



## Barium hexaferrite thick-films for ozone detection at low temperature

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### ABSTRACT

Crystalline BaFe<sub>12</sub>O<sub>19</sub> powder was synthesized by auto-combustion sol gel method, in which citric acid was used both as a fuel and chelating agent. The pre-combusted precursor was calcined at 900 °C for 1 h and characterized by laser granulometry, X-ray diffraction, scanning electron microscopy, thermal analysis and transmission electron microscopy. Sensors were prepared by screen-printing the sensing material onto α-alumina substrates with platinum interdigitated electrodes. After drying overnight, sensors were fired at 600 °C in air.

The sensor response was measured in the range 150 °C–350 °C performing all measurements in a flow chamber at a constant flow rate of 1 L/min of dry air in the range 200–500 ppb O<sub>3</sub>. Response time and recovery time (e.g., the times taken for the sensor to attain 90% of total impedance change from its initial impedance value) were determined, together with cross-sensitivity tests towards NH<sub>3</sub>, CH<sub>4</sub>, humidity, CO<sub>2</sub>, N<sub>2</sub>O and NO<sub>2</sub>.

Sensor's maximum responses were observed at 250 °C, with SR equal to 18% under 500 ppb O<sub>3</sub>, and SR of 10% under 200 ppb O<sub>3</sub>. Such results are extremely encouraging and support the exploitation of barium hexaferrite as relatively low-temperature ozone sensors.

### 1. Introduction

Ozone is one of the most reactive form of oxygen, being less stable with respect to O<sub>2</sub>. It is produced in the troposphere in a chain of photochemical reactions involving sunlight, nitrogen and hydrocarbon gases as well. Recently, tropospheric ozone level has increased due to the interaction between sunlight and a wide range of chemicals emitted in the troposphere by anthropogenic activities, like industries and vehicles. Thus, tropospheric ozone is a byproduct of industrial and urban pollution [1]. Nowadays ecologically clean “ozone” technologies are common: it is established that ozone can be widely used in medicine, as well as in different technological processes [2–4]. Despite its use in purification of gases [5] and in water deputation, ozone is hazardous to the human respiratory system, causing inflammation and congestion of the respiratory apparatus [6,7]. For these reasons, monitoring O<sub>3</sub> in atmosphere appears crucial. In 2015, EPA (United States Environmental Protection Agency) revised the National Ambient Air Quality Standards (NAAQS) for ground-level ozone to 70 ppb, in order to improve public health protection [8]. As a consequence, the analytical techniques developed to monitor ozone concentration should work in a quite wide range of concentration (0.01–10 ppm) [1]. In fact, ambient measuring needs instruments with low detection levels, while in industrial and commercial applications this characteristic is not so stringent considering that the expected concentrations are commonly in the order of some ppm.

Nowadays, a wide range of sensing technologies have been employed to determine ozone concentration, for instance ultraviolet (UV) light absorption, photometry, gas-sensitive semiconductors, potassium iodide, chemiluminescence analyzers, optical detection, direct amperometry determination and fluorescence measurements [9–16]. Among them, gas-sensitive semiconductors evidence a great potential, compared with traditional ozone measurements methods, because of their low cost, ease of operation, high long-term stability and reliability, together with a relatively moderate power dissipation.

Traditionally, the conduction mechanism of semiconducting metal oxide (SMO) is explained by gas-related modulation of Schottky barriers causing space-charge layers at grain boundaries of n-type semiconducting oxides [17–19], like in the most investigated materials: SnO<sub>2</sub>, ZnO, WO<sub>3</sub> and In<sub>2</sub>O<sub>3</sub> [19–23]. Nevertheless, the temperature of maximum sensor response depends strongly on the grain size and film thickness [24].

