Sensors and Actuators B 190 (2014) 305–310

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

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

Humidity sensing properties of $Bi_{0.5}(Na_{0.85}K_{0.15})_{0.5}Ti_{0.97}Zr_{0.03}O_3$ microspheres: Effect of A and B sites co-substitution

Run Wang [a], Ding Wang [b], Yong Zhang [a], Xuejun Zheng [a,*]

[a] Faculty of Materials, Optoelectronics and Physics, Xiangtan University, Xiangtan, Hunan, 411105, People's Republic of China
[b] School of Materials Science and Engineering, University of Shanghai for Science & Technology, Shanghai, 200093, People's Republic of China

ARTICLE INFO

Article history:
Received 12 June 2013
Received in revised form 3 August 2013
Accepted 13 August 2013
Available online xxx

Keywords:
Humidity sensors
$Bi_{0.5}(Na_{0.85}K_{0.15})_{0.5}Ti_{0.97}Zr_{0.03}O_3$ microspheres
Element substitution
Humidity sensing properties

ABSTRACT

$Bi_{0.5}(Na_{0.85}K_{0.15})_{0.5}Ti_{0.97}Zr_{0.03}O_3$ (BNKTZ) sensing materials were successfully synthesized via a simple metal–organic decomposition method. Their morphological feature was characterized as regular shaped microspheres, and it was observed that a large quantity of nanoparticles with the size, of 50–100 nm were present on microspheres surfaces. The introduction of a small quantity of Zr^{4+} in, the reaction system was played an important role in the size-control. At room temperature, humidity, sensing properties of the BNKTZ were investigated in detail. At 100 Hz, the curve of impedance versus relative humidity (RH) was of good linearity and the variation of BNKTZ humidity sensor's impedance was more than four orders of magnitude when humidity changed from 11% to 95% RH. The response time and recovery time were found to be about 18 s and 60 s, respectively. Furthermore, the maximum, hysteresis was only 4% RH. Comparing with A site substituted materials, with the similar response and sensing range, the A and B sites co-substituted BNKTZ humidity sensor possessed lower impedance, better linearity and wider operating frequency. The results indicated that BNKTZ microspheres have broader application for fabricating high performance room temperature humidity sensors.

1. Introduction

In the last decade, humidity sensor, as an important chemical sensor, has gained considerable attention due to its practical applications in industrial, agricultural, meteorology, medicine and aeronautics [1–3]. Many scientific and technological efforts have been spent on improving humidity sensing properties such as high sensitivity, linear response and fast response speed [4–7]. The humidity sensor relied on the change of impedance is one of the most commonly used sensors and it is compatible with the electronic circuitry. Usually, most of sensing materials exhibit high impedance under low relative humidity (RH) and low frequency conditions. The high impedance requires complex amplifying circuit or strict testing condition, which lead these sensing materials to low practicability [8]. Wang et al. had prepared the humidity sensor based on ZnO/TiO_2 composite nanofibers with high sensitivity and quick response/recovery speed. However, the impedance of the ZnO/TiO_2 sensor was greater than 100 MΩ at low frequency, which was difficult to test [9]. Hence, it is required to design novel sensing materials with high response and low impedance.

ABO_3-type complex metal oxide, as a kind of potential humidity sensing materials, has been extensively studied because of its excellent stability and reliability in oxidizing or reducing atmospheres [10–15]. However, some shortcomings, such as low response and high impedance in low frequency, should be improved [8,16]. ABO_3-type complex metal oxide can be substituted on the A site with an alkaline earth element or/and B site with a transition metal element, which brought interesting modifications in their electronic properties as well as their catalytic properties [13]. Substitution of proper metal ions in ABO_3-type complex metal oxide may also improve the humidity sensing properties [17]. In our previous work [15], it was difficult to get the electric signal of the A-site substituted Bi(Na, K)TiO_3 (BNKT) humidity sensor's impedance at operating frequency less than 100 Hz because of the high impedance, which was similar with Wang's results [9]. Therefore, the decreasing of the ABO_3-type complex metal oxide impedance is useful for enhancing the width of operating frequency.

