Synthesis and atom-scale microstructure of Ba$_6$Mn$_5$O$_{16}$

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Abstract

Layered manganate Ba$_6$Mn$_5$O$_{16}$ was prepared by a traditional solid-state reaction method and its microstructure at atomic level was investigated in detail by means of high-resolution transmission electron microscopy (HRTEM). Although the sample shows, from the XRD data, a nearly single-phase $n = 5$ layered Ba$_6$Mn$_5$O$_{16}$ phase of the hexagonal Ba$_{n+1}$Mn$_n$O$_{3n+1}$ homologous series, the presence of numerous structural defects, especially intergrowth faults of the hexagonal Ba$_{n+1}$Mn$_n$O$_{3n+1}$ homologous series with different $n$ in it, was revealed by HRTEM. Furthermore, a minor 2H BaMnO$_3$ phase was also found to coexist with the layered Ba$_6$Mn$_5$O$_{16}$ phase. These defects could have a correlation with the magnetic properties of the sample, i.e. the $T_N$ being very broad and the appearance of the Curie tail in the susceptibility.

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1. Introduction

The perovskite-related oxides with the general formula ABO$_3$ have been extensively studied because of their intriguing structural and physicochemical properties. Structurally ABO$_3$ related perovskites can be described on the basis of packed AO$_3$ layers with B cations occupying a fraction of octahedral sites. The stacking sequence of the AO$_3$ layers can be cubic (c), hexagonal (h) and a combination of the both. Different stacking sequence leads to different perovskite-related structures. From a structural point of view, the Ba–Mn–O system can be regarded as one of the most fruitful systems since numerous BaMn$_{3−y}$O$_y$ varieties can be stabilized for different values of $y$ [1–6].

Recently, the layered Ba–Mn containing manganates, Ba$_4$Mn$_3$O$_{10}$ [7] and Ba$_6$Mn$_5$O$_{16}$ [8], have been stabilized. Both the layered oxides belong to the hexagonal A$_n+1$B$_5$O$_{3n+1}$ homologous series which are based on such a building principle: blocks of $n$ face-sharing octahedra linked one to each other by two of the three terminal corners forming a two-dimensional sheet [9]. For $n = 1$, the A$_3$BO$_3$ composition, like the X$_2$YO$_4$ derived from $n = 1$ Ruddlesden–Popper (RP) X$_{n+1}$Y$_{n}$O$_{3n+1}$ series [10], stabilizes a layered K$_2$NiF$_4$-type [11] structure. When $n = ∞$, one-dimensional 2H ABO$_3$ structural type, such as BaMnO$_3$ [1] and CsNiF$_3$ [12], is obtained. In fact, the layered Ba$_4$Mn$_3$O$_{10}$, isosctructural to Cs$_4$Ni$_3$F$_{10}$ [13] and Sr$_4$Mn$_3$O$_{10}$ [14], can be related to the 9R–BaMnO$_{3−y}$ with a $(hh)$ stacking sequence [15]. In a similar way, the layered Ba$_6$Mn$_5$O$_{16}$, isosctructural to Cs$_6$Ni$_5$F$_{16}$ [16], can be associated with the 15R–BaMnO$_{3−y}$ with a $(hh)(hh)$ stacking sequence [3]. The transformation of the 9R and 15R BaMnO$_{3−y}$ polytypes, respectively, into the layered Ba$_4$Mn$_3$O$_{10}$ and Ba$_6$Mn$_5$O$_{16}$ was described in Ref. [9]. Fig. 1 shows the [100] projection of the Ba$_6$Mn$_5$O$_{16}$ layered structure built up from Mn$_3$O$_8$ units of five face-sharing octahedra linked via their apexes.
Interestingly, the magnetic measurements on the manganate Ba$_n$Mn$_{5n}$O$_{16}$ revealed a broad $T_N$ and a noticeable Curie tail in the magnetic susceptibility [8]. These magnetic characteristics of the broad $T_N$, as well as the appearance of the Curie tail (which could be related to the uncoupled end chain spins) in the susceptibility, indicate that some structural defects such as intergrowth faults could exist in the material since magnetoresistance properties strongly depend on the number of octahedra that stack in a perovskite block [17]. However, no detailed microstructure analysis has been carried out on this layered compound. Bearing in mind this information, we decided to reinvestigate the Ba$_n$Mn$_{5n}$O$_{16}$ system, first to see whether the $n=5$ Ba$_5$Mn$_{25}$O$_{16}$ phase of the hexagonal Ba$_n^{+1}$Mn$_n$O$_{3n}^{+1}$ homologous series can be stabilized using a synthesis method different from that reported in Ref. [8], then to see whether the microstructure has a correlation with the magnetic properties in this system.

