Sensors and Actuators B 221 (2015) 499–506

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

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

CO_2 gas sensing response of YPO_4 nanobelts produced by a colloidal method

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ARTICLE INFO

Article history:
Received 2 March 2015
Received in revised form 19 June 2015
Accepted 27 June 2015
Available online 2 July 2015

Keywords:
YPO_4
Nanobelts
Colloidal method
CO_2 sensor
Impedance measurements

ABSTRACT

YPO_4 has been studied as host lattice for luminescence materials; however, little is known about its gas sensor properties. In this work, YPO_4 was synthesized by a colloidal method using yttrium nitrate, phosphorous acid and CTAB (as surfactant). The calcination at 500 °C produced single-phase YPO_4 nanobelts, having length between 3 and 10 μm, and width between 70 and 250 nm. In order to optimize the synthesis of YPO_4 nanobelts, several surfactants and different concentrations of CTAB were tested. Impedance measurements were performed on thick films made with the as-prepared YPO_4 nanobelts. The results show repeatability in the detection of variations in the concentration of CO_2 of 200 ppm, from 350 °C. However, the response was improved, when an operating temperature of 400 °C was used. At this temperature YPO_4 responded in a wider frequency range, from 100 Hz to 100 kHz. Quantitative detection of CO_2 was proposed in terms of the variation on the dielectric constant of the carbonate film, formed on its surface. Preliminary results obtained from carbon monoxide sensing characterization revealed a periodic detection pattern, with short response time. These results indicate a p-type semiconductor behavior for YPO_4.

1. Introduction

Yttrium phosphate (YPO_4) has been studied as a host lattice for luminescent materials [1]. Ropp investigating the luminescence properties of phosphors found that the color emitted by YPO_4:Ln^{3+} (Ln^{3+} = Eu^{3+}, Sm^{3+}, Dy^{3+}, Tb^{3+}, Pr^{3+} and Er^{3+}) is determined by the rare earth doping [2]. Other applications of YPO_4 and YPO_4:Ln^{3+} can be found in environmental barrier coatings [3], photocatalytic generation of hydrogen [4], lithium ion batteries [5] and therapies for cancer treatment [6].

Due to luminescence properties depend on the microstructure, numerous methods to synthesize doped and undoped yttrium phosphate have been investigated. The resulting materials were nanoparticles of irregular shape, nanofibers, microflakes, microbundles, hexagonal microprisms and ellipsoid nanoparticles, among others [7–14]. Of particular interest for this work, Lai et al. using the hydrothermal method produced nanospheres, nanorods and microprisms, by adding citric acid, oxalate and EDTA (ethylenediaminetetraacetic acid), respectively [15]. In another work, the same authors reported the synthesis of ellipsoid YPO_4 nanoparticles, using the hydrothermal method and CTAB (hexadecyltrimethylammonium bromide) [16]. Hou et al. synthesized YPO_4 microbelts by electrospinning [17]. In this case, the amount of YPO_4 produced was limited by the rate at which the polymer solution was pumped through a syringe (0.5 ml/h). Furthermore, a high voltage (20 kV) must be applied to extract the YPO_4 microbelts.

On the other hand, the emission of CO_2 by human activities promotes the global climate change, which is observed by severe droughts, hail storms, tornadoes and rain falls, to name a few [18]. To evaluate the concentration of CO_2, chemical sensors based on K_2CO_3 [19], K_2CO_3-polyethylene glycol [20], CuO-$BaTiO_3$ [21], $Na_3Zr_2Si_2PO_{12}$ (NASICON) [22–25], $SmCoO_3$ [26] and $CoSb_2O_6$ [27] have been studied. Among these materials NASICON has been one of the most studied, which suggests that other phosphates may be suitable for this application. It is worth to mention that due to its outstanding physicochemical properties, another phosphate ($LiFePO_4$) is widely used as cathode for rechargeable lithium batteries [28].

