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Synthesis of $Bi_2Fe_4O_9$ via PVA sol–gel route

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ABSTRACT

$Bi_2Fe_4O_9$ powders were synthesized by a sol–gel process using polyvinyl alcohol (PVA) as a complexing agent. Differential scanning calorimetry (DSC), thermogravimetric (TG), Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD) and Field emission scanning electron microscope (FSEM) techniques were used to characterize precursor and derived oxide powders. The effect of the ratios of positively charged valences to hydroxyl groups of PVA (M^{n+}/–OH) on the formation of $Bi_2Fe_4O_9$ was investigated. XRD analysis showed that single-phase $Bi_2Fe_4O_9$ was obtained from the M^{n+}/–OH = 2:1 and M^{n+}/–OH = 1:1 precursors at the temperature of 700 °C. For the precursor with M^{n+}/–OH = 4:1, pure $Bi_2Fe_4O_9$ formed at the temperature of 800 °C. $Bi_2Fe_4O_9$ powders clacined at 700 °C from M^{n+}/–OH = 2:1 precursor shows weak ferromagnetism.

1. Introduction

$Bi_2Fe_4O_9$ (BFO) is an important functional material because of its potential applications as a semiconductor gas sensor [1]. Moreover, its catalysis for ammonia oxidation to NO is of current interest because it will possibly replace the high-cost, deficiency, and unrecoverable loss of commercial catalysts (platinum, rhodium, and palladium alloys) in the industrial process of nitric acid manufacturing [2,3]. $Bi_2Fe_4O_9$ is known to have an orthorhombic structure with lattice constants of $a = 7.965$ Å, $b = 8.440$ Å, and $c = 5.994$ Å. It is paramagnetic at room temperature and undergoes a transition to an antiferromagnetic state at $T_N \approx 264$ K. Early in 1964, $Bi_2Fe_4O_9$ have been synthesized by the method of solid-state sintering at temperatures over 850 °C [4]. Park et al. [5] have employed a molten salt technique for the synthesis of submicron-sized $Bi_2Fe_4O_9$ cubes and they obtained phase-pure $Bi_2Fe_4O_9$ at 820 °C for 3.5 h. However, because of some disadvantages of solid state reaction such as high temperature, easy impurity contamination, relatively larger dimension, and difficult control of synthesis conditions, new synthesis methods have been investigated until now. Yang et al. [6] prepared successfully densely packed $Bi_2Fe_4O_9$ nanowires arrays by a citrate-based sol–gel method combined with porous AAO template at 800 °C for 3 h. Xiong et al. [3] prepared $Bi_2Fe_4O_9$ nanoscale powders at 180 °C via a hydrothermal process. Sun et al. [7] synthesized phase-pure $Bi_2Fe_4O_9$ at 180 °C for 48 h and Wang et al. [8] successfully synthesized $Bi_2Fe_4O_9$ nanoparticles by a hydrothermal method at the temperature of 100 °C for 9 h. Han et al. [9] successfully prepared $Bi_2Fe_4O_9$ samples at the temperature of 180–270 °C for 72 h and the effect of hydrothermal conditions on the morphology has been investigated. Ruan and Zhang [10] reported a tunable hydrothermal process for the synthesis of $Bi_2Fe_4O_9$ crystals and found that $Bi_2Fe_4O_9$ nanoplates can act as photocatalysts for methyl orange degradation under visible light irradiation, while the $Bi_2Fe_4O_9$ microplates only exhibit this performance under UV light. Zhang et al. [11] synthesized $Bi_2Fe_4O_9$ via the hydrothermal reaction of bismuth nitrate, iron nitrate, and poly (vinylacohol) (PVA) as the surfactant, NaOH or nitrate as catalyst.

Poly (vinyl alcohol) solution polymerization method has been used successfully to synthesize various monophase, fine, and pure mixed-oxide powders [12–16] but no literature reported the synthesis of $Bi_2Fe_4O_9$ by PVA sol–gel method. In present paper, a simple sol–gel method based on polyvinyl alcohol is used to prepare $Bi_2Fe_4O_9$ powders. The effect of PVA content on the formation of $Bi_2Fe_4O_9$ was investigated.

