GRAIN GROWTH DEPENDENCE OF MICROSTRUCTURE
IN La_{0.67}Ba_{0.33}MnO_3+6 OXIDES

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Grain growth dependence of microstructure in La_{0.67}Ba_{0.33}MnO_3+6 oxides has been studied in detail. The result shows that the crystals grew along three vertical axes with a concentric terrace pattern in the sample sintered at 1673K while the oxides sintered at 1573K grew with a lateral growth manner. However, the concentric terrace growth pattern resulted in twin microstructure in the cooling processing and the lateral growth manner produced non-twin microstructure in the oxides at ambient, respectively. It was found that the oxide with twin microstructure has a much higher saturation magnetization than the non-twin oxide. This may be due to the easier alignment of the domains in the twin-grained oxide through the rearrangement of dislocations in twin-boundaries.

1 Introduction

Perovskite lanthanum manganese oxides, La_{1-x}A_xMnO_3+δ (A = Ca, Sr, Ba etc.) that possess colossal magnetoresistance (CMR) properties, have attracted great interest in recent years because of their potential technological applications.\textsuperscript{1-3} It is believed that CMR properties arise from the double exchange effect, a process where carrier hopping is greater between aligned spins than between anti-aligned spins due to the energy cost of flipping the carrier spin.\textsuperscript{4} Recently, the CMR properties of single crystal and polycrystalline materials are found to be significantly different.\textsuperscript{5,6} It was reported that the microstructures play an important role in determining the magneto-transport properties of thin films; and the grain boundaries strongly affect the low field MR behavior in bulk materials due to the associate strain field. Research results also showed that the high field magnetoresistance depends on the connectivity between the grains rather than the size of the grains; and the large MR component in polycrystalline materials is attributed to the spin polarized tunneling between grains.\textsuperscript{7,8} However, the grain growth effects on the microstructure, which dominated the physical properties of La_{2/3}Ba_{1/3}MnO_3+6 oxides, are not fully understood. In the present work, the grain growth dependence of microstructure has been investigated in detail by using transmission and scanning electron microscopy (TEM and SEM). The effects of microstructure on the

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transition behavior of La$_{2/3}$Ba$_{1/3}$MnO$_{3+δ}$ oxides have also been studied. The understanding obtained from this work can be used to further develop CMR materials and to optimize their fabrication parameters.

2 Experimental

La$_{2/3}$Ba$_{1/3}$MnO$_{3+δ}$ oxide was prepared by mixing La$_2$O$_3$, BaCO$_3$ and MnO$_2$ powders in a nominal cation ratio of La:Ba:Mn = 2:1:3. The mixture of powder was decomposed at 1073K for 24 hours and then ground and pressed into pellets. To investigate the effect of sintering temperature on the grain growth manner and microstructure, the pellets were sintered at 1573K and 1673K for 60 hours respectively. The La$_{2/3}$Ba$_{1/3}$MnO$_{3+δ}$ oxides formed during the sintering process. The heating/cooling rates were ±5K/min. The surface morphology and the microstructure of the La$_{2/3}$Ba$_{1/3}$MnO$_{3+δ}$ oxide were characterized using Scanning Electron Microscope (SEM) and Transmission Electron Microscope (TEM). Selected area electron diffraction was employed to identify the crystallographic orientations. The magnetization of the La$_{2/3}$Ba$_{1/3}$MnO$_{3+δ}$ oxides was measured from 1.6K to 400K with absence of magnetic field.

3 Results and discussion

Fig.1 shows the SEM micrograph of the morphology of La$_{2/3}$Ba$_{1/3}$MnO$_{3+δ}$ crystals sintered at 1673K. It reveals that the crystals grew along three vertical axes with a concentric pattern of ~250 nm high terraces. TEM micrograph in Fig.2(a) exhibits that lamella structure of ~79 nm mean period uniformly dominated the microstructure of the 

![Fig.1 SEM morphology of La$_{2/3}$Ba$_{1/3}$MnO$_{3+δ}$ oxides sintered at 1673K for 60 hours.](image)

![Fig.2 (a) TEM micrograph showing lamella microstructure of La$_{2/3}$Ba$_{1/3}$MnO$_{3+δ}$ oxide sintered at 1673K, (b) SAED pattern showing that the lamella microstructure consists of twin La$_{2/3}$Ba$_{1/3}$MnO$_{3+δ}$ crystals.](image)
sample sintered at 1673K. The selected area electron diffraction (SAED) pattern in Fig. 2(b) shows two sets of diffraction patterns – \( P_M \) (marked with solid line) and \( P_7 \) (marked with dotted line) in the lamella area. The reciprocal lattice points in these patterns were \([2\overline{4}3]_{\text{Matrix}}\) and \([2\overline{4}3]_{\text{Twin}}\), respectively. From the diffraction patterns, it can be deduced that twin plane of the \( \text{La}_{2/3}\text{Ba}_{1/3}\text{MnO}_{3+\delta} \) crystals was \((001)\) and twin axis was \([001]\). Fig. 3(b) also shows that if the reciprocal lattice point \((\overline{1}22)\) in \( P_M \) moved \( \frac{a}{5}[210] \) along \((210)\) direction, it would get to the reciprocal lattice point \((1\overline{1}2)\) in \( P_7 \).

Hence, the twin crystallization could simply take place as the matrix lattice glide along \((210)\) for a distance of \( \frac{\sqrt{5}}{5}a \) (0.175 nm).

Fig. 3 shows the grain boundary morphology of the twin lamellae, revealing that the grain boundary consists of dislocations. These dislocations may be caused by the incoherent twin boundary. On the other hand, the difference between the height of concentric terraces and the mean period of lamella reveals that lamella structure was not formed during the crystal growth but resulted by the diffusionless phase transformation during the cooling processing after sintering.

