Ceramics International 42 (2016) 12581–12585

Contents lists available at ScienceDirect

Ceramics International

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

Ethanol sensing evaluation of sol–gel barium calcium ferrite

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ARTICLE INFO

Article history:
Received 11 February 2016
Received in revised form
22 March 2016
Accepted 26 March 2016
Available online 28 March 2016

Keywords:
Hexaferrites
Ethanol sensors
XPS

ABSTRACT

Hexaferrites are very attractive materials for high-frequency circuits and operating devices, nevertheless their use for sensing application is very rare. In the present work, $BaCa_2Fe_{16}O_{27}$ hexaferrite was synthesized by a simple sol–gel technique. Structural and microstructural information have been obtained by X-ray powder diffraction (XRD), Scanning electron microscopy (SEM), Transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). The gas sensing performance of $BaCa_2Fe_{16}O_{27}$ hexaferrite-based sensors was investigated for the detection of some common volatile organic compounds and gases like ethanol, acetone, methane and carbon monoxide. The results showed the sensors to exhibit high sensitivity, quick response/recovery and good reproducibility and stability towards 100 ppm ethanol. Moreover the sensors proved to be highly selective from measurements of cross sensitivity.

1. Introduction

Nanocrystalline ferrites are considered as one of the most attracting class of materials due to their applications like in transformer cores, recording head, memory devices, magnetic imagining pigments, anti-radar coating etc. Ferrites are usually comprised of cubic and hexagonal symmetries. Hexagonal ferrites are very attractive materials for high-frequency circuits and operating devices. They are preferably used as permanent magnets, high-density magnetic recording media and microwave devices. Numerous new hard and soft ferrites and their composites have been developed recently, with large potential applications including gas [1,2] and humidity sensors [3], bio-sensors and microwave absorbers. It is also well known that spinel type ferrites are used as gas/alcohol sensors. The main advantage is that compared to traditional sensor materials based on metal oxide semiconductor (MOS); it has that the ability of regulating the type of conductivity and resistivity by changing the cation composition, stoichiometry and annealing conditions. In recent years due to environmental pollution and health concern, globally research activities are going on towards finding newer, more efficient and low cost sensors selective to a specific gas/vapor. Ferrites such as $BiFeO_3$, $LaFeO_3$ and $GdFeO_3$ exhibit different gas sensing ability [3–5]. The hexaferrites are basically complex oxides and their behavior is similar to semiconductor and hence they may resemble MOS sensors in detection of toxic and inflammable gases. Hexaferrites have high Curie temperature, large magnetocrystalline anisotropy, high coerecivity and magnetization and hence they are mostly used in magnetic recording materials [6,7]. They are also used in data storage; microwave devices; wireless communications and smart technology [8,9].

Literature survey revealed that recently only one group have studied the acetone and ethanol sensing properties of barium hexaferrite compound [10]. But to our knowledge, the gas/vapor sensing properties of barium calcium ferrite have not been investigated till date. Large scale applications of ferrite materials have promoted the development of various chemical methods like co-precipitation, hydrothermal, sonochemistry, combustion, sol–gel etc [11,12]. Hence an attempt was made to study the sensing properties of a new hexaferrite i.e. barium calcium hexaferrite synthesized by sol–gel route, which may pave a new path avenue towards the development of hexagonal ferrite sensors. Moreover, the material exhibited p-type gas sensing property which can be considered as a promising material platform for developing the new functionalities of chemiresistors.

2. Experimental

2.1. Materials and synthesis

$BaCa_2Fe_{16}O_{27}$ (BCF) compound was synthesized by the sol–gel auto-combustion method. $Ba(NO_3)_2$(Sigma-Aldrich),$Ca(NO_3)_2 \cdot 4H_2O$(sd Fine-Chem, India) and $Fe(NO_3)_2 \cdot 9H_2O$ (Sigma-Aldrich) were taken as the starting materials. Stoichiometric amount of the

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http://dx.doi.org/10.1016/j.ceramint.2016.03.201
0272-8842/

metal nitrates were taken and a solution was prepared in distilled water. The metal nitrate solution was vigorously stirred on a hot plate magnetic stirrer and citric acid equivalent of the metal ions was added to it. Citric acid (Sigma-Aldrich) was used as the combustion/chelating agent because its decomposition generates high temperature during burning process, leading to the complete formation of the ferrite phase. The final solution was heated at 150 °C for about 6 h until a reddish-brown gel was obtained. The gel was dried in a vacuum oven at 120 °C for 20 h to obtain xerogel which was further ground and calcined at 950 °C for 4 h.

2.2. Characterization

Thermal analysis (TGA/DTA) of the dried gel was done from room temperature to 1000 °C at the heating rate of 10 °C/min using Perkin Elmer Thermal Analyser. The powders were subjected to the evaluation of structural properties by a High Resolution X-Ray Diffractometer (D8 Advance Davinci (Bruker) XRD system). The shape and particle size of the calcined powders was investigated using transmission electron microscope (Techno $G^2$30 STwin). The characteristic vibrational modes present in the powder was analyzed by Fourier Transform Infrared Spectroscopy (FT-IR, Shimadzu) in the range of 4000–400 cm^{-1} wave number. The chemical state and the electronic structure of the materials were investigated using X-ray photoelectron spectroscopy (XPS). The surface area was measured using a NOVA Surface Area Analyser system. The magnetic properties were investigated using Vibrating Sample Magnetometer (Lakeshore).

