



## Characterization and photocatalytic properties of Ba doped $\text{Bi}_{12}\text{TiO}_{20}$

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### Abstract

Doping of  $\text{Bi}_{12}\text{TiO}_{20}$  with Ba ions was prepared by a chemical solution decomposition (CSD) method. Crystal structures of the prepared powders were confirmed by XRD and IR methods. Photocatalytic activities of the prepared samples were evaluated using methyl orange as a model organic compound. The result shows doping with 0.5 at.%  $\text{Ba}^{2+}$  can significantly increase the photoactivity of the  $\text{Bi}_{12}\text{TiO}_{20}$  crystals.

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### 1. Introduction

Recently photocatalytic methods, using semiconductors, such as  $\text{TiO}_2$ , has attracted extensive attention, because they provide a promising strategy for cleaning polluted air or water [1]. Previous studies have shown that such semiconductors can degrade most kinds of persistent organic pollutant, such as dyes, pesticide, detergents and volatile organic compounds, under UV-light irradiation [1–4]. However, the fast recombination rate of photogenerated electron/hole pairs hinder the commercialization of this technology [1,2]. It is, therefore, of interest to develop new photocatalysts with higher photocatalytic properties. In an earlier study, the author has found that  $\text{Bi}_{12}\text{TiO}_{20}$  is a new photocatalyst showing high

photocatalytic activity against methyl orange [5]. It is known that transition metal ions doped into catalysts can increase the quantum efficiency of the heterogeneous photocatalytic property by acting as electron (or hole) traps and by altering the  $e^-/h^+$  pair recombination rate [6,7]. So it is of great interest to investigate the influence of metal nanoparticle deposition on the photocatalytic property of  $\text{Bi}_{12}\text{TiO}_{20}$ .  $\text{Bi}_{12}\text{TiO}_{20}$  crystals belong to a family of sillenite compounds with the general formula  $\text{Bi}_{12}\text{MO}_{20}$  where M represents a tetravalent ion or a combination of ions, which gives an average charge of  $4^+$ . The overall structure of the  $\text{Bi}_{12}\text{TiO}_{20}$  crystal may be described in terms of the seven-oxygen coordinated Bi polyhedra, which share corners with other identical Bi polyhedra and with  $\text{TiO}_4$  tetrahedra. This body centered cubic structure of sillenite bismuth titanate facilitate the solubility of novel metal ions in the crystals, because the tetrahedron of oxygen atoms surrounding the M atoms is able to expand or contract without a major effect on

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the remaining atomic arrangement [8]. In this paper,  $\text{Ba}^{2+}$  ions were doped into  $\text{Bi}_{12}\text{TiO}_{20}$  crystals by a chemical solution decomposition (CSD) method, and the dependence of dye oxidation rate on the dopant concentration was investigated.

## 2. Experiment

The precursor materials of Ba doped bismuth titanate crystals were prepared by a chemical solution decomposition method. The dopant concentrations mentioned in this work are the nominal atomic concentration, which is based upon the assumption of quantitative incorporation of the dopant.  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ ,  $\text{Ba}(\text{NO}_3)_2$  and  $\text{Ti}(\text{OC}_4\text{H}_9)_4$  were selected as starting materials, glacial acetic acid ( $\text{CH}_3\text{COOH}$ ) was used as a solvent.  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  and the stoichiometric amount of  $\text{Ba}(\text{NO}_3)_2$  were initially dissolved in  $\text{CH}_3\text{COOH}$ , then  $\text{Ti}(\text{OC}_4\text{H}_9)_4$  was added dropwise with constant stirring. The formed solution was diluted with 2-methoxyethanol ( $\text{CH}_3\text{OCH}_2\text{OH}$ ) to adjust its viscosity and surface tension. Dust and impurities were removed by filtering through 0.2  $\mu\text{m}$  syringe filters. To keep the solution stable longer, certain amount of acetylacetone ( $\text{C}_5\text{H}_8\text{O}_2$ ) was added. After stirring for 0.5 h by using of a magnetic stirrer, the solution was dried at 100 °C to remove the solvents and some organic matters. Then the obtained powder was calcined at higher temperature for 10 min to remove other organic matters and produce crystallinity. X-ray powder diffraction patterns of the prepared samples were carried out on a Rigaku D/MAX- $\gamma$  A X-ray diffractometer using  $\text{Cu K}\alpha$  radiation. The infrared spectra were measured using KBr pellets made from a mixture of as-prepared powder. The pellet thickness varied from 0.5–0.6 mm. The IR spectra were examined from 400–4000  $\text{cm}^{-1}$  with a Nicolet-5DX FT-IR spectrometer.