2. Experimental

Polycrystalline Ba$_5$Mn$_{25}$O$_{16}$ was synthesized using traditional solid-state reaction method. The starting materials, BaCO$_3$ (>99%) and MnCO$_3$ (99.9%) taken in stoichiometric ratio, were thoroughly mixed in a motorized agate mortar. Then the powders were calcined at 1000 °C, reground, pelletized and annealed in air at 1230 °C for 30 h. The X-ray powder diffraction (XRD) pattern was recorded with Cu K$_\alpha$ radiation to characterize the crystal structure of Ba$_5$Mn$_{25}$O$_{16}$ sample. The magnetization measurement was carried out in a SQUID magnetometer.

Thin samples for transmission electron microscopy (TEM) studies were prepared by crushing the Ba$_5$Mn$_{25}$O$_{16}$ bulk specimen in an agate mortar filled with alcohol, and then dispersing the fine fragments suspended in alcohol on Cu grids coated with holey carbon supported films. A Tecnai F20 field-emission electron microscope installed at Beijing Laboratory of Electron Microscopy, Beijing National Laboratory for Condensed Matter Physics, was used for selected area electron diffraction (ED) and high-resolution transmission electron microscopy (HRTEM) experiments. The Cs (the spherical aberration coefficient of the objective lens) and the Del (the halfwidth of a Gaussian spread of focus due to chromatic aberration) values of the microscope are 1.2 mm and 57 Å, respectively. All the TEM studies were carried out at 200 keV.

3. Results and discussion

Fig. 2 shows the XRD pattern for the Ba$_5$Mn$_{25}$O$_{16}$ sample, which is very similar to that reported by Boualahya et al. [8]. All the peaks in the pattern can be indexed on the base of the Cmca orthorhombic structure with the lattice parameters $a = 0.57071$ nm, $b = 1.31856$ nm and $c = 1.99273$ nm refined by Boualahya et al. [8], and the indices of most main peaks have been marked in the pattern (we have not marked all the peaks as high dense peaks are included in the pattern). The layered structure of the perfect Ba$_5$Mn$_{25}$O$_{16}$ phase is further reinforced by the resultant ED and high-resolution TEM data. Fig. 3 shows a HRTEM image taken along the [1 0 0] zone-axis direction, where the contrast forms clearly a zigzag path along c-axis. The corresponding ED pattern taken along the [1 0 0] zone-axis direction is shown on the top left-hand corner of Fig. 2, and also indicates the details about the layered structure. Image simulations based on the structure model proposed previously [8] were carried out on the simulation program Cerius 2.0 using multi-slice theory of dynamical scattering. The Cs and Del values used for simulations are 1.2 mm and 57 Å, respectively. The simulated results show that a simulated image for a defocus value of $-45$ nm and a thickness of 5 nm, superimposed...
onto the image, appears to be in good agreement with the experimental one.

