Magnetoresistance Plateau in La$_{2/3}$Ca$_{1/3}$Bi$_x$Mn$_{1-x}$O$_3$
Granular System

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Abstract: The effect of doping additional Bi on the magnetoresistance (MR) of La$_{2/3}$Ca$_{1/3}$Bi$_x$Mn$_{1-x}$O$_3$ was investigated. It is found that traditional colossal magnetoresistance (CMR) peak can only be observed in the $x$<0.05 samples and the peak value decreases with the increase of $x$, but the $x$$\geq$0.05 samples show a magnetoresistance plateau above 200 K because of the presence of additional (La,Ca,Bi)-O layers. Moreover, this MR plateau is enhanced for the segregation of the La, Ca, and Bi elements.

Key words: perovskite manganite; phase segregation; composite; magnetoresistance plateau

1 Introduction

Colossal magnetoresistance (CMR) observed in AMnO$_3$-type perovskite manganites (A=RE$_{1-x}$AE$_x$, here RE and AE are trivalent rare-earth elements and divalent alkaline-earth elements, respectively) has attracted much research worldwide because of its importance both for fundamental research in solid-state physics and for practical application in magneto-electronics$^{[1,2]}$. However, the so-called CMR is usually found on a large magnetic field of the order of several teslas and in a narrow temperature range, which seriously limit its practical applications. Recently, the discovery of low-field magnetoresistance (LFMR) in the polycrystalline of perovskite manganites has shone a light on the practical research of them. It is proposed that the LFMR in these materials is closely related to spin dependent scattering and tunneling at the grain boundaries and interfaces$^{[3,4]}$. Further research revealed that the introduction of a secondary phase, usually a nonmagnetic or an antiferromagnetic inorganic insulator, into the granular system of ferromagnetic manganites could effectively decorate the grain boundaries and interfaces and lead to an improved MR$^{[5-11]}$.

Our latest work had successfully fabricated granular metal/insulator composites by doping Zr in the Mn-site of La$_{2/3}$Sr$_{1/3}$MnO$_3$$^{[12]}$. Because of the low solid solubility of Zr ions in La$_{2/3}$Sr$_{1/3}$MnO$_3$, most Zr ions segregate as the secondary phases during the sintering process. In other words, the existence of the secondary phases in the composites is not by introduction, but by segregation. Comparing with the preparation of composites in the previous research$^{[5-11]}$, we think the distribution of each phase in our samples is more homogeneous, which should be beneficial to LFMR and reproduction. In the present paper, we made granular metal/insulator composites by doping additional Bi in La$_{2/3}$Ca$_{1/3}$MnO$_3$ and found magnetoresistance plateaus in high Bi-content samples.

2 Experimental

The samples with nominal compositions La$_{2/3}$Ca$_{1/3}$Bi$_x$Mn$_{1-x}$O$_3$ ($x=0, 0.01, 0.05, 0.1, 0.2$) were prepared by sol-gel method$^{[12]}$. Here we decrease Mn content at the same time to enhance the effect of Bi. The final sintering process was carried out at 950 $^\circ$C for 10 h. The structure of the samples was characterized by X-ray diffraction (XRD) (Bruker D8-ADVANCE X-ray Diffractometer) and the morphology was probed by a field emission gun (FEG) scanning electron microscope (SIRION SEM, FEI, the Netherlands). DC magnetization measurements were performed on a superconducting quantum interference device (SQUID) magnetometer. The resistance was measured with a standard four-probe method in the
warming process and the magnetoresistance (MR) ratio is defined as \( MR = \frac{(R_0 - R_H)}{R_0} \), where \( R_0 \) and \( R_H \) are the resistance in a zero field and an applied magnetic field, respectively.

### 3 Results and Discussion

Fig.1 shows the X-ray powder diffraction patterns of all the samples. It is shown that the crystal structure of the \( x \leq 0.05 \) samples is a single perovskite structure. But it is clear that additional diffraction peaks are present in the patterns of the \( x > 0.05 \) samples. These additional peaks were indexed as bismuth oxides and bismuthate (we classify them as the secondary phases). The result indicates that only a small amount of Bi could enter the lattice of \( \text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3 \) and the perovskite phase in the samples with Bi addition is a kind of Mn deficient phase with chemical formula \( \text{A}_{1+\delta}\text{Mn}_{1-\delta}\text{O}_3 \) \((\delta < 0.1)\)\(^{[13]}\).

For the close correlation between the magnetic, electrical properties and the microstructure of polycrystalline manganites, the fracture morphologies of all samples were imaged by SEM (as depicted in Fig.2). Obviously, the average grain size of the \( x \leq 0.05 \) samples increases with the increase of Bi, but the \( x \geq 0.05 \) samples show sligter difference in the grain size. It should be noticed that the morphology of the \( x=0.05 \) sample is similar to those of the \( x=0.1 \) and \( 0.2 \) samples, which maybe mean that the segregation of La, Ca and Bi had already happened when \( x=0.05 \) and \( \delta \) in chemical formula \( \text{A}_{1+\delta}\text{Mn}_{1-\delta}\text{O}_3 \) should be less than 0.05 \((\delta < 0.05)\). The reason of no clear signals of the secondary phases in the XRD pattern of the \( x=0.05 \) sample is because of the small amount of the secondary phases in it. Under this hypothesis, the change of the average grain size could be understood. For the low melting behavior of the bismuth oxide\(^{[14]}\), the doping Bi element served as additive to improve the growth of the grains, which results in the accretion of grains in the \( x < 0.05 \) samples. In the \( x \geq 0.05 \) samples, the appearance of the secondary phases could block the further growth of the grains and lead to the slighter difference in grain size of them. With the increase of the grain size, the the pore volume of the samples decreases simultaneously in the \( x < 0.05 \) samples. But in the \( x \geq 0.05 \) samples, still for the low melting behavior of the bismuth oxide\(^{[14]}\), the secondary phases were melting and filled in the interfaces of the grains during the sintering process, which results in the further decrease of pore volume and better connectivity between the grains in these samples.

The measurement of DC magnetization (\( M \)) indicates that all the samples transform from paramagnetism to ferromagnetism (PM-FM) with decreasing temperature. Fig.3(a) illustrates the \( dM/dT \) versus temperature curves of all the samples (normalized with the peak value of \( dM/dT \)). The Curie temperature \( T_C \) (defined as the temperature where \( dM/dT \) reaches the minimum) is 271, 265, 264, 257, 258, and 258 K for the \( x=0, 0.01, 0.025, 0.05, 0.1, 0.2 \) samples, respectively. The decrease of \( T_C \) in the \( x \leq 0.05 \) samples should be attributed to the weakening of the double-exchange (DE) interaction caused by