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Synthesis of $TbMnO_3$ nanoparticles via a polyacrylamide gel route

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ABSTRACT

We report here the synthesis of $TbMnO_3$ nanoparticles via an acrylamide gel route. XRD, TG analysis, DSC analysis, and FTIR spectroscopy are combinatively used to investigate the thermal decomposition process of precursor xerogels and the formation of $TbMnO_3$ phase. It is demonstrated that high-phase-purity $TbMnO_3$ nanoparticles can be prepared by using different chelating agents at a sintering temperature of 800 °C. SEM observation and XRD analysis reveal that the particle size and morphology of the products have a dependence on the chelating agent. The particles prepared using citric acid as the chelating agent appear to be regularly spherical in shape and highly uniform in size with a diameter of ~67 nm, while the sample prepared by using the chelating agent EDTA mainly consists of sphere-, ellipsoid-, and rod-like particles and exhibits a relatively broad particle size distribution with an average particle size centered around 115 nm. The use of a combination of citric acid and EDTA generally results in sphere- and ellipsoid-like particles with an average particle size between those of the samples prepared separately by using the two chelating agents.

1. Introduction

Multiferroics are known to be an important class of multifunctional materials, which possess not only single ferroelectric, ferromagnetic and ferroelastic properties, but also multiferroic coupling effects. Due to their intriguing properties, multiferroic materials hold promise for potential applications in novel electronic devices like the emerging field of spintronics, multiple-state memory elements and magnetic-electric sensors [1,2]. Perovskite rare-earth manganites $RMnO_3$ (R = Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Y, etc.) are a representative example of multiferroic materials. Depending on ionic radius of the rare-earth elements, the $RMnO_3$ multiferroic manganites crystallize into either an orthorhombic structure with space group *Pbnm* (R = Gd, Tb, and Dy with relatively large ionic radius) or a hexagonal structure with space group $P6_3cm$ (R = Ho, Er, Tm, Yb, Lu, and Y with relatively small ionic radius) [3,4]. The hexagonal manganites generally present ferroelectricity with T_C = 700–1000 K and antiferromagnetism with T_N = 80–100 K [5,6], where the two ferroic ordering temperatures differ by an order. In contrast, the orthorhombic manganites have comparable ferroelectric and antiferromagnetic ordering temperatures (T_C = 17–28 K and T_N = 38–42 K) [7–9], indicating a possible direct coupling between them. Among these materials, $TbMnO_3$, which stabilizes in the orthorhombic structure, has been the focus of research interest owing to its giant magnetoelectric and magnetocapacitance effects [7]. Upon cooling, $TbMnO_3$ undergoes two magnetic phase transitions from paramagnetic to an incommensurate sinusoidal antiferromagnetic ordering at T_N = ~42 K and subsequently to a spiral antiferromagnetic ordering at T_{lock} = ~28 K [7,10]. A spontaneous electrical polarization along the *c*-axis appears below T_{lock}, which has been suggested to arise from the spiral ordering of Mn spin moments [11–13]. This direct relationship between the magnetic structure and polarization leads to a strong magnetoelectric effect in the compound.

It is well known that the properties of functional materials depend highly on their morphologies, dimensions, sizes and defects. Especially at the nanoscale, the materials are expected to display enhanced properties or a completely new set of properties which are usually absent in their bulk forms. Therefore it is important and interesting to study the nanosized systems of multiferroic materials. For the famous multiferroic system $TbMnO_3$, much work has been devoted to the two-dimensional nanofilms epitaxially grown on a range of substrates including $SrTiO_3$, $LaAlO_3$ and $NdGaO_3$ [14–16]. However, to date, there has been little work concerned with the synthesis of substrate-free nanostructures of $TbMnO_3$ [17]. Han et al. reported the synthesis of matchbox-like $TbMnO_3$ particles via a convenient hydrothermal route, which, however, have a size generally in the order of 10 μ [18]. Here we report a polyacrylamide gel route for the synthesis of $TbMnO_3$

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