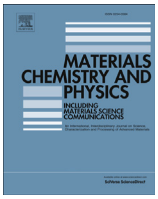
Materials Chemistry and Physics xxx (2016) 1–8

Contents lists available at ScienceDirect

Materials Chemistry and Physics

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



Synthesis and effect of annealing temperature on the structural, magnetic and photocatalytic properties of $(La_{0.5}Bi_{0.2}Ba_{0.2}Mn_{0.1})FeO_{(3-\delta)}$

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HIGHLIGHTS

- A novel perovskite-type ferrite $La_{0.5}Bi_{0.2}Ba_{0.2}Mn_{0.1}FeO_{3-\delta}$ was synthesized.
- An increase in annealing temperature (T_A) caused a decrease in surface area.
- Coercive fields increased with increase in T_A but magnetization decreased.
- The materials showed photoluminescence activity in the visible region.
- Powders showed good photocatalytic activity for rhodamine B photodegradation.

ARTICLE INFO

Article history:
Received 4 January 2016
Received in revised form
2 April 2016
Accepted 2 May 2016
Available online xxx

Keywords:
Magnetic materials
Nanostructures
Sol-gel growth
Annealing

ABSTRACT

Novel $La_{0.5}Bi_{0.2}Ba_{0.2}Mn_{0.1}FeO_{3-\delta}$, with a perovskite-like structure, was synthesized by using the citric acid sol-gel route. The powder was precalcined at 400 °C and then separate portions were annealed at temperatures of 500, 600, 700, 800 and 900 °C. Transmission electron microscopy and powder X-ray diffraction analysis of the powders showed that they contain crystalline rhombohedral perovskite-type nanoparticles. The BET specific surface areas ranged between 4.19 and 27.8 $m^2\ g^{-1}$, decreasing with increasing annealing temperature. Vibrating sample magnetometer analysis of the hysteresis loops showed an increase in coercive field with increasing annealing temperature. Very large coercive fields of about 5.60 kOe were obtained for samples annealed at 900 °C. This could prove useful in making magnetic recording materials. Photoluminescence spectroscopy showed that all the powders were active in the visible region and could be useful for visible light photodegradation of pollutants. The powders were all screened for photocatalytic activity against an organic dye (rhodamine B) in the visible region of the solar spectrum and the photocatalytic activities were good particularly for powders annealed at 900 °C.

1. Introduction

Perovskite solid-solutions are a large family of multifunctional materials that exhibit fascinating properties which are of interest in emerging technologies. Solid solutions with multiferroic properties have received considerable attention in recent years due to their potential for application in various fields of advanced technologies. They have been found to exhibit intriguing magnetic and electric (ferromagnetic, ferroelectric and ferroelastic) properties [1–6], dielectric, piezo and pyroelectric properties [7–9], and catalytic as well as photocatalytic properties [10–12]. Perovskite-like materials are built on a flexible structure which allows for easy substitution and replacement of the ions on either the A- or B-site, and by selecting atoms with suitable properties, materials with novel properties can be produced [13,14]. The multiferroic properties exhibited by $BiFeO_3$ are due to the coupling of the electric field due to the lone pair of electrons on the Bi^{3+}, the magnetic field due to the Fe^{3+}, and the structural geometry of the FeO_6 octahedra [13,15]. The properties of perovskite-like materials can also be influenced by partial replacement (doping) of either sites of the material with

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http://dx.doi.org/10.1016/j.matchemphys.2016.05.007

smaller divalent ions (e.g. Ca, Sr, and Ba) [16]. This doping method has been used to synthesize materials with required properties for applications in areas of interest. Orthoferrites are perovskite-like systems in which a rare-earth (RE) metal occupies the A-site in the material lattice (i.e $REBO_3$) and have also been shown to display interesting characteristics [17–23].

In this work, we synthesize a novel orthoferrite solid solution with the general formula $(La_{0.5}Bi_{0.2}Ba_{0.2}Mn_{0.1})FeO_{(3-\delta)}$ via a solution route with a view to obtaining materials with good magnetic and photocatalytic properties, and analyze the effect of annealing temperature on their specific surface area, magnetic as well as photocatalytic properties.

2. Experimental

2.1. Materials

$Fe(NO_3)_3.9H_2O$ (98%) (Saarchem), La_2O_3 (99.9%) (BDH Chemicals), $Bi(NO_3)_3.5H_2O$ (97%), $Ba(NO_3)_2$ (99%), $Mn(CH_3OO)_2$ (99%), $K_2Cr_2O_7$ (99%), Ag_2SO_4 (99%) (Saarchem), citric acid (99.7%) (BDH Chemicals), chemically pure concentrated H_2SO_4 (98%), $HgSO_4$ (99%) and $(NH_4)_2Fe(SO_4)_2.6H_2O$ (99%) (Merck), ethylene glycol (99%) (Promark Chemicals), chemically pure concentrated HCl (37%) and HNO_3 (55%) (Promark Reagents), rhodamine B (The Coleman and Bell Co), and H_2O_2 30% vol. (100 vol) (Minema Chemicals) were used as received. Deionized water from a Millipore Milli-Q Elix 5 UV water purification system was used throughout and is hereafter referred to as Milli-Q water.

