Materials Chemistry and Physics 116 (2009) 599–602

Contents lists available at ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys

Synthesis and magnetic properties of $BiFeO_3$ and $Bi_{0.98}Y_{0.02}FeO_3$

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ARTICLE INFO

Article history:
Received 17 January 2009
Received in revised form 26 April 2009
Accepted 1 May 2009

Keywords:
Magnetic materials
Chemical synthesis
Chemical techniques
Magnetic properties

ABSTRACT

Multiferroic $BiFeO_3$ and $Bi_{0.98}Y_{0.02}FeO_3$ samples were prepared by a solution combustion method using oxalyldihydrazide (ODH) as a fuel. The as-prepared compounds were annealed at 600 °C for 3 h to obtain single-phase materials. The crystal structure examined by X-ray powder diffraction (XRD) indicates that the samples were of single phase and crystallize in a rhombohedral (space group, *R*-3*c* no.161) structure. Magnetic measurements were carried out on the resultant powders from 300 to ∼0 K. A significant increase in magnetization was observed for Y-doped $BiFeO_3$.

1. Introduction

Among multiferroics materials, $BiFeO_3$ enjoys a unique position as the material has found itself in potential technological applications in emerging electronic devices such as multiple-state memories and new data-storage media [1–3]. The perovskite $BiFeO_3$ exhibits ferromagnetism, ferroelectricity, and ferroelasticity—all in the same phase. The perovskite $BiFeO_3$ is an attractive material, exhibiting high Curie temperature ($T_C = 1103$ K) and high Néel temperature ($T_N = 643$ K) with a weak magnetism at room temperature due to a G-type canted spin AFM structure [4,5].

The synthesis of $BiFeO_3$ is challenging as several competing phases prevent the formation of single-phase material and accordingly the $BiFeO_3$ phase is formed with various impurities such as $Bi_2Fe_4O_9$, $Bi_{36}Fe_{24}O_{57}$, and $Bi_{25}FeO_{40}$ [6,7]. Several synthesis techniques like solid-state route [8], co-precipitation [9], sol–gel [10], combustion method [11,12], hydrothermal [13], flux method [14], and molten salt synthesis method [15] have been reported in the literature to make $BiFeO_3$ type materials. The known synthesis techniques contained several disadvantages like longer reaction times due to slow diffusion, complex, labor intensive procedures, inability to scale up, all of which we desire to overcome. It has been shown that a small amount of metal doping (either divalent or trivalent) helps in stabilizing the required phase, as well as in forming single-phase material with improved physical properties. For example, divalent doped (Ca, Sr, Pb, and Ba) $BiFeO_3$ resulted in single-phase formation which showed the existence of weak ferromagnetism [16]. Gd^{3+} doping in $BiFeO_3$ resulted in desired phase formation without impurities and the compounds showed reduced antiferromagnetic Néel temperature compared to the parent compound [17]. Partial substitution of Bi^{3+} by rare-earth element ions (La^{3+}, Nd^{3+}, Tb^{3+}, Sm^{3+}) resulting in enhancement of magnetization has been reported [8,18–21]. We have been interested in the effect of the trivalent rare-earth ion, Y^{3+}, in the stabilization of the $BiFeO_3$ phase, and in studying the effect on the magnetic properties of the system. Study of (Bi, Y)FeO_3 is a current topic of interest and accordingly we have established a structure–property relationship in this novel system. To synthesize such compounds we have applied the solution-based combustion method using oxalyldihydrazide (ODH) as a fuel, which is synthesized in-house. Specific advantages of using ODH are that it decomposes at lower temperatures (240 °C) to CO, HNCO, and NH_3. This method does not leave much residual carbon like glycine and other fuels. Novel (Bi, Y)FeO_3 materials synthesized by a simple, low temperature process have not been reported so far.

2. Experimental

$(Bi_{1-x}Y_x)FeO_3$ was synthesized by the solution combustion method using oxalyldihydrazide (ODH) as a fuel. The detailed procedure for calculating the metal nitrates to fuel ratio has been described elsewhere [22]. Stoichiometric amounts of $Bi(NO_3)_3{\cdot}5H_2O$ and $Fe(NO_3)_3{\cdot}9H_2O$ were dissolved in a minimum amount of water in a Pyrex dish. Calculated amounts of the fuel ODH were added. The ODH dissolved and formed a clear solution which was introduced into a muffle furnace preheated to 500 °C. The mixture boiled, followed by frothing, and ignited with the evolution of a large amount of gas. The flame persisted for about a minute, leaving behind a residual black-colored fine powder. The chemical reaction occurring in the combustion process can be written as:

$$Bi(NO_3)_3 + Fe(NO_3)_3 + C_2H_6N_4O_2 \rightarrow BiFeO_3 + 2CO_2 + 5N_2 + 3H_2O + 10[O] \quad (1)$$