Only few studies have discussed the sensitivity of doped ferrites, like SmFeO<sub>3</sub> and BaFe<sub>12</sub>O<sub>19</sub> under oxidizing atmospheres [25–27]. Thus, the aim of this work is to investigate the properties of a novel p-type semiconductor metal oxide in the form of a thick-film of barium hexaferrite (BaFe<sub>12</sub>O<sub>19</sub>) towards ozone exposure under sub-ppm concentration range. This ceramic sensor was developed by screen-printing technique, in place of thin-films that have already been investigated as ozone efficient detection material [27].

Among different synthesis routes as hydrothermal synthesis and

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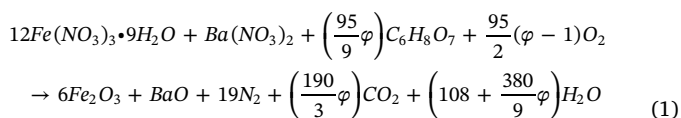
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solid-state reaction [28–30], barium hexaferrite powder was synthesized by a sol-gel auto-combustion process based on the gelling and the subsequent combustion of a solution containing salts and organic fuel. This process has the advantages of the use of inexpensive precursors, an easy and fast preparation and a noticeable scalability.

## 2. Materials and methods

### 2.1. Powder synthesis

BaFe<sub>12</sub>O<sub>19</sub> powder was prepared by auto-combustion sol gel method [31] starting from iron nitrate nonahydrate, barium nitrate, citric acid and ammonium hydroxide solution (28% v/v). In a typical synthesis, Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (ACS reagent, > 98%, Aldrich) and Ba(NO<sub>3</sub>)<sub>2</sub> (ACS reagent, < 99%, Aldrich) were mixed at 50 °C in the proper molar ratio (12:1) and dissolved in distilled water, until a clear red solution was obtained. Then, citric acid (99 + %, Alfa Aesar was added to the solution (with a citric acid to nitrates molar ratio equal to 1 [32]). The pH was adjusted to 7.0 by adding NH<sub>4</sub>OH (Fluka, 28%). Here, the citric acid displayed a twofold role: fuel and chelating agent for Fe<sup>3+</sup> and Ba<sup>2+</sup> ions [31]. According to a study [33], the total reaction of combustion can be written as depicted in Eqs. 1 and 2, since the compositions of the prepared barium hexaferrite particles can be represented by BaO·6Fe<sub>2</sub>O<sub>3</sub>:



In order to outline the combustion process, some simplifications were carried out. First, the formation of the two oxides (Fe<sub>2</sub>O<sub>3</sub> and BaO) was considered separately in the reaction scheme in accordance with SCS (solution combustion synthesis) [33]. Moreover, ammonium hydroxide contribution to the total balance of oxidants and reductants was neglected because of the small quantities compared to the other reactants involved in the reaction.

After 1 h stirring, the solution was evaporated by heating at 80 °C under permanent agitation, until the formation of a brownish viscous gel was observed. Ethanol (≥ 99.8%, Aldrich) was added at the end of evaporation process to limit particles agglomeration. The gel precursor was then pre-combusted by increasing the temperature up to 180 °C directly on the hotplate. A brownish fibrous structure was formed after a violent ignition phenomenon. Nonetheless, the obtained material showed magnetic behavior, as verified by means of a small magnet. At the end, the pre-combusted precursor was finally calcined at 900 °C for 1 h (heating and cooling rate of 5 °C/min), to ensure crystallinity of the final barium hexaferrite powders [32].

### 2.2. Powder and film characterization

The particle size distribution of barium hexaferrite powder was determined by laser granulometry (Mastersizer 3000, Malvern, UK). The powder was manually ground by means of an agate mortar and an agate pestle, sieved under 45 μm and dispersed for 5 min in absolute ethanol under sonication in an ultrasonic bath, before analysis.

Thermogravimetric-Differential Thermal Analysis (TG-DTA, STA 409, Netzsch, Germany) was performed on BaFe<sub>12</sub>O<sub>19</sub> precursor and on 350 °C calcined powder in the temperature range 25–925 °C with a heating ramp of 10 °C/min under static air.