2.2. Synthesis of $(La_{0.5}Bi_{0.2}Ba_{0.2}Mn_{0.1})FeO_{(3-\delta)}$

$(La_{0.5}Bi_{0.2}Ba_{0.2}Mn_{0.1})FeO_{(3-\delta)}$ powders were prepared by a Pechini-type sol-gel process. A solution of $Fe(NO_3)_3.9H_2O$ was prepared by dissolving 0.03 mol of the salt in Milli-Q water (20 cm^3). La_2O_3 (0.0075 mol), $Ba(NO_3)_2$ (0.006 mol), $Mn(CH_3OO)_2$ (0.003 mol) and $Bi(NO_3)_3.5H_2O$ (0.006 mol) were dissolved in dilute nitric acid (about 25 cm^3, 6 mol dm^{-3}) solution to give the amount of metals required for the stoichiometry of the material. The two solutions were mixed thoroughly, made up to 200 cm^3 by adding Milli-Q water and then gradually poured into a burette. This solution was then added (dropwise) to a citric acid solution (400 cm^3, 0.15 mol) in a beaker, which was continuously being stirred by a magnetic stirrer at room temperature, to form a clear solution. Once the addition was complete and while still stirring, the temperature of the mixture was raised to 90 °C and the solution continuously evaporated until the volume of the solution was reduced to about 50 cm^3. Ethylene glycol (100 cm^3) was added and the heating and stirring continued until a thick gel formed. The gel was then removed from the beaker and placed in a crucible in an oven at 120 °C for 24 h to dry. The dry gel was subsequently precalcined at 400 °C for 4 h to remove all organic components present. Separate sample portions of the powders were subsequently annealed in a muffle furnace for 4 h at 500, 600, 700, 800 and 900 °C.

2.3. Characterization

Transmission electron microscopy (TEM) (JEOL JEM 1010) was used to analyze the morphology of the crystals. The crystal lattice structure was determined by powder X-ray diffraction (PXRD) analysis by using a Bruker D8 Advance diffractometer equipped with a Cu K_α radiation source. The crystallite sizes of the powder crystals were calculated by using the Scherrer equation, $D = K\lambda/\beta cos\theta$ (where D is the average crystallite size of the material, K is the Scherrer constant, λ is the wavelength of the radiation and β is the full width at half maximum). The surface areas of the synthesized materials were determined by nitrogen adsorption and the BET equation method by using a Micromeritics Tristar II 3020 fully automated three-station surface area and porosity analyzer. The magnetic properties of the powders at room temperature were analyzed by using a Lakeshore 735 vibrating sample magnetometer (VSM) which had been calibrated with a standard Ni sphere for magnetization measurements. The maximum applied field was 14 kOe. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements were obtained for each sample by using a TGA/DSC thermal analyzer (TA Instruments SDT-Q600 thermal analyzer) in air. The temperature range of the analysis was between 25 and 1000 °C. A PerkinElmer Spectrum 100 Fourier transform infrared (FTIR) spectrometer coupled to an attenuated total reflectance accessory was used to collect the FTIR spectra of the samples. The photoluminescence emission spectra of the powders were monitored at 590 nm by carrying out the excitation at a wavelength of 390 nm by means of a PerkinElmer LS 55 spectrofluorimeter equipped with a high energy pulsed xenon source for excitation.

2.4. Photocatalytic screening

The photocatalytic activity of each sample was tested on rhodamine B (RhB) dye in the presence of H_2O_2 at room temperature. The irradiation was from a 26 W fluorescent lamp (Osram Dulux D, 26 W, 1800 lm) placed in a quartz jacket at about 7 cm above the dye solution. A mass of 1.5 g dm^{-3} of the synthesized material was used first, in the absence of H_2O_2, and then in the presence of H_2O_2 (3.0×10^{-5} mol dm^{-3}). The degradation of the RhB dye solution was monitored by using a Biochrom Libra S6 spectrophotometer at the wavelength of maximum absorbance (λ_{max}) for RhB of 556 nm. A 30-min period was allowed for equilibration before the photodegradation process began. The chemical oxygen demand (COD) for the degraded solution was determined by using the procedure described in literature [24].

3. Results and discussion

Fine powdered samples were obtained with colour varying from brown for samples calcined at 400 °C, to black for samples annealed at 700 °C and above. The samples were labelled LaBa followed by the temperature at which the powder was annealed (e.g. LaBa500, LaBa600 and LaBa900 for samples annealed at 500, 600 and 900 °C respectively).

3.1. Phase characterization

The powder X-ray diffraction (PXRD) analysis conducted on the samples (Fig. 1) shows that the perovskite peaks begin to form very early at the pre-calcination stage ($T_A = 400$ °C). All the perovskite peaks can be seen in the diffractogram of the sample calcined at 400 °C with low intensities. The formation of these peaks indicates that the nucleation and growth of the crystals has already begun at this temperature. The presence of several other peaks, however, shows that the powder is composed mainly of mixed oxides at this stage. As the annealing temperature (T_A) increased, the intensity of the perovskite peaks also increased and the powder crystallizes in a single phase rhombohedral lattice with space group R3C at T_A of 600 °C. The absence of any impurity peaks at $T_A = 600$ °C is an indication that all the ions have been incorporated into the perovskite lattice. The broadness of the peaks is due to the nanosize nature of the crystallites. The broadness decreases as T_A increases, showing that the crystallite sizes increase with increase in T_A. At T_A of 700 °C and above, some tiny peaks (labelled *) begin to emerge

Please cite this article in press as: I. Abdulkadir, et al., Synthesis and effect of annealing temperature on the structural, magnetic and photocatalytic properties of $(La_{0.5}Bi_{0.2}Ba_{0.2}Mn_{0.1})FeO_{(3-\delta)}$, Materials Chemistry and Physics (2016), http://dx.doi.org/10.1016/j.matchemphys.2016.05.007