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Preparation and Characterization of Hexagonal W-type Barium Ferrite Nanoparticles

Abstract  New chemical synthesis procedure for preparation of nickel-zinc doped W-type hexagonal, nickel-zinc doped barium ferrite nanoparticles has been developed, using the nitrate-citrate sol–gel auto-combustion method (NCSAM). The crystalline phase attributes, microstructure, morphology, thermal behavior of the as-burnt phase and the sintered powders were characterized using XRD, SEM, TG-DTA, FT-IR measurements. The pure W-type ferrite phase is formed during 4 h annealing at a temperature of 1200 °C.

Keywords  Ceramics · Hexaferrite · Nanoparticle · Self-combustion · Sol–gel

Introduction

Hexagonal ferrites are a wide family of ferromagnetic oxides, with peculiar and useful properties. The crystal structure of the different known types of hexagonal ferrites (M, W, X, Z, and U) is very complex and can be considered as a superposition of R and S blocks along the hexagonal c axis, RSR*S* for M-type and RSR*S*S* for W-type, where R is a three-oxygen-layer block with composition BaFe₆O₁₁, S (spinel block) is a two-oxygen-layer block with composition Fe₆O₈, and the asterisk means that the corresponding block has been turned 180° around the hexagonal axis [1, 2]. Among the hexagonal ferrites W-type compounds with a general formula AMe₂Fe₁₆O₂₇ (A = alkali earth metals, usually Ba, Sr, Ca, and Me = d-block metals, Zn, Co, Ni, etc.) have created interest due to the main magnetic parameter values, that are more suitable for microwave applications than those of other hexagonal ferrites [3].

A variety of techniques have been developed to synthesize W-type hexaferrites. The most used method for the preparation of barium ferrite in industrial and technical application is the classical ceramic method, which results in a material that is inhomogeneous at a microscopic scale [4]. The conventional mechanical grinding [5] and glass crystallization method [6] for W-type hexaferrites preparation have disadvantages such as time consuming and introducing impurities into material composition. Furthermore, the high calcination temperature (≥ 1300 °C) results in the formation of coarse aggregation and the vaporization of some volatile components. Nowadays, new wet chemical methods have been developed for the preparation of nanograined hexagonal W-type ferrites. Various advantages such as low processing cost, energy efficiency and high production rate [7] are among the benefits of the sol–gel combustion synthesis method, which has been applied to the preparation of various high performance materials including ceramics, intermetallics, and composites [8, 9]. In this paper, sol–gel auto-combustion method has been used to synthesize nanocrystalline, nickel and zinc doped W-hexaferrite. The synthesis process and characterizations of nanocrystalline ferrite is reported.
**Experimental**

**Materials**

Nickel-zinc W-type barium hexaferrite powders were prepared by nitrate-citrate sol-gel auto-combustion method (NCSAM). The starting materials were Ba(NO$_3$)$_2$ (≥ 99%), Ni(NO$_3$)$_2$ · 6H$_2$O (≥ 97%), Zn(NO$_3$)$_2$ · 6H$_2$O (≥ 99%), Fe(NO$_3$)$_3$ · 9H$_2$O (≥ 97%), citric acid anhydrous (≥ 99.5%) and ammonia (∼ 25%), all of analytical purity. All the reagents were purchased from Fluka, and were used without any further purification.

**Preparation**

The preparation process can be described as follows. The stoichiometric amounts of barium, nickel, zinc nitrates and iron nitrates were dissolved together in distilled water, under continuous stirring during 30 min. The calculated amount of citric acid was poured into this mixture, changing the colour of the solution from orange to brownish-yellow. The metal nitrates to citric acid molar ratio were chosen to be 1 : 2. After a subsequent 30 min of stirring, the pH was adjusted to the value of 2, by adding concentrated ammonia solution, followed by 6 h of continuous stirring at room temperature. The dark green coloured clear sol was heated on a hot plate at circa 110$^\circ$C under continuous stirring, until the 3/4 volume of the water evaporated, and suddenly the gelation occurred, resulting a viscous dark green gel, which was further dried in a drying chamber at 140$^\circ$C. During this process, the gel burnt in a self-propagating combustion manner (Fig. 1) to form a dark-grey colored fluffy, loose powder, which was heat-treated in air atmosphere at various temperatures between 900–1200 $^\circ$C.

**Characterization**

**X-ray Diffraction Spectroscopy (XRD).** XRD patterns of the samples treated at various temperatures were recorded in the range of 2θ = 10–70$^\circ$, with a scanning speed of 0.04$^\circ$ min$^{-1}$ on a Philips PW 105 diffractometer, operated at 40 kV, 35 mA and using Cu K$_\alpha$ radiation. The average crystallite size in the sample was calculated using the Scherrer equation:

$$D = \frac{K \lambda}{h_{1/2} \cos \Theta},$$

where $D$ = average size of the crystallites, $K$ = Scherrer constant, $\lambda$ = wavelength of radiation (1.54186 Å), $h_{1/2}$ = peak width at half height and $\Theta$ corresponds to the peak position.

**Elemental Analysis by Inductively Coupled Plasma Spectroscopy (ICP).** The stoichiometry analysis of the heat treated powders was carried out using a inductively coupled plasma spectrometer. The results were almost equal with the initial, calculated composition.

**Transmission Electron Spectroscopy (TEM).** The micrograph and the crystallite size of the calcined samples were examined using a MORGAGNI 268D TEM (100 kV; W filament, top-entry; point-resolution = 0.5 nm) transmission electron microscope.

**Fourier Transformed Infrared Spectroscopy (FT-IR).** The infrared spectra of the samples were recorded using a THERMO Nicolet AVATAR 320 FT-IR spectrometer (laser frequency 15 798.8 cm$^{-1}$) in the range of 4000–400 cm$^{-1}$. The number of sample and background scans was 32 each. The recorded spectra were evaluated with the spectrometer’s software (EZ OMNIC version 6.1a). Sample preparation included mixing ∼ 0.7 mg powdered sample with 250 mg dried KBr and pressing them into pellets.

**Scanning Electron Microscopy (SEM).** Scanning electron micrographs and analysis of the morphology of the samples were carried out on a JEOL JSM-6100 scanning microscope, operated at 15 kV high voltage, with EDAX EDS detector system.

**Thermogravimetry and differential thermal analysis (TG-DTA).** The thermal behavior of the powders was investigated with thermo gravimetric analysis (TG) and differential thermal analysis (DTA), using a Setaram Setsys 16/18 TG-DTA instrument. Experimental conditions were: flowing synthetic air atmosphere (80% N$_2$, 20% O$_2$), in the temperature range 25–1300 $^\circ$C, with a heating rate of 10 K/min, using 100 µl Al$_2$O$_3$ crucibles. The spectra were evaluated using the thermogravimeter’s software (SETSOFT, ver. 1.54).