



Structural study, photoluminescence, and photocatalytic activity of semiconducting BaZrO₃:Bi nanocrystals

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ABSTRACT

Wide band gap nanocrystalline bismuth doped barium zirconate is synthesized by a facile hydrothermal method at 100 °C. The obtained cubic perovskites are characterized by powder X-ray diffraction (XRD), UV–VIS diffuse reflectance spectroscopy, photoluminescence (PL) spectroscopy, and photocatalytic activity. The estimated band gap in the 2.4–4.9 eV range, depending on Bi concentration, suggests nanocrystalline BaZrO₃:Bi as a useful visible-light activated photocatalyst under excitation wavelengths <800 nm. Displacement of main XRD pattern peaks suggest that bismuth ion mostly substitutes into Zr⁴⁺ sites within the BaZrO₃ host lattice. It is found that BaZrO₃:Bi decomposes methylene blue (MB) under both UV and visible light irradiation. The photocatalyst efficiency depends strongly on Bi content and induced defects.

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1. Introduction

The increasing necessity of a stable and durable green photocatalyst has been the motivation of many investigations on different materials. In particular, perovskites oxides have attracted attention for their chemical stability. Among transition metal oxide perovskites barium zirconate (BaZrO₃, BZO) has been intensively studied. As a result of intensive research on this ceramic, diverse properties of BZO are now known, like: high melting point (~2600 °C), ideal cubic structure, small coefficient of thermal expansion and poor thermal conductivity [1]. In addition, among the cubic oxide perovskites, BZO is the only one who remains cubic in the range from 1600 K down to 4 K [2]. As concluded by Moreira et al., particle size, shape and composition are important parameters of the material to control via the synthesis method. They found that photoluminescence (PL) emission of BZO depend not only on the size but also in the shape of the synthesized powder. PL measurements and first principles calculations have been conducted in order to understand the origin of BZO intrinsic emission. Such emission is being related to structural disorder in the constituent polyhedrons of BZO system, the octahedral ZrO₆ site and the dodecahedral BaO₁₂ site [3]. Narrow band gap energies

and the presence of intermediary energy levels in disordered BZO powders have been associated to oxygen vacancies (V_O) in structural disordered ZrO₆/ZrO₅ clusters [4]. Thus, the origin of the PL emission in BZO is related to electron–hole recombination as well as the relaxation and trapping processes at intermediary band gap energy levels [4]. It has been reported that the bond angle between metal–oxygen–metal (M–O–M) is a critical parameter in perovskites systems like ATaO₃ (A=Li, Na and K), Sr₂Nb₂O₇ and Sr₂Ta₂O₇. It has been found that as the bond angle approximates to 180°, the easier the excitation energy is delocalized, and the photocatalytic activity is favored [5,6]. Yuan et al. studied BZO as water splitting photocatalyst for the first time [7]. They were able to split distilled water over pure BZO under UV-light irradiation. Experimental results showed that BZO valence and conduction bands are dominated by O 2p and Zr 4d orbitals, respectively. They concluded that production of O₂ and H₂ gasses after water splitting photocatalysis on BZO under UV-light was due to the intrinsic structural properties of cubic BZO perovskite, such as: a 180° Zr–O–Zr bond angle, largely dispersed conduction band, and highly negative potential photoinduced electrons. The above mentioned properties make BZO an attractive system to be used as a photocatalyst. In addition the good diffusion of defect-generated photocarriers (electron–hole pairs) to the BZO nanocrystals surface promotes better photocatalytic reactions [7]. Visible light-active photocatalyst are now subject of investigation in order to develop new materials with a more efficient use of natural sunlight. Incorporation of Sn⁴⁺

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in BZO has proved to shift the water splitting photocatalytic activation spectra of BZO toward visible light ranges up to 600 nm [8]. Sn⁴⁺ incorporation into the Zr⁴⁺ octahedral sites promotes reduction of the band gap of BZO as a consequence of the contribution the Sn 5s orbitals to the conduction band of the BZO [8]. The notable impact of Sn⁴⁺ incorporation to BZO optical and photocatalytic properties is attributed to the increased electronegativity of the Sn⁴⁺ as compared to the Zr⁴⁺ ion [8]. Photocatalytic activity of β -Bi₂O₃ under visible light has been studied by Wang et al. Their results showed better stability of β -Bi₂O₃ during photocatalytic degradation of dye molecules when doped with titanium. They concluded this improvement was due to titanium stabilized the host crystal lattice. Titanium incorporation into the system avoid the phase transition of β -Bi₂O₃ during photocatalytic reaction. Suggestions made by this group are that upon doping β -Bi₂O₃ with different rare earths or transition metals, phase stabilization could be achieved and visible-light photocatalytic activity improved [9]. BaBiO₃ is another bismuth based compound with good photocatalytic activity under visible light. Tang et al. succeeded on creating a BaBiO₃ compound with a 2.05 eV band gap. Such a narrow band gap, along with high contribution of Bi 6s orbitals to the valance and conduction bands, allowed high mobility of photocarriers, and consequently efficient decompose of organic contaminants [10]. Thus, in the search for better visible light activated photocatalyst, we propose cubic nanocrystalline bismuth doped barium zirconate (BaZrO₃:Bi) perovskite as a good candidate. In this work the structural, morphological, photoluminescent properties, and photocatalytic activity of such system are investigated. Decomposition of methylene blue solutions under UV and sunlight irradiation was done at different concentrations of bismuth ion.

