



Hydrothermal synthesis of bismuth niobates and their application in azo-dyes photo-discoloration



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ABSTRACT

Bismuth niobates were obtained by hydrothermal synthesis using bismuth (III) nitrate pentahydrate [Bi(NO₃)₃·5H₂O] and a Lindqvist potassium hexaniobate [K_{8-x}H_xNb₆O₁₉·nH₂O] as soluble precursors. Pure crystalline Bi₅Nb₃O₁₅, β-BiNbO₄ and α-BiNbO₄ were obtained as pure phases through co-precipitation at pH = 8, followed by hydrothermal treatment and calcination at 600, 700 or 800 °C, respectively, which are milder temperatures than those used in solid state, citrate sol-gel and ball milling methods. Band gap energies of α-BiNbO₄ and β-BiNbO₄ were estimated by UV–vis diffuse reflectance spectroscopy (DRS) as 3.2–3.4 eV, which are higher than experimental values reported in the literature. The materials were evaluated in the methyl orange azo-dye photo-discoloration under UV irradiation and complete bleach was attained. The triclinic phase presented a better efficiency as a photocatalyst than the orthorhombic phase. Unexpectedly, the mixture of both phases resulted in the highest photocatalytic efficiency, similar to that found for Degussa P25 commercial catalyst.

1. Introduction

The bismuth niobates (BiNbO₄) are known as strategic materials in advance technology studies due to their luminescence efficiency, ferroelectric, dielectric and optoelectronic properties [1,2]. They have been investigated for its use as photocatalysts, since BiNbO₄ presents a high efficiency as a semiconductor in reactions involving photon absorption, such as in the water splitting to produce hydrogen [3–9] and in the photocatalytic decontamination of domestic or industrial effluents [10–12]. Several studies indicate that the main reason of BiNbO₄ high efficiency on photodegradation under UV–vis light is the contribution of bismuth 6s orbitals to the valence band formation results in the narrowing of its band gap [13].

The BiNbO₄ has two main crystalline structures, the orthorhombic phase (α-BiNbO₄) and the triclinic phase (β-BiNbO₄), these polymorph present different electronic band structures and, consequently, different properties. The orthorhombic phase usually results in a higher activity than triclinic ones [5].

The triclinic phase band gap energy (E_g) is slightly higher than the orthorhombic one, but it depends on the synthesis method. The

orthorhombic phase presents a band gap energy (E_g) varying from 2.6 to 2.8 eV, when synthesized by conventional solid state method [10,5], and 2.56 eV, when synthesized by the citrate method [14]. The triclinic phase shows an E_g ~ 3.4 eV for a sample prepared by the solid state method. For the citrate method, that produces a triclinic phase stable at low temperatures, also known as “low β”, different results were reported in the literature. Zhai et al. [14] measured an E_g value of 2.79 eV, Ullah et al. [15] reported a value of 2.93 eV, and finally Wang et al. [16] estimated an absorption edge of 370 nm, which results in a band gap energy of 3.35 eV. These differences might be accounted to their synthesis method and particle size.

There are several methods of preparing BiNbO₄, being the conventional solid state method the most used one. Bismuth and niobium oxides are mixed and calcined. From 900 °C to nearly 1020 °C the orthorhombic phase can be obtained, however, at temperatures above 1040 °C the triclinic is more stable [10, 17–20]. In addition to the high synthesizing temperature, this method causes several problems to photocatalysis such as large grain growth, segregation of components and loss of stoichiometry due to the volatilization of bismuth at high temperature.

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High-energy ball-milling (HEM) has been studied as an alternative treatment to mitigate the synthesizing conditions of solid-state reactions [20]. HEM main advantage is to provide activation through mechanical energy instead of heating energy [1, 20]. Pure orthorhombic phase was reported to be obtained at 700 °C [20]. However, no reports on obtaining the triclinic phase have been published.

Another promising methods are citrate and Pechini methods. The difference between these two methods is the introduction of a polyhydroxy alcohol, such as ethylene glycol, followed by the polymerization process between metal citrates and the polyhydroxy alcohol, resulting in immobilization of metal complexes in a rigid organic framework, thus ensuring the compositional homogeneity [21]. The homogeneous dispersion of the citrate sol-gel precursors resulted in a reduction of synthesizing temperatures. Initially β -BiNbO₄ is obtained at 600 °C, from 700 to 900 °C β phase coexist with α one. A nearly pure orthorhombic phase can be obtained from 900 to 1020 °C [2; 17–19]. At approximately 1040 °C the triclinic phase is formed once again [22, 23]. Although this method obtained the triclinic phase at a milder temperature, no pure phases were observed and the polymeric precursors used are more expensive than the precursors of solid state reaction method.

In the co-precipitation method bismuth and niobium precursors are co-precipitated and calcined. It was reported that α -BiNbO₄ could be obtained at lower temperatures than the solid state reaction method [24–26]. However, this experimental procedure was reproduced by the present authors and the BiNbO₄ could not be obtained, but phase mixtures.

The hydrothermal synthesis method synthesizes was used to obtain amorphous powders that, after receiving calcination treatment, resulted in nanosized crystalline Bi₅Nb₃O₁₅ [27]. As far as we know, no reports on obtaining α - or β -BiNbO₄ by hydrothermal synthesis have been published.

