Journal of Alloys and Compounds 665 (2016) 152–157

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Multiferroicity in $SmFeO_3$ synthesized by hydrothermal method

Chenyang Zhang [a], Mingyu Shang [b], Milan Liu [c], Tingsong Zhang [d], Lei Ge [a], Hongming Yuan [a, *], Shouhua Feng [a]

[a] *State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, Jilin University, Changchun 130012, PR China*
[b] *College of Earth Sciences, Jilin University, Changchun 130012, PR China*
[c] *College of Physics, Jilin University, Changchun 130012, PR China*
[d] *College of Science, Changchun University of Science and Technology, Changchun 130022, PR China*

ARTICLE INFO

Article history:
Received 1 November 2015
Received in revised form
2 January 2016
Accepted 7 January 2016
Available online 9 January 2016

Keywords:
Hydrothermal synthesis
Orthoferrite
Multiferroic
Perovskite

ABSTRACT

The perovskite orthoferrite $SmFeO_3$ was synthesized by the hydrothermal method. The Néel temperature of this material was found to be 655 K by temperature-dependent magnetization measurements. Magnetic field-dependent magnetization of the material at 300 K revealed typical weak ferromagnetic behaviour. Dielectric analysis showed a ferroelectric phase transition at 480 K. The structural and magnetic properties of $SmFeO_3$ were also characterized using Mössbauer spectra, which also confirmed this structural transition. The remanent polarization determined by the positive-up-negative-down (PUND) method was approximately 0.012 $\mu C/cm^2$ at 173 K. Therefore, the results presented here indicate that $SmFeO_3$ is multiferroic at temperatures above room temperature. Our analysis shows that the material's non-centrosymmetric *Pna2₁* structure is likely to be responsible for the ferroelectricity in $SmFeO_3$ rather than the *Pbnm* structure or the magnetic structure.

1. Introduction

In recent years, multiferroics, which exhibit magnetic and ferroelectric ordering simultaneously, have attracted intense interest because of their promising applications in spintronics and data storage [1–3]. However, the two orderings have different occupation rules for d orbital electrons that are not compatible with each other and thus lead to a lack of multiferroic materials [4]. This problem could be overcome using two strategies that have been widely applied in this field. The first is an approach where the magnetic and ferroelectric orderings originate from different subsystems, and the second is an approach where the ferroelectric ordering is induced by breaking the magnetic ordering symmetry. For example, in $BiFeO_3$, the ferroelectric (Curie temperature $T_C = 1103$ K) and antiferromagnetic (Néel temperature $T_N = 643$ K) orderings result from the lone pair electrons of Bi^{3+} ions and the spin of Fe^{3+} ions, respectively [5,6]. In $TbMnO_3$, the non-collinear spiral magnetic structure is responsible for the generation of spontaneous polarization at temperatures below the corresponding magnetic temperature ($T_N = 27$ K) [7].

From the perspective of practical application of these materials, multiferroics should have working temperatures that are close to room temperature, but few have met this requirement to date. In addition to $BiFeO_3$, CuO ($T_C = 230$ K) and hexaferrites ($T_C \approx$ room temperature) also exhibit multiferroicity near room temperature, with ferroelectricity that arises from their spiral magnetic structures [8,9]. Recently, as the search for high temperature multiferroics continues, perovskite orthochromites ($RCrO_3$) and orthoferrites ($RFeO_3$) have received considerable attention. It has been reported in the literature that these two systems demonstrate ferroelectricity driven by magnetic ordering [10,11]. For the orthochromites, only materials with paramagnetic R^{3+} ions show ferroelectricity below the antiferromagnetic ordering temperature. However, in recent reports on $RCrO_3$ (where $R =$ Sm, Lu, Er and Ho), ferroelectricity appears at temperatures that are higher than the corresponding magnetic ordering temperature, indicating the different origins of the magnetic and ferroelectric orderings [12–14]. Structural analysis has shown that rotation of the CrO_6 octahedra and R^{3+} displacement result in ferroelectricity and point towards a distortion structure with a non-centrosymmetric *Pna2₁* space group rather than a centrosymmetric *Pbnm* space group. In a previous paper, we reported on the ferroelectricity of $YFeO_3$ ($T_C = 420$ K) synthesized by the hydrothermal method; the ferroelectricity occurs far below its Néel temperature of 655 K, thus

---

* Corresponding author.
E-mail address: hmyuan@jlu.edu.cn (H. Yuan).

http://dx.doi.org/10.1016/j.jallcom.2016.01.042

indicating the multiferroicity of this compound [15]. It should be noted here that no anomalous magnetization is observed near the Curie temperature. In addition, according to the inverse Dzyaloshinskii-Moriya (DM) interaction or spin current models, the cancellation of the adjacent local polarization meant that the spin-canted magnetic structure could not give rise to net electric polarization [16,17]. Therefore, our results also show that the magnetic structure could not be the source of the ferroelectricity in $YFeO_3$.

In this context, we extended our research to another orthoferrite, $SmFeO_3$, with paramagnetic R^{3+} ions. $SmFeO_3$ shows weak ferromagnetism below 655 K. Dielectric and ferroelectric analyses reveal that $SmFeO_3$ exhibits ferroelectricity below 480 K. Therefore, the results presented here indicate multiferroicity above room temperature in the sample material.