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doi:10.1016/j.matchemphys.2009.05.001

Similarly, $Bi_{0.98}Y_{0.02}FeO_3$ was synthesized by taking stoichiometric amounts of $Bi(NO_3)_3{\cdot}5H_2O$, $Y(NO_3)_3$, $Fe(NO_3)_3{\cdot}9H_2O$, and ODH fuel. The as-prepared samples were subjected to 600 °C for 3 h to get single-phase materials. The fuel oxalyldihydrazide $C_2H_6N_4O_2$ (ODH) was prepared, by the drop-wise addition of 1 mol diethyl oxalate to 2 mol of ice-cooled hydrazine hydrate (99.9%) with constant stirring. The product was washed with alcohol and finally with distilled water.

$$(COOC_2H_5)_2 + 2N_2H_4 \cdot H_2O \xrightarrow{0-5\,^{\circ}C} (CON_2H_3)_2 + 2C_2H_5OH + 2H_2O \tag{2}$$

The reaction of ODH with the metal nitrates and the corresponding redox reaction are mildly exothermic (compared to glycine) and autocatalytic, going to completion without requiring any further heat from external sources.

The phase purity and crystal structure were examined by a Bruker X-ray diffractometer using Cu K_α radiation with a nickel filter. For Rietveld refinement, data was collected at a scan rate of 0.5° min^{-1} and a 0.02° step size for 2θ from 10° to 100°. The data were refined by using the Rietveld analysis program, "*FullProf*" [23]. The morphology of the powder was examined using a JEOL JSM-840A scanning electron microscope fitted with an energy dispersive X-ray analyzer (EDX). Magnetic measurements were performed with a vibrating sample magnetometer in a physical property measuring system (PPMS, Quantum Design, USA).

3. Results and discussion

Fig. 1a and b shows the powder XRD patterns of solution combustion—synthesized $BiFeO_3$ and $Bi_{0.98}Y_{0.02}FeO_3$ samples crystallized in the rhombohedral structure with space group *R*-3*c*(161). The powder samples were annealed at 600 °C in order to get the desired crystallinity. From Fig. 1, it can be seen that almost a single-phase rhombohedrally distorted perovskite $BiFeO_3$ is obtained. Small amounts of $Bi_2Fe_4O_9$ and $Bi_{25}FeO_{39}$ were also observed. The lattice parameters estimated by the Rietveld method are $a = b = 5.5768$ Å and $c = 13.864$ Å (Table 1), which are consistent with reported values [24]. The structural parameters were refined by the Rietveld method using the *FullProf* program. In Fig. 2, observed, calculated, and difference XRD patterns of the refined XRD patterns of (a) $BiFeO_3$ and (b) $Bi_{0.98}Y_{0.02}FeO_3$ compounds are given. There is a good agreement between observed and calculated patterns. The refined structural parameters for all samples are summarized in Table 1.

Fig. 3a and b shows SEM images of $BiFeO_3$ and $Bi_{0.98}Y_{0.02}FeO_3$ samples, where one can see that the particles are agglomerated. A high interconnection of the grains can be seen. The morphology of the particles seemed to be approximately dumb-bell in shape. Particles in both the samples are aggregated into clusters which are from less than a micrometer to about one micrometer in size.

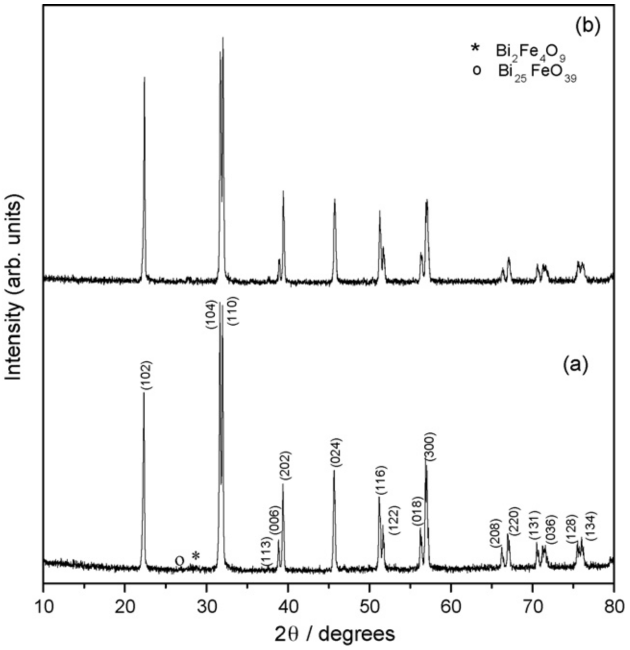

Fig. 1. Powder XRD patterns of (a) $BiFeO_3$ and (b) $Bi_{0.98}Y_{0.02}FeO_3$ samples.