For gas sensing applications, particle size and morphology play a key role, being the nanostructured materials those that shown a better performance [29]. Among the numerous available shapes, two-dimensional (2D) nanostructured materials possess less crystal defects, which facilitate the charge carrier flow [30]. Therefore,

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http://dx.doi.org/10.1016/j.snb.2015.06.119
0925-4005/

this work was focused in the synthesis of YPO_4 nanobelts and the evaluation of its CO_2 gas sensing properties.

2. Experimental

YPO_4 was prepared by dissolving separately 0.41 g phosphorous acid (99%, Aldrich), 1.915 g yttrium (III) nitrate hexahydrate (Alfa Aesar, 99.9%) and 0.2 g CTAB (Sigma, 99%), in 5 ml of ethyl alcohol (J.T. Baker, 99.5%). Once clear solutions were obtained, the resulting mixture was stirred for 18 h at room temperature. The evaporation of the solvent was done by applying microwave irradiation, using a home microwave oven (Panasonic). The resulting material was dried at 110 °C using an oven, and later it was calcined at 300, 400 and 500 °C in air (5 h) in a programmable temperature furnace. The samples were cooled at room temperature inside the furnace. For comparative purposes, YPO_4 was also prepared in absence of surfactants, and using 0.1 and 0.4 g of CTAB, as well as with 0.2 g PVP (polyvinylpyrrolidone, Sigma–Aldrich) and 0.2 g AOT (dioctyl sulfosuccinate, Sigma, 99%).

X-ray powder diffraction (XRD) patterns were obtained at room temperature, using a Rigaku Miniflex diffractometer (Cu $K\alpha_1$ radiation). Field emission scanning electron microscopy (FESEM), using a Tescan (Mira) microscope and transmission electron microscopy (TEM, Jeol JEM-1010) were used to observe the morphology of samples. Prior to TEM observation, the powders were sonicated in isopropyl alcohol and cast onto formvar-coated copper grids. Specific surface area measurements (BET analysis) were performed with a Horiba 9601 MP surface area analyzer. For this purpose, the powder was degassed at 300 °C, prior to nitrogen adsorption at 77 K. The gas sensing characterization was performed on YPO_4 thick films, which were prepared by depositing a suspension of the powder using a syringe. The suspension was made by dispersing 70 mg YPO_4 in 5 ml of ethyl alcohol absolute. To confine the suspension, an alumina ring having 3 mm of inner diameter was used. Gold wires (Aldrich, 99.9%) were attached to the alumina ring as electrodes; Fig. 1 shows a drawing of the sensor device. Prior to the evaluation of the gas sensing properties the films were sintered at 400 °C for 5 h, in air. The latter was done to improve the mechanical strength of the film, and to remove the solvent used in its preparation. Then, the sensor device was placed inside a test chamber, which was previously described [27]. Extra dry CO_2 (99.8%), CO (100%) and air (used as base gas) were supplied by a mass flow controller (MKS Instruments, 647C). The concentration of CO_2 in air was measured using a portable CO_2 analyzer (Extech, EasyView 80). Impedance measurements were carried out at fixed frequencies, from 100 Hz to 100 kHz, using a LCR meter (Agilent 4263B). Polarization curves (*I–V*) were recorded with a potentiostat (Solartron 1285A).

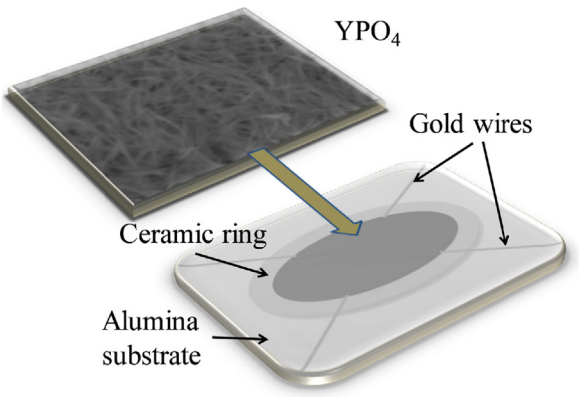

Fig. 1. Scheme of the sensor device used for gas sensing characterization.