2. Experimental details

2.1. Material synthesis

In a typical synthesis procedure, 4.44 g of $Sm(NO_3)_3 \cdot 6H_2O$ and 4.04 g of $Fe(NO_3)_3 \cdot 6H_2O$ were dissolved in 30 mL of distilled water in a beaker by continuously stirring them to form a solution. Then, 60 g of KOH was added on stirring and cooling to room temperature. The final mixture was then transferred into a 90 ml Teflon-lined stainless steel autoclave with a filling capacity of 70%. Crystallization was carried out under autogenous pressure at 513 K for 3 days. After the autoclave was cooled and depressurized, the sample was washed thoroughly with distilled water and sonicated by direct immersion of a titanium horn (Vibracess, 20 kHz, 200 W/cm^2). Dark red crystals were subsequently obtained at the bottom of the beaker.

2.2. Material characterization

The sample morphology was checked with a JEOL JSM-6700F scanning electron microscope (SEM). The sample compositions were determined by inductively-coupled plasma (ICP) spectroscopy using a Perkin–Elmer Optima 3300DV spectrometer and X-ray energy dispersive spectroscopy (EDS) coupled to the microscopy process. X-ray diffraction (XRD) patterns were obtained from 15° to 90° with steps of 0.02° and a counting time of 2 s per step using a Rigaku D/Max 2500 V/PC X-ray diffractometer with Cu Kα radiation ($\lambda = 1.5418$ Å) at 40 kV and 200 mA. The valence states of the sample were determined by X-ray photoelectron spectroscopy (XPS, ESCALAB250, USA). DC and AC magnetic measurements were performed using a superconducting quantum interference device vibrating sample magnetometer (Quantum Design). For the electrical measurements, the sample was ground and pelletized, and was then annealed at 1073 K for 24 h. Silver paste was attached to the two faces of the pellet as electrodes. Dielectric measurements were carried out using an LCR meter (Agilent E4980A) using a home-made setup. The polarization-electric field (*P-E*) hysteresis loop was measured using a Radiant Precision II and the positive-up-negative-down (PUND) method. The Mössbauer spectra were recorded in transmission mode using a ^{57}Co γ-ray source in a platinum matrix and a multi-channel analyser. The spectrometer was calibrated using α-Fe and the spectra were fitted using a computer program based on the least squares method.

3. Results and discussion

3.1. Structural and thermal stability analysis

Fig. 1 shows SEM images of the sample. The powder crystals have cubic shapes and a uniform size of approximately 20 μm. Compositional analysis by ICP shows that the Sm:Fe ratio is 1:1, which agrees well with the theoretical value and is further confirmed by the EDS results (Table SI and Fig. S1).

Fig. 2 shows the XRD pattern of the sample at room temperature. All peaks can be indexed to a single-phase orthorhombic structure with *Pbnm* space group. To obtain the unit cell parameter information, we performed a Pawley refinement, and the results were $a = 5.3985(1)$ Å, $b = 5.5950(1)$ Å, $c = 7.7107(39)$ Å, and $\alpha = \beta = \gamma = 90^\circ$.

The samples were initially annealed at selected temperatures and then the thermal stability of each sample was checked by analysis of the XRD patterns. Fig. 3 shows the XRD patterns of samples annealed in the 973 K–1473 K range. When the annealing temperture was less than 1173 K, no new peaks appeared and the patterns of the annealed samples remained the same as that of the as-synthesized sample, indicating that no structural changes occurred. When the annealing temperature was raised to 1273 K and higher, peaks from Sm_2O_3 and Fe_2O_3 were clearly observed. It should be noted here that the reaction temperature at which the solid state method is performed for orthoferrite synthesis is usually higher than 1473 K [18,19]. Therefore, the samples that were synthesized by the hydrothermal method have lower thermal stability than samples that were synthesized by the solid state reaction, which indicates the possible difference between the samples that are synthesized by these two methods.

3.2. XPS analysis

Fig. 4 shows the XPS spectrum of the Fe2p core level of the sample at room temperature. The Fe2p peak appears at 711.1 eV, which is consistent with the Fe2p peak position for Fe^{3+} in Fe_2O_3 [20,21]. Accordingly, the oxide state of the Fe ion in the sample is +3.

3.3. Magnetization analysis

Fig. 5 shows the temperature dependences of the zero field-cooled (ZFC) and field-cooled (FC) susceptibilities of the sample under an applied magnetic field of 100 Oe in the temperature range from 300 to 723 K. The Néel temperature determined by the onset of magnetization is 655 K. The ground state of orthoferrites is G-type antiferromagnetic. Because of the DM interaction, the spins of Fe^{3+} are slightly canted and the sample shows ferromagnetic-like behaviour or weak ferromagnetism below the Néel temperature [22]. The allowed spin configuration in $SmFeO_3$ is $G_xA_yF_z$ in Bertaut's notation. With decreasing temperature, a broad downturn occurs at approximately 460 K in both the ZFC and FC curves, and this is also observed in other orthoferrites with paramagnetic R^{3+} [10,23]. This corresponds to the spin-reorientation of the sample, and the spin configuration turns into $F_xC_yG_z$. In addition to the two characteristic transitions above, both the ZFC and FC curves for our sample show an anomaly at 566 K; this anomaly is not observed in $SmFeO_3$ when synthesized by other methods, and therefore clearly indicates some type of difference. When the temperature is cooled to 150 K, the magnetization decreases rapidly (Fig S2). This suggests that the ordering of the Sm^{3+} spin moment in the exchange field generated by the Fe^{3+} sublattice and the direction of the net Sm^{3+} moment is opposite to that of the net Fe^{3+} moment [10,23].

Fig. 6 shows the magnetic field (*H*)-dependent moment (*M*) curves at 300 K. The *M-H* loop exhibits typical weak ferromagnetic behaviour. As the magnetic field increases, the moment also increases linearly and does not reach saturation at the magnetic field of 60 kOe. The high field linear part of the *M-H* loop can be represented by the relationship $M = M_s + \chi_{AFM}H$, where M_s is the net