2. Experimental procedure

The synthesis procedure of $Bi_2Fe_4O_9$ through the polyvinyl alcohol route was outlined in Fig. 1. Bi_2O_3 powders (purity of >98.9%, Shanghai Institute of Precision Chemical Reagent), $Fe(NO_3)_3{\cdot}9H_2O$ (purity of >98.5%, Sinopharm Chemical Reagent Co., Ltd.), PVA (Chengdu Institute of the Joint Chemical Reagent) and 65–68% nitric acid (guaranteed reagent, Shanghai Chemical Reagent No. 3 Factory) were employed as the starting ingredients. A 5% PVA solution was made by adding PVA (MW = 79,000) to deionized water. The polymer was dissolved by stirring at 70 °C. Bi_2O_3 powders

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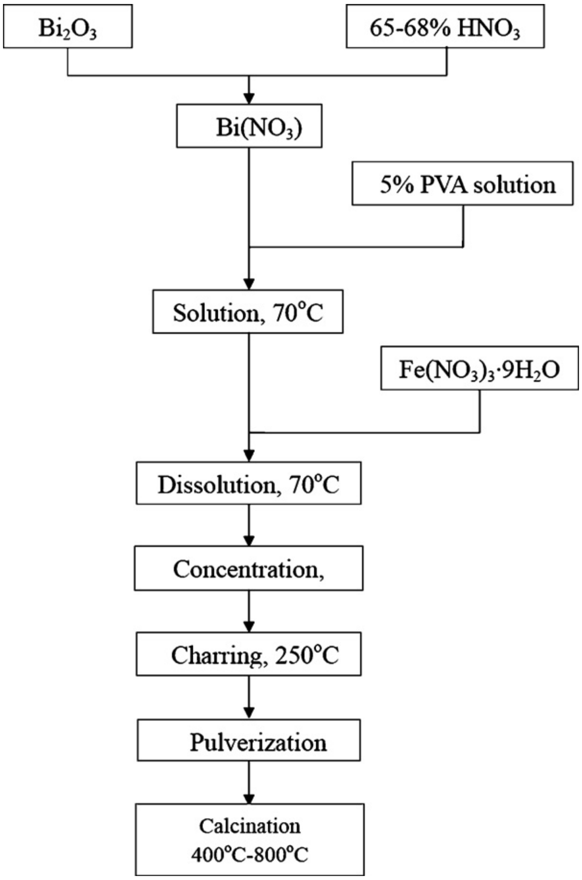

Fig. 1. Flow diagram for the preparation procedure of the $Bi_2Fe_4O_9$ powder.

(4 mol% excess) were dissolved in nitric acid solution to obtain $Bi(NO_3)_3$. Then, mixing $Bi(NO_3)_3$ and 5% PVA solution by stirring at the temperature of 70 °C and 2 ml nitric acid was added to prevent $Bi(NO_3)_3$ from hydrolysis. Finally a stoichiometric $Fe(NO_3)_3\cdot 9H_2O$ was added to the solution. During the process, the molar ratios of positively charged valences to hydroxyl groups (M^{n+}/–OH) of PVA were 1:1, 2:1 and 4:1, respectively. With continuous heating at 70 °C under constant stirring to evaporate superfluous water, the volume of the solution decreased and the solution viscosity increased continuously. A colloid was formed with evolution of NO_x gas resulting from decomposition of nitrate ions. Throughout the process, no signs of precipitation were observed. Then the sample was removed from the hot plate and heated in an oven at 250 °C for 2 h. The resulting mass was slightly ground into a fine powder and $Bi_2Fe_4O_9$ precursor was obtained. The precursor was calcined at 400–800 °C for 2 h in static air to obtain $Bi_2Fe_4O_9$ powder.

Simultaneous differential scanning calorimetry (DSC) and thermogravimetric (TG) analysis (NETZSCH STA 449C) at a heating rate of 10 °C/min in static air were employed to analyze the decomposition and the oxidation process of the precursor. Fourier transform infrared spectroscopy (FT-IR, Vertex 70, Bruker) was used to determine the chemical bonding of the $Bi_2Fe_4O_9$ precursor and powders. The phases were identified by powder X-ray diffraction (XRD) using CuKα radiation (X′Pert PRO, PANalytical B.V.). Field emission scanning electron microscopy (S-4800, HitachiLtd., Tokyo, Japan) was used to observe the grain size and the morphology of $Bi_2Fe_4O_9$ powders. Magnetic properties were measured using physical property measurement system (PPMS, Quantum Design).