X-ray diffraction (XRD) was also carried out on BaFe<sub>12</sub>O<sub>19</sub> precursor calcined at 350 °C and 650 °C and on calcined BaFe<sub>12</sub>O<sub>19</sub> powder. Spectra were recorded on a diffractometer (X'Pert Pro, PanAnalytical, The Netherlands) operating with CuKα radiation (0.154056 nm) in the range 5–70° 2θ, with a step size of 0.05° of 2θ and an acquisition time

per step of 5 s. Diffraction patterns were indexed by means of the Powder Data File database (P.D.F. 2000, International Centre of Diffraction Data, Pennsylvania, USA).

The average crystallite size was estimated according to the Scherrer equation, for a qualitative comparison with the available data in literature (Eq. (3)):

$$D = k\lambda/\beta\cos\theta \quad (3)$$

where *k* is a constant assumed to be equal to 0.9, *λ* is the CuKα wavelength (0.154056 nm), *θ* is the half of Bragg (radians) and *β* is the full width at half maximum of the X-ray diffraction peaks, which are commonly associated with the crystallite size, presence of defects, and peak broadening caused by the instrument [34].

Moreover, FESEM (Zeiss Supra-40, Germany) observations were performed both on powders and screen-printed films in order to study the morphology of the surface, after Cr metallization process.

Finally, observations of the synthesized sample were performed by using an HR-TEM coupled with energy dispersive X-ray spectroscopy (TEM-EDS). Investigations were carried out using a JEOL 3010-UHR (Peabody, MA, USA) instrument, operating with an acceleration potential of 300 kV and equipped with an Oxford Inca Energy TEM 200 EDS X-rays analyzer.

### 2.3. Gas sensing tests

Sensors were prepared by screen-printing technique onto α-alumina substrates (Coors Tek, USA; ADS-96: 96% alumina, 0.85 cm × 1.7 cm) with platinum interdigitated electrodes (ESL 5545, USA). These electrodes were fired at 980 °C (2 °C/min heating and cooling ramps) for 18 min obtaining a high-grade adhesion and optimizing their electrical conductivity, as per manufacturer's recommendations.

Electrodes present a thickness of 400 μm and are spaced 450 μm each other. In addition, the edge of an electrode belonging to one comb and the vertical connection of the second comb are separated by 400 μm.

Inks for screen printing were fabricated by mixing BaFe<sub>12</sub>O<sub>19</sub> powder with an organic vehicle (ethylene glycol monobutyl ether, Emflow, Emca Remex, USA), to achieve the proper rheological characteristics, and polyvinyl butyral (PVB) acting as temporary binder for the powder before thermal treatment.

After screen-printing deposition with a 325-mesh steel mask, sensors were dried at room temperature overnight and fired at 600 °C in air for 1 h (2 °C/min heating and cooling ramps). This process is required for removing organic residues from the solvent and for ensuring the adhesion with the substrate.

Once fabricated, sensors were tested in a home-made system (Fig. 1), where ozone was generated by a UV lamp (Ultra-Violet Products Ltd., SOG-01, UK) from a constant air flow of 1000 sccm (standard cubic centimeter) of compressed air. Ozone concentration was modulated by varying the length of lamp exposed and was determined by means of the calibration curves given by the manufacturer.

Ozone losses due to adsorption or reactions in pipe lines and measuring chamber was prevented by utilizing suitable materials like polyvinylidene fluoride (PVDF) and polytetrafluoroethylene (PTFE) tubes.

Finally, cross-sensitivity tests were additionally performed adopting the same operating conditions. Target gas was diluted with air by means of flow meters (Teledyne Hastings Instruments HFM 300, HFC 302, USA). All the sensors were heated by a Ni-Cr wire, located underneath the sensor, alimented with a DC power supply (Peak Tech, China). A PT1000 resistance temperature detector was used for temperature determination of sensors.

During tests in a dynamic flow system under constant gas flow, film impedance and resistance were measured by means of a LCR meter (Hioki 3533-01, Japan). Impedance's measurements were carried out by means of a constant AC tension of 1 V at 1 kHz, and sensors were

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