2. Experimental

2.1. Synthesis

Pure BZO and bismuth doped BaZrO₃:Bi samples were prepared by a facile hydrothermal process [2]. As synthesized Bi concentrations were 0.01 mol%, 0.1 mol%, 0.5 mol%, 1 mol%, 5 mol% and 10 mol% of Bi₂O₃. Precursor materials: barium nitrate (99%), zirconyl chloride (99%) and bismuth nitrate (98%) were analytical grade and were used without further purification. In a typical procedure, the precursor materials were dissolved in a 200 ml solution with equal volume of water and ethanol, stirred for 30 min at room temperature (RT) in a glass autoclave of 250 ml capacity. CTAB (98%) was used as dispersant agent at a molar concentration of 11 mM. The precipitant agent (NaOH) was added to the solution and continued under strong stirring for 1 h. After this, the solution was sonicated for 30 min and placed into a sealed glass autoclave. The solution was heated at 100 °C inside a furnace for 24 h for the hydrothermal reaction to happen. After cooled down to RT, the solution was washed several times to eliminate the precipitate and dried overnight at 100 °C. Finally, all samples were annealed at 1000 °C for 3 h in air atmosphere.

2.2. Characterization

The X-ray diffraction patterns of annealed samples were measured in a θ - θ Bruker D-8 Advance diffractometer having the Bragg-Brentano geometry, Cu K α radiation, a Ni 0.5% Cu-K β filter in the secondary beam and a one-dimensional position sensitive silicon strip detector (Bruker, Lynxeye). Diffraction intensity as a function of the angle 2θ was measured between 20° and 110° with a 2θ of 0.01946° and a counting time of 53 s per point. Barium Zirconium oxide crystalline structure was refined via the Rietveld method using the Fullprof code [11] under the space group

Table 1

Relative atoms positions of BZO, space group $Pm\bar{3}m$ and of ZrO₂ space group $P21/c$.

Atom	x	y	z
Ba	0.0	0.0	0.0
Zr	0.5	0.5	0.5
O	0.0	0.0	0.0
Zr	-0.256(1)	0.486(2)	0.152(1)
O	0.485(5)	0.708(4)	0.433(4)
O	-0.184(2)	0.449(3)	0.367(2)

$Pm\bar{3}m$, and zirconium dioxide was refined under the space group $P21/c$. The used atom positions are shown in Table 1. Crystalline morphology was modeled by using spherical harmonics as base functions [12], while the background was modeled with a polynomial function that, in addition to the constant, linear, quadratic, and cubic terms in 2θ , also contained the terms $(1/2\theta)$ and $(1/2\theta)^2$. Transmission electron microscopy (TEM) was performed in a JEM-2200FS microscope with an accelerating voltage of 200 kV. The microscope is equipped with a Schottky-type field emission gun, and an ultra high resolution configuration (Cs = 0.5 mm; Cc = 1.1 mm; point-to-point resolution = 0.19 nm). Local chemical analysis was performed in a Noran instrument attached to the microscope using the energy dispersive X-ray spectroscopy (EDXS) technique. The optical absorption spectra were obtained with a Perkin-Elmer UV-VIS-NIR Lambda 900 spectrophotometer in diffuse reflectance mode using a 1.5 in integrating sphere (Labsphere Co.). Photoluminescence characterization measurements were performed on an Acton Research modular 2300 spectrofluorometer. The excitation source is a 75 W Xenon lamp. The fluorescent emission from the sample was focused onto a SP-500i spectrograph (Acton Research) and detected by a photo multiplier tube R955 (Hamamatsu) connected to an Acton Research SpectraHUB and a PC that collected all data. All photoluminescence measurements were done at room temperature. Low band pass filters (cut off at 350 and 400 nm) were placed before the monochromator to prevent spurious excitation and its harmonics to reach the detector.

2.3. Photocatalytic activity

Photocatalytic activity of bismuth doped BZO samples was studied by measuring methylene blue (MB) degradation in a 46 μ M solution under UV-light and solar irradiation. The reaction was done in a home made reactor with three 4 W UV-light lamps, disposed in a circular configuration. The lamps emission is centered at 366 nm with a FWHM of 16 nm. 25 mg of milled pure BZO, or BaZrO₃:Bi(x%), x = 0.1 mol%, 1 mol%, and 10 mol%, photocatalyst powder were placed in a 20 ml of 46 μ M MB solution and vigorously stirred with a magnetic stirrer. Air cooling was used to keep reactor temperature at 30 °C. Samples of 400 μ L were extracted off at regular time intervals and centrifuged at 14,000 rpm for 5 min to precipitate the photocatalyst. The MB degradation was monitored by measuring MB absorption at the characteristic 665 nm peak of 200 μ L of the centrifuged solutions. Control photolysis of MB in absence of photocatalyst were performed simultaneously for each BZO and BZO:Bi samples. The average degradation of MB was 3.5% after 10 h irradiation with the three 4 W UV lamps and the reactor set at 30 °C. In order to estimate the MB degradation under natural solar-light irradiation, the magnetic stirrer and solutions were place outdoors for 6 h under direct sunlight in a sunny day (9 am to 15 pm). The process followed to measure the photocatalytic activity of BaZrO₃:Bi powders under sunlight was the same as explained above.

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