Interestingly, although the sample shows a single-phase layered $\text{Ba}_6\text{Mn}_5\text{O}_{16}$ phase from the XRD data, the presence of numerous structural defects, especially intergrowth faults of the hexagonal $\text{Ba}_{n+1}\text{Mn}_n\text{O}_{3n+1}$ homologous series with different $n$, is revealed by TEM. The intergrowth structures can be analyzed by HRTEM along both the [1 0 0] and [0 1 0] zone-axis directions. As examples, Fig. 4(a) shows the [1 0 0] zone-axis HRTEM image of an area containing $n = 7$ member hexagonal structure, and Figs. 4(b) and (c) present the [0 1 0] zone-axis HRTEM images of different areas containing intergrowth structures with $n = 1, 3, 5$ and 7 members. It should be noted that in the hexagonal $\text{A}_{n+1}\text{B}_n\text{O}_{3n+1}$ homologous series the structure with $n = 1$ is isotopic to layered $\text{K}_2\text{NiF}_4$-type [11] structure with only corner-sharing octahedra, and the structures with even $n$ members may reasonably be missing from the series. In order to well understand the formation of the intergrowth faults, we show schematically in Fig. 4(d) the [1 0 0] projection of the $n = 5 \text{Ba}_6\text{Mn}_5\text{O}_{16}$ structure containing blocks with $n = 1, 3, 5$ and 7 members. It can been seen that a kind of $n$ member intergrowth block is generated by the substitution of a group of $[\text{Mn}_n\text{O}_{3n+3}]$ units with face-sharing octahedra (where $n$ is odd) for a group of $[\text{Mn}_3\text{O}_{18}]$ units with five face-sharing octahedra. The positional parameters of the atoms of each kind of intergrowth block, as shown in Fig. 4(d), can be derived approximately from the crystallographic data of the $\text{Ba}_6\text{Mn}_5\text{O}_{16}$ structure [8]. To see whether the intergrowth faults as shown in Fig. 4(d) are reasonable, image simulations from them were also carried out. The simulated images of different intergrowth faults were revealed to be in good agreement with the experimental images. As an example, a simulated image ($\Delta t = 7 \text{ nm}$ and $\Delta f = -48 \text{ nm}$) from the area containing one $n = 1$ intergrowth block (see Fig. 4(d)), superimposed onto the image of Fig. 4(c), appears to be in good agreement with the experimental one. In fact, the $n = 1$ intergrowth structure as depicted in Fig. 4(d) is visible in many $\text{Ba–Mn containing ABO}_3$ perovskite-related polytypes such as the 12R polytype [18].

An attempt was made to estimate the content of the intergrowth faults, although the TEM results usually suffer from poor statistics due to the observation of a limited number of individual grains. In our evaluation, we conclude, by observing 30 grains, that about 30% of the grains show clear intergrowth faults.