The aim of the present work was to study the synthesis conditions to obtain both α - and β -BiNbO₄. Soluble precursors were used to obtain 1:1 stoichiometric proportion. The pH was chosen in order to achieve precipitation of both precursors. The photocatalytic properties were assessed by using the photo-discoloration of azo-dye methyl orange (MO) as a model reaction.

2. Experimental

2.1. Hydrothermal synthesis

In order to obtain the bismuth niobates, 3.3 g of Bi(NO₃)₃·5H₂O (VETEC PA) was dissolved in 20 mL of distilled water, acidified by adding 8 mL of nitric acid (HNO₃ 65%, Merck) and stirred until complete homogenization. Then, a solution prepared by dissolving 1.47 g of a Lindqvist niobate (K_{8-x}H_xNb₆O₁₉·nH₂O) in 20 mL of distilled water was added dropwise, under stirring.

The precursors solubility has been reported to be strongly influenced by pH [24; 25], so a rigorous pH control is fundamental to warrant the incorporation of both Bi³⁺ and Nb⁵⁺. While the niobium precursors (K_{8-x}H_xNb₆O₁₉·nH₂O) are soluble in basic medium and precipitates on pH below approximately 9.0, the bismuth precursor, Bi(NO₃)₃·5H₂O, is soluble in acid medium and significantly precipitates on pH above nearly 7.0 at room temperature and ambient pressure. Thus, three values of pH were chosen to perform the essays: 7.0, 8.0 and 9.0.

After the suspension preparation, it was transferred to a PTFE-lined steel autoclave and submitted to hydrothermal treatment at 150 °C for 24 h. After that, the solid was filtered, washed with distilled water and dried for 48 h in a desiccator containing silica gel. The solids were calcined at 600, 700 and 800 °C, for 6 h.

2.2. Characterization

The X-ray diffraction patterns (XRD) of the materials were collected using a Shimadzu XRD-6000 diffractometer, which operates with a CuK α radiation at 40 kV, 30 mA and graphite monochromator in the region from 1.4 to 50° 2 θ at a scanning speed of 2° min⁻¹. The results were compared with patterns found at the ICSD collection.

The values of the crystalline diameters were estimated using the Scherrer's Eq. (1).

$$D = \frac{0,89\lambda}{B \cos\theta} \quad (1)$$

In which D is the crystallite diameter, λ is the wavelength of X-rays, B is the half width and θ is the Bragg angle to the diffraction peak obtained with the (hkl) plane.

The FTIR spectra were collected with KBr pellets (1 wt.%) using a Shimadzu IR Affinity-1 spectrometer, between 4000 and 400 cm⁻¹, with a resolution of 2 cm⁻¹ and 20 scans.

The UV-vis spectra were collected using a Thermo Scientific Evolution 600 spectrophotometer on diffuse reflectance mode, at the wavelength range from 200 to 900 nm, using BaSO₄ as reference. The band gap energy values were determined by both the geometrical and the 1 st. derivative methods.

The morphological characterization of the samples were studied using scanning electron microscopy (SEM), transmission electron microscopy (TEM) and the specific surface area was measured by a Brunauer–Emmett–Teller (BET) method. The equipment used to obtain the SEM micrographs was the Hitachi S-3400N microscope and the mapping surface results were obtained using a Bruker EDS probe QUANTAX 200. TEM images were collected on a Zeiss EM109 microscope. The BET method apparatus was the Micromeritics ASAP2020 using N₂ adsorption/desorption method.

2.3. Photocatalytic tests

The study of the photocatalytic activity of bismuth niobates was performed by photo-discoloration reaction of the methyl orange (CI # 13025, Acid Orange 52) in aqueous solution (40 mg L⁻¹). The commercial Degussa P25 photocatalyst was used as a standard and the reaction parameters were first optimized with this catalyst.

The solutions concentrations used on the analytical curve determination of the photo-discoloration reaction were from 1.0 to 40.0 mg L⁻¹. The azo-dye was used without the utilization of any previous purification process.

The reaction parameters were: Hg vapor lamp (Phillips), used as a source of UV radiation (λ_{max} = 365 nm and 125 W); 1 g L⁻¹ catalyst and 1 hour of prior adsorption in the dark. An air flow of 100 mL min⁻¹ was bubbled in the solution during the irradiation period to warrant the supply of molecular oxygen. A 10 mL aliquot was periodically withdrawn, centrifuged to remove the spent catalyst and then analyzed in a UV-1650 PC Shimadzu spectrophotometer, operating at 416 nm. Temperature was kept constant at 25 °C by using a thermostatic bath.

3. Results and discussion

3.1. Synthesis and characterization

All samples obtained after hydrothermal treatment resulted in white powders. After calcination, some known structures were identified by XRD analysis. The X-ray diffraction patterns of the samples obtained at pH 7, 8 and 9, after hydrothermal treatment (as-synthesized) and calcination at different temperatures, are shown in Fig. 1.

The as-synthesized samples at pH 7, 8 and 9 have shown XRD patterns of typical amorphous materials (Fig. 1). The XRD pattern of the sample prepared at pH 7 after calcination at 600 °C is compatible with Bi₅Nb₃O₁₅ phase (ICSD#245707) [28]. When calcined at 700 °C the β -

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