In this paper, the A and B sites co-substituted $Bi_{0.5}(Na_{0.85}K_{0.15})_{0.5}Ti_{0.97}Zr_{0.03}O_3$ (BNKTZ) microspheres were prepared by metal–organic decomposition method (MOD), which were compared with the A-site substituted BNKT sensing materials in our previous research [15]. The effects of A and B sites co-substitution on humidity sensing properties were investigated and the sensing mechanism of BNKTZ microspheres sensor was explored. These researches may offer useful guidelines to design humidity sensors and understand the substitution effects of ABO_3-type complex metal oxide.

* Corresponding author. Tel.: +86 731 58293648; fax: +86 731 58298119.
E-mail address: zhengxuejun@xtu.edu.cn (X. Zheng).

0925-4005/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.snb.2013.08.048

2. Experimental

2.1. Synthesis

All chemicals used in the present work are AR grade from Shanghai Chemical Co. and used as received without further purification.

In a typical procedure, BNKTZ precursor solution was prepared by firstly dissolving an appropriate amount of bismuth nitrate [$Bi(NO_3)_3{\cdot}5H_2O$] (99.5%), sodium nitrate [$NaNO_3$] (99%), potassium nitrate [KNO_3] (99%), and zirconium nitrate [$Zr(NO_3)_4{\cdot}5H_2O$] (99%) in acetic acid solution. The molar ratio of $Bi(NO_3)_3{\cdot}5H_2O$, $NaNO_3$ and KNO_3 was 1:0.85:0.15. At the same time, the tetrabutyl titanate was dissolved in 2-methoxyethanol [$CH_3OCH_2CH_2OH$] solution. And then, a stoichiometric amount of tetrabutyl titanate solution was added to above solution. The molar ratio of zirconium nitrate to tetrabutyl titanate is 3:97. After that, the acetylacetone [$CH_3COCH_2COCH_3$] (99%) was added to prevent the reactant hydrolysis caused by the moisture in the air. The obtained solution was stirred constantly about 24 h until a transparent and stable light yellow precursor solution was obtained. The precursor solution was first dried at 250 °C for 300 s and then pyrolyzed at 480 °C for 300 s and finally annealed at 700 °C for 3 h to obtain yellow powder. The yellow powder was washed with deionized water and ethanol successively and then dried at 60 °C in air for 24 h.

2.2. Characterization

The crystalline structure of BNKTZ materials was assessed by X-ray diffraction (XRD) using a Bruker D8 Advanced with Cu Kα radiation at 1.5418 Å. Field-emission scanning electron microscopy (FE-SEM) images were performed on a Carl Zeiss LEO1525 microscope with an accelerating voltage of 20 kV. Compositions of the BNKTZ microspheres were verified by energy dispersive X-ray spectroscopy (SEM S3500, Hitachi; 20 kV).

2.3. Humidity sensor measurements

The BNKTZ sensing materials were mixed with deionized water in a weight ratio of 4:1 to form a paste. The paste was spin-coated onto an Al_2O_3 ceramic substrate (6 mm × 3 mm, 0.5 mm in thick) with five pairs of Ag–Pd interdigitated electrodes (electrodes width: 0.15 mm) to form a film. And then, the film was dried in air at 60 °C for 5 h. The properties of BNKTZ humidity sensor were measured by a ZL-5 model LCR analyzer. The AC voltage in the test was 1 V, and the frequency varied from 40 Hz to 100 kHz. The humidity environments were achieved with supersaturation aqueous solutions of LiCl, $MgCl_2$, $Mg(NO_3)_2$, NaCl, KCl and KNO_3 in a closed glass vessel, which corresponded to 11%, 33%, 54%, 75%, 85% and 95% RH, respectively [18]. There was a standard humidity probe (Model 6517-RH Humidity probe, Keithley Instruments, USA) in our system to monitor the RH value in the glass vessel. The saturated salts solution atmosphere in the chamber was tested until equilibrium (about 10 h), which ensured the humidity environment of closed glass vessels accurate [19]. The response time and recovery time are defined as the time taken by a sensor to achieve 90% of the total impedance change in the case of adsorption and desorption [20]. The hysteresis was measured by switching the humidity sensor between the chambers of 11%, 33%, 54%, 75%, 85% and 95% RH, and then transferring back. The humidity of the laboratory atmosphere was maintained at 25% RH by using an automatic drier. Temperature is an important factor for estimating humidity sensing properties. However, in our experiment, all sensors without any heating device were tested in our experiment, and the controlled humidity environments were achieved using saturated aqueous solutions of different salts, which will be affected by the changed of the atmosphere temperature. So, all of these measurements were performed at 25 °C.