Table 1
Structural parameters of $BiFeO_3$ and $Bi_{0.98}Y_{0.02}O_3$.

	$BiFeO_3$	$Bi_{0.98}Y_{0.02}FeO_3$
Crystal system	Rhombohedral	
Space group	*R*-3*c*(161)	
Lattice parameters		
$a = b$ (Å)	5.5768(3)	5.5758(4)
c (Å)	13.8642(6)	13.8599(1)
Cell volume (Å^3)	373.418	373.166
R_f (%)	3.95	3.91
R_{Bragg}	4.71	4.31
R_p	7.72	8.72
R_{wp}	9.95	11.1
χ^2	1.19	1.18

The results of the magnetic measurements on $BiFeO_3$ and $Bi_{0.98}Y_{0.02}FeO_3$ samples obtained by the combustion route are presented in Fig. 4. Fig. 4a shows the evolution of magnetization as a function of applied magnetic *M*(H) for $BiFeO_3$ and Y-doped $BiFeO_3$ samples measured at 300 K with a magnetic field sweep of

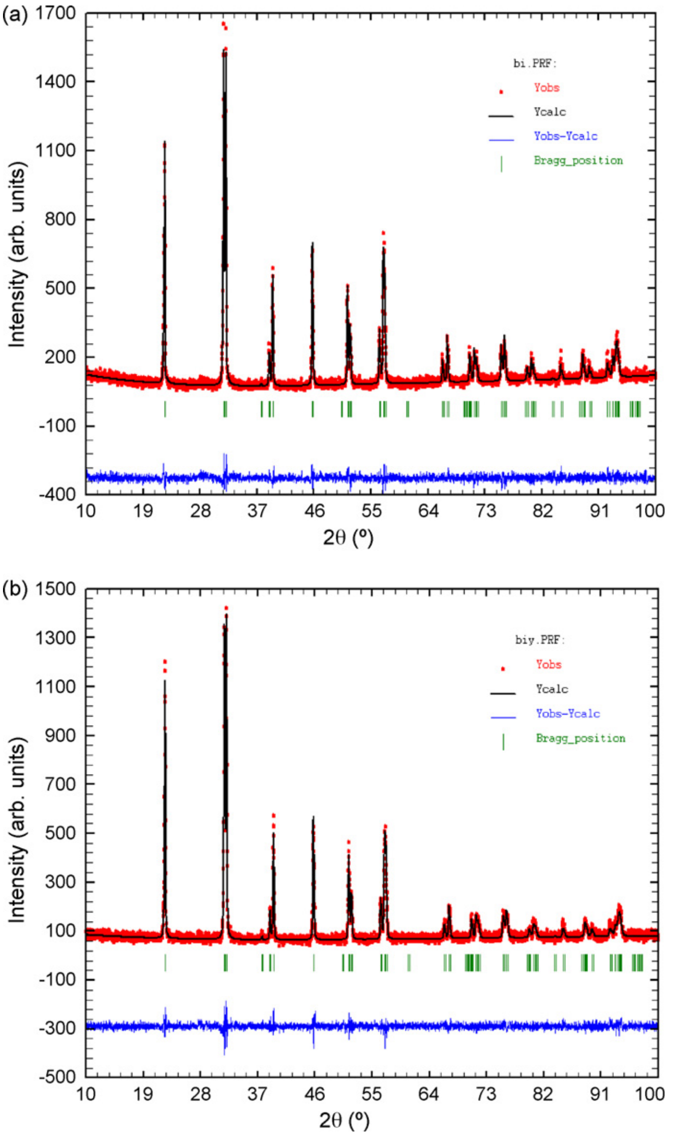

Fig. 2. Typical, observed, calculated and difference Rietveld refined XRD patterns of (a) $BiFeO_3$ and (b) $Bi_{0.98}Y_{0.02}FeO_3$ samples.