2.3. Fabrication and measurement of sensor

For fabrication of sensors, the powders were mixed with required amount of isopropanol to form a paste. The paste was then coated (coating thickness ~100 μm) on alumina substrates. The gold electrode and platinum lead wires were attached to the end of the tubes by curing at high temperature before applying the paste. After coating with the paste, the tubes were fired at 400 °C for 10 min. The details of the sensor packaging arrangements are described in details elsewhere [11]. The measurement was done by using an indigenously developed static flow gas sensing measurement in which a given amount of test gas was injected into the test tube by micro syringe and the sensors was inserted inside the chamber with environmental air humidity about 25% at room temperature (about 25 °C). The required concentration of test gases was calculated by the following equation:

$$C = (22.4 \times ø \times \rho \times V_1)/(M \times V_2) \times 1000$$

where C (ppm) is the test gas concentration, $ø$ is the desired liquid volume (g/mL), ρ is the density of the liquid, V_1 is the volume of liquid, V_2 is the volume of the test chamber, and M (g/mol) is the molecular weight of the liquid. The change in resistance was measured using an Agilent B2901A source meter and the data were recorded using LabView based graphical user interface (GUI). The sensor response was calculated using the following equation $S=[(R_a-R_g)/R_a]*100$, where R_g is the resistance under a given gas atmosphere at the operating temperature and R_a is the base resistance at ambience at the same temperature. Before characterization, the sensors were aged at the operating temperature (350 °C) for 12 h to obtain a constant stable resistance in air. The voltage–current characteristics was measured by Agilent B2910A Precision source meter at room temperature.

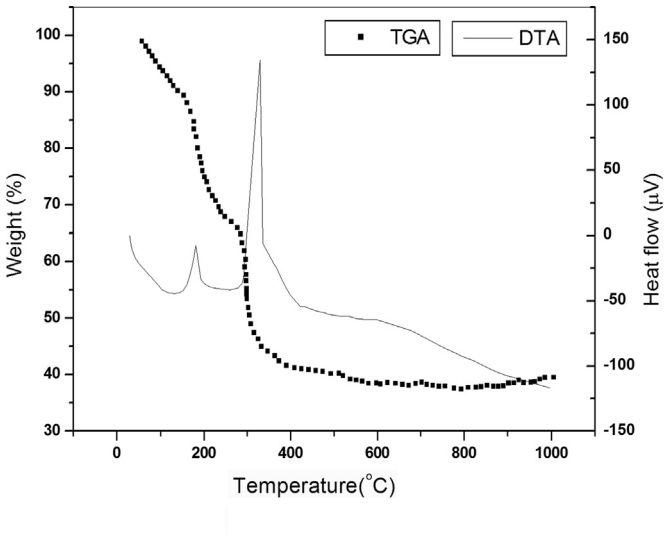

Fig. 1. TGA/DTA curve of the compound.

3. Results and discussion

3.1. Crystal structure and morphology

The TGA/DTA curve of the compound is shown in Fig. 1. From the TGA graph, it was observed that the mass weight loss has taken place in three stages. The first stage between 34.8 °C and 172.5 °C was accompanied by a 13.67% weight loss owing to the removal of water and other solvents. The second stage is between 172.5 °C and 387.9 °C with a loss of 44.44% due to the removal of excess citric acid which was used as a chelating agent. The third minor loss of ~2.06% occurred between 387.9 °C and 700 °C mostly because of the decomposition of the metal nitrates and organic groups. The corresponding DTA curve shows two exothermic peaks at ~182.9 °C and ~332.1 °C which can be ascribed to the combustion of citric acid ligand and decomposition of nitrate salts. Fig. 2 depicts the XRD pattern which was used to determine the phase composition of calcined powders. The formation of the compound was confirmed by matching with the reported peaks of $BaFe_{16}O_{27}$ [10]. The compound has its characteristics peak for the hkl plane at (114) with $2\theta=34.38°$. An average

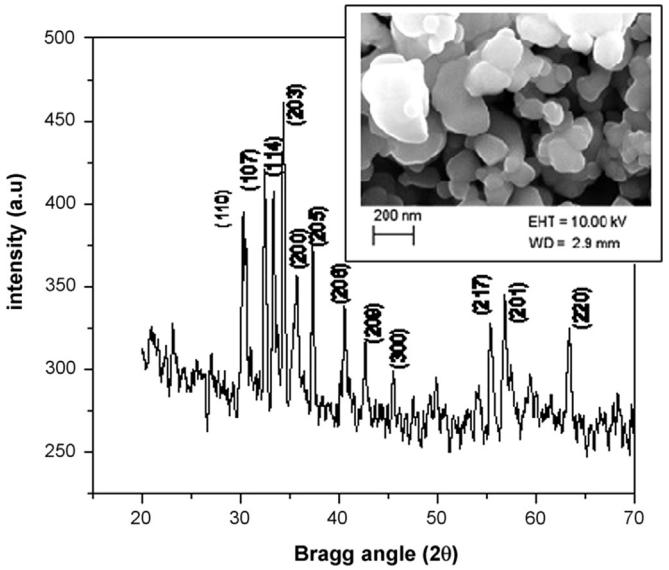

Fig. 2. XRD pattern of compound with SEM micrograph at inset.