If one block of $[\text{Mn}_3\text{O}_{18}]$ units with five face-sharing octahedra in the $\text{Ba}_6\text{Mn}_5\text{O}_{16}$ layered structure was replaced by $[\text{Mn}_n\text{O}_{3n+3}]$ units with $n = \infty$, structural phase separation would take place. The replacing $[\text{Mn}_n\text{O}_{3n+3}]$ units form the well-known one-dimensional $2\text{H BaMnO}_3$ phase with infinite strings of face-sharing $\text{MnO}_6$ octahedra parallel to $c$-axis. Christensen and Ollivier [1] and Cussen and Battle [19] identified the $2\text{H BaMnO}_3$ with space group $P6_3/mmc$ at room temperature. Such phase separation was occasionally observed in our $\text{Ba}_6\text{Mn}_5\text{O}_{16}$ sample. Figs. 5(a) and (b) display HRTEM images of different areas, showing the coexistence of the layered $\text{Ba}_6\text{Mn}_5\text{O}_{16}$ phase and the $2\text{H BaMnO}_3$ phase. In Fig. 5(a), the [1 1 0] direction of the
The \( \text{Ba}_6\text{Mn}_5\text{O}_{16} \) phase is parallel to the incident beam, while the [11\( \bar{1} \)] direction of the 2H \( \text{BaMnO}_3 \) phase is along the incident beam. The coherency phase boundary is along the direction indicated by the white thick arrow. In Fig. 5(b), the coexistence of the two phases is also clearly seen and the phase boundary is marked by the white thick arrow. Obviously in this image, the [0 1 0] direction of the \( \text{Ba}_6\text{Mn}_5\text{O}_{16} \) phase is parallel to the incident beam, while the [1 2 2\( \bar{1} \)] direction of the 2H \( \text{BaMnO}_3 \) phase is along the incident beam. In order to further confirm the two phases from a chemical point of view, electron energy-loss spectroscopy (EELS) studies were also carried out. Fig. 5(c) shows the EELS spectra obtained from the domains \( A \) and \( B \) in (b). Each spectrum includes the O–K, Mn–L\text{2,3} and Ba–M\text{4,5} absorption edges. The insert is the magnified Ba–M\text{4,5} edges obtained after the two spectra are normalized to have the same Mn–L\text{2,3} integrated counts. It is clear that the Ba–M\text{4,5} edge obtained from the domain \( A \) is higher than that from the domain \( B \). Further quantifications from the EELS spectra using an EELS quantitative program suggest that the domains \( A \) and \( B \) are compositionally the \( \text{Ba}_6\text{Mn}_5\text{O}_{16} \) phase and the \( \text{BaMnO}_3 \) phase, respectively. In general, the separated 2H \( \text{BaMnO}_3 \) phase and the matrix layered \( \text{Ba}_6\text{Mn}_5\text{O}_{16} \) phase share a perfect plane at the phase boundary. The orientation relationship between them can be well described as:

\[
(0 0 1)_O || (0 1 1)_H,
\]

\[
[1 0 0]_O || [1 0 0]_H,
\]

where O and H represent the layered \( \text{Ba}_6\text{Mn}_5\text{O}_{16} \) phase and the 2H \( \text{BaMnO}_3 \) phase, respectively. Fig. 5(d) shows the schematic representation of the phase boundary in which the orientation relationship between the \( \text{Ba}_6\text{Mn}_5\text{O}_{16} \) phase and the 2H \( \text{BaMnO}_3 \) phase is clearly depicted.

Occasionally some areas containing stacking faults were also observed, and the corresponding HRTEM image of
one of the examples is shown in Fig. 6. In this image, some intergrowth faults as mentioned above are also clearly seen.

Fig. 7 shows the temperature profile of magnetization for \( \text{Ba}_6\text{Mn}_5\text{O}_{16} \) sample at an applied external field of 1 kOe. The main characteristics of the magnetic-susceptibility, in principle similar to the reported results in Ref. [8], are a broad maximum centered around 150 K and a drop in the magnetic susceptibility below 100 K. The final increase below 40 K which could be a Curie tail is also clearly visible in the susceptibility. Such magnetic characteristics of the broad \( T_N \), as well as the appearance of the Curie tail in the susceptibility, could have a correlation with the defects as described above.

4. Conclusions

The layered manganate \( \text{Ba}_6\text{Mn}_5\text{O}_{16} \) was prepared by a traditional solid state reaction method different from that reported in Ref. [8] and its microstructure at the atomic level was investigated in detail by means of HRTEM. Although the sample shows a nearly single phase from the XRD data, the presence of numerous intergrowth faults of the hexagonal \( \text{Ba}_{3n+1}\text{Mn}_{3n}\text{O}_{3n+1} \) series with different \( n \), as well as a number of stacking faults in it, was revealed by HRTEM. In addition, a minor \( 2\text{H} \) \( \text{BaMnO}_3 \) phase was also found to coexist with the layered \( \text{Ba}_6\text{Mn}_5\text{O}_{16} \) phase. These structural defects could be related to the magnetic properties of the sample, i.e. the very broad \( T_N \) and the appearance of the Curie tail in the susceptibility.

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References