Facile and rapid synthesis of multiferroic TbMnO$_3$ single crystalline

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ABSTRACT

The pure single phase of multiferroic material TbMnO$_3$ powders were successfully synthesized by one-step molten salt synthesis (MSS) method in the NaCl–Na$_2$SO$_4$ eutectic salts at the temperature as low as 800 °C for 1 h. The temperature of synthesized high purity TbMnO$_3$ is limited in a very narrow range. Prolonging the sintering time will not have an effect on the purity of samples, and either lower or higher salt concentration is not conducive to form pure TbMnO$_3$. The obtained TbMnO$_3$ was indexed to an orthorhombically distorted perovskite phase. The as-prepared crystals exhibit uniform and regular rhombic-like morphology with an average size of about 2 μm in edge length and 1–2 μm in thickness. The elements Mn and Tb in TbMnO$_3$ exist dominantly as Mn^{3+} and Tb^{3+}, respectively. The magnetic measurements of the TbMnO$_3$ powders exhibit antiferromagnetism. Because of the simplicity and generalizability of the MSS method, it is reasonable to expect that the MSS method could also be exploited in future works which involves the nanoscale investigation of ferroelectric, ferromagnetic and multiferroic materials.

1. Introduction

A single-phase multiferroic [1] material is one that possesses more than one of so-called 'ferroic' properties: ferroelectricity, ferromagnetism, ferroelasticity and ferrotoroidicity. [2] In the past several years, this kind of materials has received revival of interest because of their promising applications in novel devices, such as magnetoelctric sensor, multiferroic memory and four-state memory based on the mutual controls of magnetic and electric fields. [3,4] However, there are quite few materials in which these properties coexist in nature. [5] So much effort has been devoted to discovering new multiferroic materials and investigating multiferroic properties of present metal oxides, such as perovskite-type BiFeO$_3$, [6,7] BiMnO$_3$, [8,9] RMnO$_3$ (R = Y, Gd–Lu),4, [10–13] RMn$_2$O$_5$ (R = Gd–Lu) [14] and double perovskite Bi$_2$MnNiO$_6$. [15] Recently, TbMnO$_3$ has attracted much attention due to its magnetoelectric effect as one of the rare earth manganates multiferroic materials. Since its ferroelectricity, combined with giant magnetocapacitance and magnetoelectric effects which were discovered by Kimura et al. in 2003, [16] many works have been

focused to TbMnO$_3$. [17–23] Experimentally it is known that, in TbMnO$_3$, a sinusoidal antiferromagnetic ordering is caused by the effect of spin frustration below ∼41 K, and below ∼27 K a spontaneous polarization induced by modulated magnetic structure appears. [16] From the research of multiferroic TbMnO$_3$, the mentioned frustrated spin systems involve an area to search for magnetoelectric media, which may provide opportunities to explore a new type of magnetoelectric functionality. Therefore, it is very significant to investigate the magneticoelectric mechanism of TbMnO$_3$.

Since morphology and dimension or size of materials play a very important role on their properties, the synthesis method to obtain the desired multiferroic materials is crucial to exploiting their ferroelectric, ferromagnetic and other properties. For most multiferroic perovskite oxides, previous work has involved a number of different synthetic routes, such as solid state method, hydrothermal method, sol–gel method and so on [6–9]. While for most of these methods, a high-temperature or high-pressure technique has to be required to gain a single phase, which is undesirable for saving time and energy [7,9]. Some methods get the powders with serious particle agglomeration, and some yield only small quantities of desired structures. Furthermore, in some cases, extremely toxic and unstable organic precursors were employed, and some substances which are harmful to human beings will be produced. Therefore, it is important to develop a simple method that is environmental friendly and low cost. It has been widely demonstrated that the molten salt synthesis (MSS)