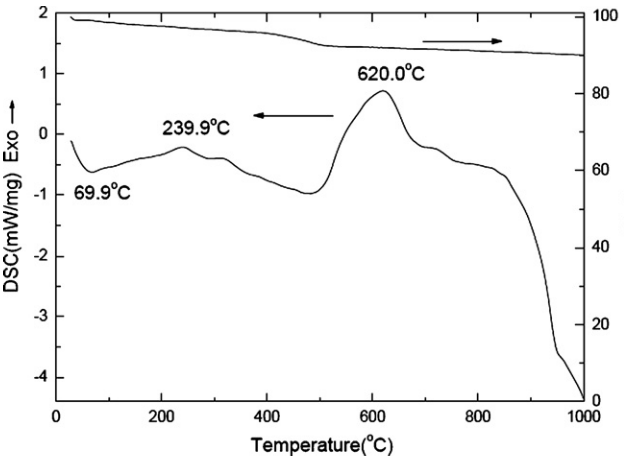

Fig. 2. DSC/TG curve of $Bi_2Fe_4O_9$ precursor powders (M^{n+}/–OH = 2:1).

3. Results and discussion

Fig. 2 shows the DSC/TG curves of the $Bi_2Fe_4O_9$ precursor (M^{n+}/–OH = 2:1). The endothermic peak in the DSC curve around 69.9 °C is indicative of the dehydration of the precursor. The small exothermic peak around 239.9 °C, accompanied by a relative larger weight loss (~5%) in the TG curve, can be attributed to the burnout of organic species in the powder precursor and the decomposition into oxides [15]. TG shows almost no weight loss after this exothermal peak. The exothermic peak around 620.0 °C is associated with the crystallization of $Bi_2Fe_4O_9$. The latter XRD patterns indicate that a large amount of $Bi_2Fe_4O_9$ formed at 600 °C.

Fig. 3 shows the FT-IR spectra of $Bi_2Fe_4O_9$ precursor and powders calcined at different temperatures. For the $Bi_2Fe_4O_9$ precursor with M^{n+}/–OH = 2:1(Fig. 3a), the broad absorption band around 3439 cm^{-1} is associated with the O–H stretch of intermolecular hydrogen bonds or molecular water. The peak at 1467 cm^{-1}, 1048 cm^{-1} and 840 cm^{-1} are related to carbonate ions [17]. Carbon in PVA can react with metal ions to form carbonate species and carbonate ions can usually be observed during sol–gel process employing complexing agent [13]. The bands located at around 1383 cm^{-1} indicated the existence of nitrate ions [18]. The absorption features at 450 cm^{-1} is attributed to the Fe–O bending vibrations, being characteristics of the octahedral FeO_6 groups in the perovskite compounds [19]. An absorption band at about 1634 cm^{-1} can be due to the stretching vibration of the free O–H group of water [20]. Calcining the precursor at 500 °C for 2 h, all the peaks of nitrate and carbonate disappeared. For precursor heated at 700 °C for 2 h, the absorption bands at 438, 483, 528, 599, 640, and 814 cm^{-1} is observed. Since later XRD analysis shows that single-phase $Bi_2Fe_4O_9$ formed at 700 °C for 2 h, these absorption bands can be assigned to $Bi_2Fe_4O_9$. The spectrum is consistent with that Voll et al. reported [21]. As shown in Fig. 4, there are two different sites of four iron atoms in $Bi_2Fe_4O_9$: Fe_1 occupies a tetrahedral position and Fe_2 an octahedral one [22]. In the structure, columns of edge-sharing Fe_2 octahedra form chains along the *c*-axis, and these chains are linked together by corner-sharing Fe_1 tetrahedra and Bi atoms. The bands at the 814 and 640 cm^{-1} are assigned to stretching vibrations of the FeO_4 tetrahedra; the band at 599 cm^{-1} is assigned to Fe–O–Fe bending vibrations of the tetrahedral pairs; the band at 528 cm^{-1} is assigned to O–Fe–O bending vibrations of the tetrahedral pairs; the bands at the 483 and 438 cm^{-1} are assigned to stretching vibrations of the Fe cations in octahedral coordination [21]. Fig. 3b shows the FT-IR spectra of $Bi_2Fe_4O_9$ precursors and powders with M^{n+}/–OH = 1:1 and 4:1. The FT-IR spectra of $Bi_2Fe_4O_9$ precursors with M^{n+}/–OH = 1:1 and 4:1 are similar