature. All products were characterized by powder X-ray diffraction (XRD) on a Rigaku D/max-γ A diffractometer with a Ni-filtered Cu Kα radiation at room temperature. The XRD data for index and cell-parameter calculations were collected by a scanning mode with a step of 0.02° and a scanning rate of $0.2°\,min^{-1}$. Silicon was used as an internal standard. The composition of each product was analyzed by using the ICP method.

Figure 1 shows XRD pattern of $La_{0.5}A_{0.5}MnO_3$ (A = Ba, Sr, Ca). The XRD index results of $La_{0.5}A_{0.5}MnO_3$ (A = Ba, Sr) indicated that the crystalline product formed in the hydrothermal systems were the single phases. The SEM images of the as-prepared $La_{0.5}Sr_{0.5}MnO_3$ showen in Figure 2 indicated that the

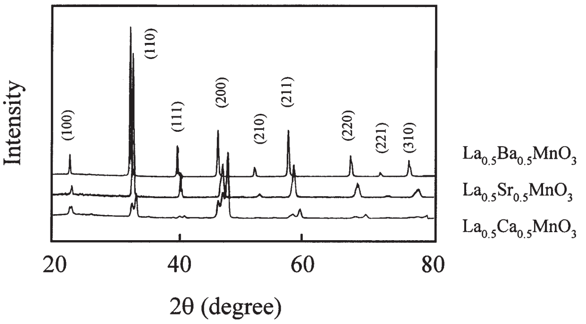

Figure 1. XRD patterns of $La_{0.5}A_{0.5}MnO_3$ (Ba, Sr, Ca).

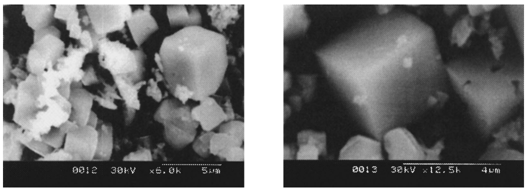

Figure 2. SEM images of the crystalline $La_{0.5}Sr_{0.5}MnO_3$.

product is cubic single crystal of about 2–5 μm in size.

In the synthesis of $La_{0.5}Sr_{0.5}MnO_3$, it was found that the sort of reactants, initial composition and alkalinity in reaction mixtures were sensitive to the formation, crystallization and purity of the products. Lanthanum nitrate, strontium hydroxide, potassium permanganate, and manganous chloride could be used as the reactants. To prepare a pure product with a formula of $La_{0.5}Sr_{0.5}MnO_3$, the molar ratio of La : Sr : Mn in initial reaction mixture was determined as 1 : 1 : 2.

The Mn(VII)/Mn(II) ratio of initial materials is a dominant factor for the preparation of $La_{0.5}Sr_{0.5}MnO_3$. According to the component of the product, it can be estimated that a hydrothermal redox reaction between Mn(VII) and Mn(II) might occur during the synthetic procedure as follows:

$$0.4\mathrm{Mn(VII)} + 1.6\mathrm{Mn(II)} \rightarrow 2\mathrm{Mn(III)}_{0.5}\mathrm{Mn(IV)}_{0.5}$$

Therefore, the molar ratio of 0.4/1.6 for Mn(VII)/Mn(II) is probably appropriate, which had been confirmed by the subsequent experimental results. When this ratio was employed, highly crystalline $La_{0.5}Sr_{0.5}MnO_3$ would be formed without any impurity. When the Mn(VII)/Mn(II) ratios of initial materials were higher or much lower than this value, an impurity phase of $La(OH)_3$ always formed with the product. Attractively, slightly lower Mn(VII)/Mn(II) ratios were also favourable for the crystallization of pure products, as a result of the oxidation environment provided by the alkaline reaction system. Since the product was crystallized under highly alkaline conditions which is of advantage for the oxidation of Mn(II), the oxidation environment can ensure the redox reaction between Mn(VII) and Mn(II) carried out completely even if the reaction synstem was a little lack of Mn(VII). An excess of Mn(VII) component in a large scale is undesirable for the formation of pure $La_{0.5}Sr_{0.5}MnO_3$. However, using H_2O_2 instead of Mn(VII) component as the oxidation agent also resulted in the formation $La_{0.5}Sr_{0.5}MnO_3$. The influence of different sources of Mn(II) (e.g. $MnCl_2$) on the purity of the products is another evidence.

The alkalinity of the reaction system, depending on the composition of initial mixture, considerably influenced the crystallization of the product. To maintain the suitable alkalinity required by hydrothermal reactions, it is essential to use alkaline mineralizers.[10] KOH and NaOH are most convenient for this purpose. Moreover, a certain concentration of OH^- ion can also provide necessary oxidizing environment for the preparation of such oxides. Pure $La_{0.5}Sr_{0.5}MnO_3$ phase can be synthesized in the $[OH^-]$ range of 5–15 M at 240 °C, and the best crystallinity was observed at the $[OH^-]$ range of 7–10 M.

Average valence states of manganese in the products were determined by iodometry. It was observed that the oxidation state of manganese varies with reaction conditions, especially the Mn(VII)/Mn(II) molar ratio in initial composition and alkalinity in reaction mixture. For the sample prepared from the typical synthesis procedure, the average valence of manganese was determined to be 3.5 and thus Mn(III)/Mn(IV) molar ratio was unit. Electrical resistance and magntoresistance were detected on disk shape pellets ($\Phi 10 \times 1$ mm). The magnetoresistance (MR) is defined as $\rho R/R_H = (R_0 - R_H)/R_H$, where R_0 and R_H are resistances at magnetic field of zero and H (1T), respectively. $La_{0.5}Sr_{0.5}MnO_3$ exhibits a sharper insulator and MR. The observed MR is 9% at 77 K (at 1T), but it is lower than those of the single crystals of $La_{1-x}Sr_xMnO_3$ with $x < 0.5$.

In summary, a magnetoresistance material, $La_{0.5}Sr_{0.5}MnO_3$ has been synthesized under mild hydrothermal conditions at 240 °C for 24 h. The alkalinity, mole ratio of Mn(VII)/Mn(II), and Mn(II) sources in the initial reaction mixture, associated with hydrothermal reaction temperature dominated the crystallization of the title compound. Hydrothermal synthesis route exhibited obvious advantages in terms of lower synthesis temperature, short reaction time, ready chemical operation for adjusting mixed valence, high purity and crystallinity of products.

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