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method is likely to meet these requirements because rapid diffusion and high reactivity of species can reduce the reaction time and make the reaction occur at a relatively low temperature in molten salt, no toxic substance is involved and the salt can be recycled. Furthermore, some simple shape control may be achieved by MSS. Thus, MSS method has been widely used to fabricate some functional materials, like $BaTiO_3$, $SrTiO_3$ [24], $BiFeO_3$ [25], $PbTiO_3$ [26], (K,Na)NbO_3 [27]. Currently, the synthesis of $TbMnO_3$ has involved several methods, of which the solid state method and the hydrothermal method are the most popular [28–30]. The synthesis of single phase $TbMnO_3$ by MSS method has not been reported yet. In the present work, the MSS method is performed to prepare $TbMnO_3$ microcrystals by utilizing NaCl–Na_2SO_4 eutectic salts. The $TbMnO_3$ powders are synthesized rapidly, and as-prepared $TbMnO_3$ micocrystals exhibit an orthorhombic phase with regular shapes and uniform morphology.

2. Experimental

In a typical synthesis, Tb_4O_7 (>99.99%), MnO_2 (>99.99%), NaCl (>99.5%) and Na_2SO_4 (>99.0%) were used as raw materials. Tb_4O_7 and MnO_2 were first mixed in an agate mortar according to stoichiometric amounts, ground for 20 min. Then NaCl–Na_2SO_4 salts with 0.5:0.5 eutectic composition were added with the molar ratio of oxides to salts for 1:2.5, [25] ground for another 20 min in ethanol. After the obtained uniform mixture was dried at 100 °C for 4 h, it was transferred to a alumina crucible, loaded into a furnace, annealed in the air atmosphere at 800 °C for 1 h with a heating rate of 5 °C/min, and subsequently gradually cooled to room temperature at an average rate of about 3 °C/min. The product was washed several times with hot distilled water to remove the salts and dried at 120 °C overnight in a drying oven, then pure $TbMnO_3$ powders were collected. The purity and crystallinity of the sample were examined by X-ray powder diffraction (XRD, TTRⅢ, Rigaku, Japan) measurements using Cu Kα radiation. The morphology and microstructure of the material were characterized with field-emission scanning electron microscope (FE-SEM, SUPRA-40, Carl Zeiss, Germany) and high-resolution transmission electron microscopy (HR-TEM, JEM-2010). X-ray photoelectron spectroscopy (XPS, AXIS ULTRA[DLD], Kratos, Japan) measurements were employed to analyze the valence state of the elements of $TbMnO_3$. The magnetism of pure $TbMnO_3$ powders was investigated by a physical properties measurement system (PPMS, Quantum Design, USA).

3. Results and discussion

The formation of $TbMnO_3$ involved the reaction between Tb_4O_7 and Mn_2O_3 as MnO_2 has transformed to Mn_2O_3 before the reaction started to occur. [31] High purity $TbMnO_3$ was prepared in NaCl-Na_2SO_4 melts (melting point 623 °C) at 800 °C for 1 h. XRD patterns of the $TbMnO_3$ powders prepared at various temperatures were shown in Fig. 1. All diffraction peaks of pure-phase $TbMnO_3$ (Fig. 1d) can be assigned to the orthorhombic phase of $TbMnO_3$ (JCPDS 72-379) with space group Pbnm (no. 62). The NaCl–Na_2SO_4 eutectic salts which provide a liquid environment for the chemical reaction dramatically decrease the reaction temperature of $TbMnO_3$. And also there was almost no degradation on the salt composition in the reaction process because the appropriate use range of the salts is from 650 °C to 920 °C, the reaction temperature 800 °C is in the range and it is much lower than the boiling point of the salts. If the soaking temperature is maintained at lower than 780 °C, such as 700 and 750 °C, the peaks of unreacted Tb_4O_7 can be detected as an impure phase (plots a and b in Fig. 1). The intensity of unreacted precursor of Tb_4O_7 peaks becomes lower and lower as the temperature increased, and disappeared when the tempera-
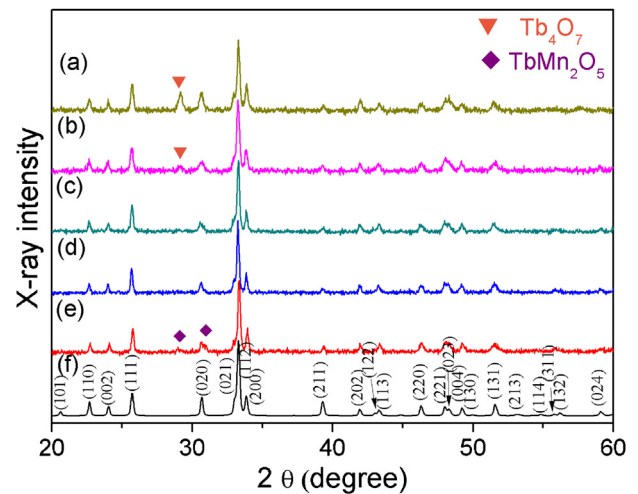