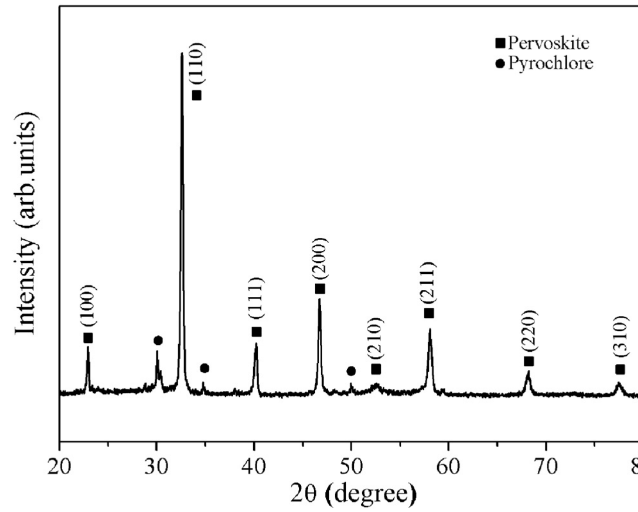

Fig. 1. XRD patterns of BNKTZ microspheres.

3. Results and discussion

3.1. Characterization of samples

The crystalline structure of BNKTZ was characterized by XRD. As shown in Fig. 1, the product is polycrystalline structure and contains the main of perovskite phase and trace amount of pyrochlore phase. The diffraction peak of perovskite phase can be indexed as $Bi_{0.5}Na_{0.5}TiO_3$, which is consistent with the reported data (JCPDS, 46-0001). The small amount of pyrochlore phase can be assigned to $Bi_2Ti_2O_7$ (JCPDS, 32-0118) [21,22]. In addition, the intensity of pyrochlore phase is very weak and low, which means that the influence of the phase is negligible [12,15]. Comparing with the XRD of A site substituted materials [15], the diffraction peak of perovskite phase is sharper and narrower, which indicate that the introduction of a small quantity of Zr^{4+} in the preparation has a great influence on the crystalline size.

The morphology of BNKTZ at low or high magnifications was characterized by FE-SEM. As shown in Fig. 2, it is obvious that BNKTZ is homogeneous spherical microstructure with the diameters in the range of 1.5–4.5 μm. In our previous research [15], the diameter range of A-site substituted BNKT was only 0.5–2 μm, which means that the particle size of BNKTZ becomes large after the Zr substitution. Furthermore, the high dense pores between the homogeneous spherical microstructures and little fragments attach on the microspheres are observed. Moreover, in Fig. 2(b), each homogeneous spherical microstructure is consisted of a large amount of nanocrystals with the size of 50–100 nm and a bottleneck shape connection is found between those homogeneous spherical microstructures. Therefore, the unique structure might be beneficial for the adsorption and desorption process of water molecules and help to improve the humidity sensing properties [15,23].

EDS was used to characterize the composition of BNKTZ microspheres. As shown in Fig. 3, BNKTZ microspheres contain the following elements: Bi (10.89%), Na (8.69%), K (1.33%), Ti (22.75%), Zr (0.71%) and O (55.63%). The appearance of Na, K and Zr peaks confirms that the Na, K and Zr atoms were successfully substituted in $BiTiO_3$. The ratio of Zr/Ti and Bi/Na/K is about 2.84:91 and 109:87:13. The ratio of Zr/Ti is almost the same with the experimental design, but the ratio of Bi/Na/K is a little inconsistence. The phenomenon is attributed to the pyrochlore phase which is formed