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Humidity sensing properties of bismuth phosphates

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ABSTRACT

Cubic sillenite-type and monoclinic bismuth phosphates were synthesized via hydrothermal methods. Structure and morphology of cubic $Bi_{13.1}PO_{\delta}$ and monoclinic $BiPO_4$ were characterized with a variety of analytical methods including powder X-ray diffraction, electron microscopy methods and surface area measurements. The humidity sensing properties of both bismuth phosphate types were investigated with respect to their capacitance characteristics. Sillenite-type cubic bismuth phosphate exhibits better response behavior than monoclinic $BiPO_4$. Cubic bismuth phosphate displays a capacitance change of up to 4 orders of magnitude over a relative humidity (RH) range from 11% to 95% together with a linear adsorption/desorption relationship. This promising humidity sensing behavior is related to the presence of a framework structure containing polarizable Bi^{3+} cations in combination with moderate phosphate doping.

1. Introduction

Humidity sensors are essential monitoring devices for process control in environmental, industrial and daily life applications [1,2]. Over the past decades, different material types have been investigated for relative humidity sensors, such as polymers, semiconductors and ceramics [3]. LiCl as a key solid electrolyte keeps attracting interest for sensor fabrication [4], but its instability in high humidity environments remains challenging [5]. Oxide materials offer the advantages of high chemical stability and humidity resistance so that they have been in the main focus of humidity sensor research with ZnO [6], SnO_2 [7], WO_3 [8], CuO [9] and ZrO_2 [10] as recent selected examples. Nevertheless, many oxide humidity sensors still have to be protected against surface contamination through hydrophilic organic layers or against etching processes induced by corrosive atmospheres [11].

This leaves room for the exploration of other easily accessible and low-cost humidity sensor materials types, such as phosphates. To the best of our knowledge, their sensing properties have not been studied beyond selected investigations into zirconium [12], boron [13], antimony [14] and glass-ceramic lithium titanate [15] phosphate sensors. Only recently photoluminescent Li_3PO_4 nanospheres have been applied for the construction of optical humidity sensors [16]. Bismuth phosphate is an exceptionally interesting new photocatalyst for the decomposition of organic dyes [17,18] and it has long been known as a valuable analytical reagent [19], photoluminescent host material [20] and catalyst [21]. However, it has never been used for humidity sensing and the only sensor application of bismuth phosphate hitherto has been reported for QCM-based gravimetric orthophosphate detection [22]. Bismuth phosphate occurs in several modifications [23] with monoclinic monazite-type $BiPO_4$ containing Bi-linked PO_4^{3-} tetrahedra as the most stable modification which undergoes a transformation into high-temperature monoclinic $BiPO_4$. $BiPO_4{\cdot}0.67H_2O$ with a related structural motif is irreversibly transformed into the monoclinic phase at room temperature [23]. A new type of hexagonal $BiPO_4$ nanorods has recently been obtained from electrochemical anodization of bismuth [24] and via sonochemical methods [25].

Cubic bismuth phosphate has mostly been accessed with solid state reactions in the $Bi_2O_3/BiPO_4$ system [26,27], and it displays a characteristic sillenite-type tunnel structure with PO_4^{3-} tetrahedra incorporated into the channels of a Bi/O-framework. This renders the Bi/P-ratio variable so that values between 13:1 and 16:1 have been obtained with solid state approaches [28]. The sillenite family encompasses a variety of compounds having the general formula $Bi_{12}(Bi_{4/5-nx}M_{5x}^{n+})O_{19.2+nx}$ ($M = M^{2+}$, M^{3+}, M^{4+} and M^{5+} (only V, As and P)) in common [29]. This renders sillenite-type cubic

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γ-Bi_2O_3 the binary structural analogue of cubic bismuth phosphate. Humidity sensing properties of γ-Bi_2O_3 have only once been investigated on films for smoke sensors that were annealed at ≥720 °C in order to exclude cross-sensitivity, and essential sensing effects were noticed at high relative humidity values (≥80%) [30]. Instead, bismuth oxides have more intensely been studied for NO detection [31] and as selective CO sensors in combination with tin oxide [32].

As bismuth oxide-based compounds in general are an excellent source for (photo)catalysts, we have studied the morphology, hydrothermal formation mechanisms and application-oriented properties of photocatalytically active bismuth vanadates, tungstates and molybdates over the past years [33]. Recently, we have furthermore demonstrated that films of *Aurivillius* type Bi_2MoO_6 (M = W, Mo) compounds display good humidity sensing properties [34]. Along these lines, we have also identified $Bi_6S_2O_{15}$ nanowires as a novel type of mixed-anionic humidity sensors [35]. In the following, we newly investigate the humidity sensing properties of bismuth phosphate as a flexible, low-cost and robust material. Cubic sillenite-type and monoclinic bismuth phosphate samples were hydrothermally synthesized and analytically characterized with special emphasis on structure, thermal stability and particle morphology. Both bismuth phosphates are compared with respect to capacitance characteristics, response behavior and response/recovery time. Sillenite-type cubic bismuth phosphate emerges as a promising candidate for humidity sensors.

2. Experimental

2.1. Synthesis of monoclinic bismuth phosphate

Ninety-seven milligram (0.2 mmol) $Bi(NO_3)_3{\cdot}5H_2O$ and 26.3 mg (0.2 mmol) $(NH_4)_2HPO_4$ were mixed with 10 mL DI water and stirred in a 15 mL Teflon liner at room temperature until a homogeneous mixture was obtained. The Teflon liner was transferred into a stainless steel autoclave and heated at 220 °C for 24 h. The product was filtered off and washed subsequently with DI water, ethanol and acetone, followed by drying in air at 80 °C.