Fig. 1. XRD patterns of samples synthesized at: (a) 700 °C, 1 h; (b) 750 °C, 1 h; (c) 780 °C, 1 h; (d) 800 °C, 1 h; (e) 820 °C, 1 h; and (f) JCPDS: 72-379.

ture rise-up to 780 °C (Fig. 1c). From the XRD pattern of the soaking temperature at 800 °C (Fig. 1e), it is observed that all peaks are in good agreement with the standard card (JCPDS 72-379), and the sharp peaks indicates a good crystallinity of the sample, thus 800 °C is the optimum temperature for the synthesis of $TbMnO_3$. While the soaking temperature was increased to 820 °C, another impurity $TbMn_2O_5$ is detected (Fig. 1e). Therefore, the temperature of synthesizing high purity $TbMnO_3$ in molten NaCl–Na_2SO_4 eutectic salts is limited in a narrow temperature range. Effects of Sintering time and the amount of salts on the experimental results were also investigated. Fig. 2 shows XRD patterns of samples synthesized at 800 °C for different times, all of the patterns indicate that pure $TbMnO_3$ powders were prepared. It can be concluded that the reaction can be completed in a very short time (1 h), and prolonging the sintering time up to 5 h will not have an effect on the purity of samples as $TbMnO_3$ is stable at this temperature. XRD patterns of various ratio of oxides to salts are shown in figure 3, it is observed that pure $TbMnO_3$ could be synthesized at the ratio of 1:2.5 and 1:5 (plots b and c in figure 3), however, peaks of Tb_4O_7 exist at the ratio of 1:1.25 and 1:10 (plots a and d in Fig. 3), this indicates that lower and higher salt concentration are both not conducive to form pure $TbMnO_3$. It is because lower salt concentration causes slower diffusing rate and lower reactivity
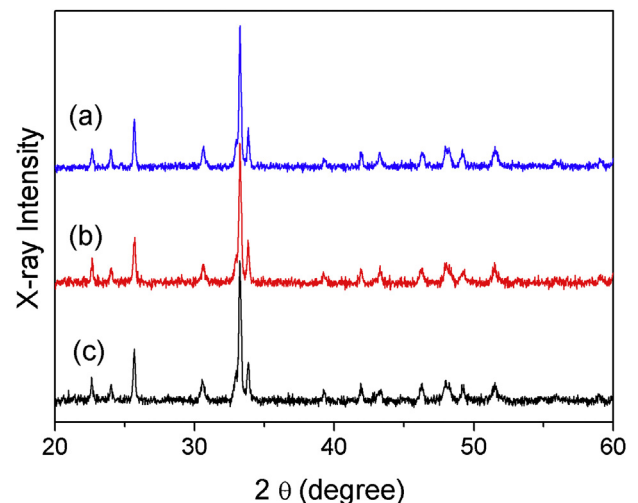

Fig. 2. XRD patterns of samples synthesized at 800 °C for different times: (a) 1 h; (b) 2 h; and (c) 5 h.