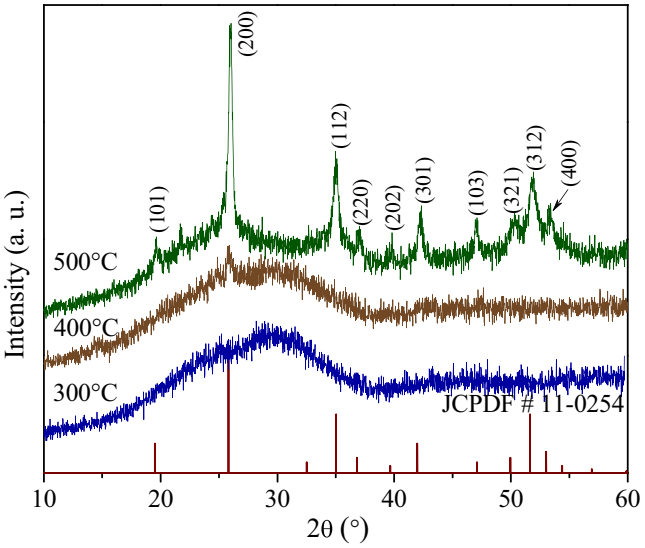

Fig. 2. XRD patterns of samples calcined at 300, 400 and 500 °C. At the bottom, diffraction lines of the JCPDF file No. 11-0254 (YPO_4).

3. Results

3.1. Crystal structure and morphology of samples

Fig. 2 shows XRD patterns of samples calcined at 300, 400 and 500 °C, as well as the diffraction lines of the JCPDF file No. 11-0254, used for the identification of YPO_4 (Xenotime). Calcination at 300 °C produced a non-crystalline material, whereas XRD patterns of samples calcined at 400 °C displayed the main diffraction line of YPO_4 ($2\theta = 25.8°$). Sample crystallinity was improved by annealing at 500 °C, where all the diffraction lines of YPO_4 were identified. YPO_4 crystallizes with the zircon-type structure ($ZrSiO_4$), which has the tetragonal unit cell [31]. YPO_4 has cell parameters $a = b = 6.904$ Å and $c = 6.035$ Å, and space group I41/amd.

Fig. 3 shows the surface microstructure (FESEM images) of samples calcined at: (A) 300, (B) 400 and (C) 500 °C. The morphology produced at 300 °C corresponds to bundles of filaments, which according to the XRD results were non-crystalline. The increase on the calcination temperature to 400 °C produced a reduction in the cross section of the filaments, caused by the thermal decomposition of the organic matter. The filaments had a length between 3 and 10 μm, randomly oriented, with some extent of agglomeration. Annealing at 500 °C produced thinner and scattered filaments, which in agreement with the XRD pattern were crystalline and single phase.

Fig. 4 shows typical TEM images of YPO_4 calcined 500 °C, in which the precise shape of the filaments can be observed. Fig. 4A displays numerous fragments of thin nanobelts, having a width in the range 70–250 nm. Fragmentation of nanobelts occurred during sonication, prior to TEM observation. An image acquired at a larger magnification (Fig. 4B) revealed a non-uniform surface, characterized by nanoporosity and nanocrystallites, with size in the range 3–7 nm. Results of BET analysis for this sample gave an average value of 37 m^2/g. This value is in the range of those reported for YPO_4 hollow microspheres, which were between 25 and 100 m^2/g [4].

The optimization in the preparation of YPO_4 nanobelts was performed testing several synthesis processes. Fig. 5 shows the morphology of YPO_4 obtained: (A) without surfactant, (B) 0.1 g CTAB, (C) 0.4 g CTAB, (D) 0.2 g PVP and (E) 0.2 g AOT; all the samples were calcined at 500 °C. In absence of surfactant the morphology was mostly irregular, with large agglomeration (Fig. 5A). The