2.2. Synthesis of cubic bismuth phosphate

Five-hundred milligram Bi_2O_3 and 700 mg K_3PO_4 were dispersed in 10 mL DI water by stirring in a 15 mL Teflon liner that was subsequently transferred into a stainless steel autoclave. The mixture was maintained under constant magnetic stirring at 120 °C for 24 h, followed by cooling to room temperature. The product was collected by centrifugation, repeatedly washed with water and air-dried at 80 °C [36].

2.3. Characterization

Products were characterized by powder X-ray diffraction (XRD) on a STOE STADI P diffractometer in transmission mode (flat sample holders, Ge monochromator and Cu $K_{\alpha1}$ radiation) operated at 40 kV and 40 mA. Scanning electron microscopy (SEM) analyses were conducted on a LEO 1530 (FEG) microscope (2 keV) with samples dispersed in ethanol and subsequently deposited on a silicon wafer. Brunauer–Emmett–Teller (BET) surface area measurements were performed on a Quantachrome Quadrasorb SI in N_2-adsorption mode. Samples were degassed at 150 °C for >3 h in vacuo prior to nitrogen adsorption measurements. High resolution transmission electron microscopy (HRTEM) was performed on a Tecnai F 30 ST (FEG, 300 kV, SuperTwin lens). Wettability measurements on static contact angle were performed with the Contact Angle System "Krüss DSA 100" and included DSA-1 software. Static contact angles were determined by the sessile drop method.

2.4. Humidity sensor fabrication

Humidity sensors were prepared as described in our previous work on bismuth tungstate and molybdate sensors [34]. Au interdigital electrodes were fabricated on a quartz substrate with finger distances set to 200 μm. 200 mg of bismuth phosphate and 0.2 mL terpinol with 5 wt% ethylcellulose were mixed with 0.04 mL acetylacetone into a homogeneous paste that was transferred onto the electrode using the "Doctor Blade" method [36]. The electrode was annealed in air for 10 min at 150 °C and the organic compounds were removed through heating for 10 min at 350 °C, followed by 30 min at 500 °C. A film with a thickness of 10 μm was obtained after cooling to room temperature.

2.5. Humidity sensing measurements

Humidity sensing measurements were performed on a TH 2617 LCR analyzer (Changzhou, China). The applied AC voltage was 1 V and the frequency was varied from 100 Hz to 100 kHz. Humidity environments were simulated by using supersaturated aqueous solutions of different salts (LiCl, $MgCl_2$, $Mg(NO_3)_2$, NaCl, KCl, and KNO_3) in a closed glass vessel, corresponding to relative humidity values of 11%, 33%, 55%, 75%, 85%, and 95%, according to standard protocols [37]. All measurements were carried out at ca. 28 °C.

3. Results and discussion

3.1. Structure and morphology of bismuth phosphate samples

Powder X-ray diffraction (PXRD) patterns of as-synthesized and thermally treated samples are compared in Fig. 1.

The lattice parameters of sillenite-type cubic bismuth phosphate (a = 10.1773(2) Å) and of monoclinic bismuth phosphate (a = 6.4717(3) Å, b = 6.9385(3) Å, c = 6.7497(3) Å, β = 103.696°) agree with literature data for cubic $Bi_{12}P_{0.86}O_{20.14}$ (PDF 44-0199, S.G. *I23*, a = 10.1761(4) Å) and monoclinic $BiPO_4$ (PDF 080-0209, S.G. $P2_1/n$, a = 6.4882(8) Å, b = 6.9516(1) Å, c = 6.7621(1) Å, β = 103.736(1)°).

Phase purity of both compounds is maintained after heat treatment for 1 h at 500 °C, and the lattice constants change only slightly to a = 10.1598(2) Å for cubic bismuth phosphate and to a = 6.4782(3) Å, b = 6.9418(3) Å, c = 6.7563(3) Å, β = 103.702(4)° for monoclinic bismuth phosphate, respectively. Elemental analyses of as-synthesized and calcined cubic sillenite-type samples revealed Bi:P ratios around 13.1:1, i.e. the obtained $Bi_{13.1}PO_\delta$ is at the lower limit of Bi:P ratios reported for Bi_xPO_δ ($13 \le x \le 16$; $\delta \sim 17$–20) compounds obtained from solid state methods [26]. Note that a precise determination of the oxygen content was not possible due to typical analytical problems with the present element combination. The structural motifs of both compounds are compared in Fig. 2. Cubic bismuth phosphate (Fig. 2a) is a member of the $Bi_{12}MO_{20}$ (M = Bi, P, Fe, Zn, V) sillenite family. Depending on the host atom incorporated into the channels of the structure, sillenites allow for manifold defect types, such as cation and oxygen vacancies or excess oxygen, respectively [26]. The presence of Bi(V) in cubic sillenite-type γ-Bi_2O_3 has been controversially discussed, but has never been experimentally verified. Instead, a structural model based on the interplay of oxygen deficiency and compensating lone pairs of Bi^{3+} was proposed [29]. Low-temperature monoclinic $BiPO_4$ (Fig. 2b) displays an entirely different monazite-type structure with layers of PO_4 tetrahedra linked by Bi atoms with interlayer contacts via longer Bi—O bonds [23].

SEM images illustrate that the cubic bismuth phosphate structure is morphologically reflected in the formation of regular particles with dimensions between 3 and 9 μm (Fig. 3a), whereas monoclinic bismuth phosphate forms smaller particles with