![Fig. 3 TEM micrograph showing the grain boundary of twin crystals](image)

Fig. 4(a) is a SEM surface morphology of \( \text{La}_{2/3}\text{Ba}_{1/3}\text{MnO}_3 \) oxide sintered at 1573K, showing a multi-step growth structure. A tip formed on a lateral-growing layer, as pointed by an arrow, can be discerned. The TEM micrograph in Fig. 4(b) indicates that the grain boundary of \( \text{La}_{2/3}\text{Ba}_{1/3}\text{MnO}_3 \) oxide consisted of multi-steps (arrowed). These results revealed that the oxide grew with a lateral growth manner during sintering at 1573K.

Although X-ray diffraction analysis indicates that the oxides, sintered at different temperatures, had the same cubic lattice structure and parameter of 0.391nm, the difference of the grain growth mechanisms resulted in the difference of the microstructures. TEM micrograph (Fig. 5) shows three \( \text{La}_{2/3}\text{Ba}_{1/3}\text{MnO}_3 \) domains, as marked with \( D_\alpha, D_\beta \) and \( D_\gamma \), in the sample sintered at 1573K. The strips in the domains may be unit cells, which had the same dipole alignment. It can be seen that the domain direction of \( D_\alpha \) is parallel to the direction of \( D_C \) while the direction of \( D_\beta \) is approximately perpendicular to the direction of both of \( D_\alpha \) and \( D_C \). The deviation of the
Fig. 4  (a) SEM surface micrograph of $\text{La}_{2/3}\text{Ba}_{1/3}\text{MnO}_3$ oxide sintered at 1573K, showing the multilayer structure of the crystals, (b) TEM micrograph showing multi-steps in the grain boundary areas.

Fig. 5  TEM micrograph showing the domain structures of $\text{La}_{2/3}\text{Ba}_{1/3}\text{MnO}_3$ oxide

Fig. 6  (a) Lamella structure of $\text{La}_{2/3}\text{Ba}_{1/3}\text{MnO}_3$ oxide, and (b) leaf-like microstructure in a lamellae domain. 

angles from 90° may be caused by the sample preparation and tilting to the polishing surface.
Although lamella structure was observed occasionally (Fig. 6(a)), its microstructure was entirely different from the oxide that was sintered at 1673K (Fig. 2(a)). Fig. 6(b) shows the details of the inner lamella structure. The leaf-like microstructures were parallel across the domain and ended on the domain boundaries. The leaves may also be the unit cells with the aligned dipoles. However, the leaf-like microstructures in one lamella were also parallel to the lamella of the its neighbor, as shown in Fig. 6(a).

Figure 7(a) presents the plate-like crystals with the La$_{2/3}$Ba$_{1/3}$MnO$_3$ domains in the sample sintered at 1573K. The domain walls can be clearly seen, with thickness of ~25 nm. The existence of the domain walls indicates that the domains had opposite direction with their neighbors. However, the characteristics of these domain walls were totally different with the domain boundaries shown in Fig. 5. The domain boundaries were thin (~2 nm) and not straight while the domain walls were thick and straight. The different thickness between the domain boundary and wall was attributed to the different interfacial energies. In general, the 90° domain boundary has one third of energy of the 180° domain wall in perovskite crystals. The lamellae domains with domain walls of ~25 nm thick were also observed, as show in Fig. 7(b). The similar thickness of the domain walls in the crystals with different microstructures reveals that the 25 nm thick domain wall is one of the microstructural characteristics of La$_{2/3}$Ba$_{1/3}$MnO$_3$ oxide sintered at 1573K.

Fig. 7 (a) The plate-like crystals with La$_{2/3}$Ba$_{1/3}$MnO$_3$ domain walls, (b) lamellae domains with domain walls.

Fig. 8 plots the magnetization (M) of the La$_{2/3}$Ba$_{1/3}$MnO$_{3+x}$ oxides versus temperature. It shows that M of the twin oxide was four times greater than that of the non-twin oxide. Although both oxides had similar ferro-to-para magnetic transition behavior at 333K, M of the non-twin oxide slightly decreased while M of the twin oxide increased around 70K (see arrows in Fig. 8). These results indicate that the T$_c$ is independent of the microstructure but the magnetization and transition behavior are strongly microstructure dependent. It is believed that the higher M was attributed to the twin microstructure, but the mechanisms are not clear.

In general, the magnetic domains of the polycrystalline La$_{2/3}$Ba$_{1/3}$MnO$_{3+x}$ oxide aligns to a certain direction spontaneously when the temperature is below the transition temperature, resulting in ferromagnetism. It is believed that the alignment of the domains in the non-twin polycrystalline oxide was restricted by the neighboring crystals that had different orientations. However, in the twin-grained oxide, the alignment was
4 Conclusion

The grain growth dependence of microstructure in La$_{2/3}$Ba$_{1/3}$MnO$_{3+x}$ oxides has been investigated in detail. The results show that the crystals grew along three vertical axes with a concentric terrace pattern in the sample sintered at 1673K while the oxides sintered at 1573K grew with a lateral growth manner. The difference of the grain growth mechanism resulted in different microstructures. Sintering the sample at 1673K, twin crystallization took place in the cooling process and formed lamella-like twin microstructural oxide. The twin plane, twin axis and twin direction were (001), [001] and [210], respectively. However, the non-twin microstructural oxide formed when the material was sintered at 1573K. The various domains with domain boundary or domain walls were observed. It was found that the oxide with twin microstructure has a much higher saturation magnetization than the non-twin oxide. This may be due to the easier alignment of the domains in the twin-grained oxide through the rearrangement of dislocations in twin-boundaries.

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References