Photocatalytic properties of as-prepared samples were evaluated using methyl orange as a model organic compound. The decolorization of methyl orange solution was carried out in a 150 ml Pyrex glass vessel with constant magnetic stirring. A 20 W UV lamp with a maximum emission at about 360 nm was used as the light source. Reaction suspension was prepared by adding the prepared samples into a 50 ml of aqueous methyl orange solution. Prior to irradiation, the

suspensions were ultrasonically sonicated for 10 min and then magnetically stirred in a dark condition for 10 min to establish adsorption/degradation equilibrium. The suspensions were then irradiated under the UV light. The distance between the liquid surface and the light source was about 5 cm. The light intensity was 0.936  $\text{mW}/\text{cm}^2$  measured by using an UV-Vis spectrophotometer. The concentrations of aqueous methyl orange were determined by measuring the absorbance at 464 nm with an UV-Vis spectrophotometer. The linear relationship between the absorbance at 464 nm ( $A$ ) and the concentration of methyl orange ( $C$ ) can be represented empirically by the equation:  $A = 0.0727 \times C$  [9].

## 3. Results and discussions

### 3.1. Characterization of the prepared powders

The XRD patterns of the Ba doped bismuth titanate powders calcined at different temperature and with different metal dopant concentration are as shown in Figs. 1 and 2, respectively. Fig. 1 shows the effects of calcinations temperature on the crystallization of 1 at.% Ba doped bismuth titanate. As shown in the figure, the prepared samples had been well crystallized when calcined at 400 °C for 10 min. According to Joint Committee on Powder Diffraction Standard data cards, the resulting Ba doped powders contain only sillenite phase of  $\text{Bi}_{12}(\text{Ti}_{0.99}\text{Ba}_{0.01})\text{O}_{32}$ . The sharp peaks in the XRD patterns indicate a well crystallinity of the prepared samples. With further increase of the annealing temperature up to 600 °C, XRD patterns of the prepared samples did not show any significant variation. All the XRD patterns can be readily identified and indexed using the Standard XRD data for the sillenite  $\text{Bi}_{12}\text{TiO}_{20}$ . XRD peaks of  $\text{Bi}_{12}(\text{Ti}_{0.99}\text{Ba}_{0.01})\text{O}_{20}$  become sharper and the full width at half maximum decreased indicating a better crystallinity and an increase in grain size when sintering at higher temperature. The effects of doped concentrations of Ba ions on the crystallization of bismuth titanate were also examined, as shown in Fig. 2, the dopant concentration of Ba ions have no great influence on the crystallization of sillenite bismuth titanates. As shown in the figure, all the prepared samples sintered at 600 °C for 10 min had been well crystallized and the XRD patterns did

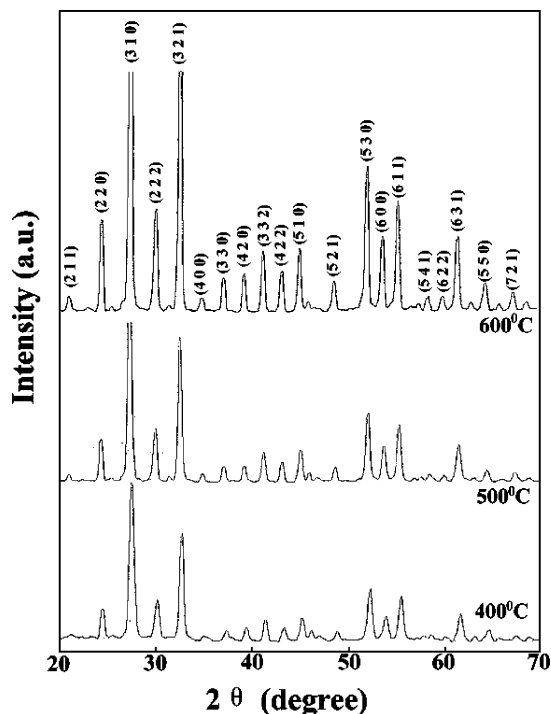


Fig. 1. XRD patterns of the prepared Ba doped bismuth titanate annealed in air from 400 to 600 °C for 10 min.

not show any significant variation with dopant concentration changed. This indicated that the Ba dopant bismuth titanate maintains a cubic structure similar to the sillenite bismuth titanate even under extensive modification by Ba ions.

It is noteworthy that in the preparation of pure sillenite  $\text{Bi}_{12}\text{TiO}_{20}$ , a metastable phase appeared during the formation of  $\text{Bi}_{12}\text{TiO}_{20}$  nanocrystals [10]. This metastable phase was found transforms gradually into the sillenite  $\text{Bi}_{12}\text{TiO}_{20}$  with the sintering temperature increases from 400 to 600 °C. The different results of Ba doped bismuth titanate crystals indicated that Ba ions doped could facilitate and stabilize the formation of sillenite bismuth titanate. Similar results was found in the study of Zn doped perovskite  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ , the author found Zn ions dopants facilitate the formation of a new phase of  $(\text{Bi}_{0.99}\text{Zn}_{0.01})_{20}\text{TiO}_{32}$ , which is thought cannot emerge at a low temperature of 400 °C, according to the conventional phase diagram of  $\text{Bi}_2\text{O}_3\text{--TiO}_2$  system [11].

The IR spectra were examined from 400–4000  $\text{cm}^{-1}$  with a FT-IR spectrometer. Fig. 3 shows the IR spec-

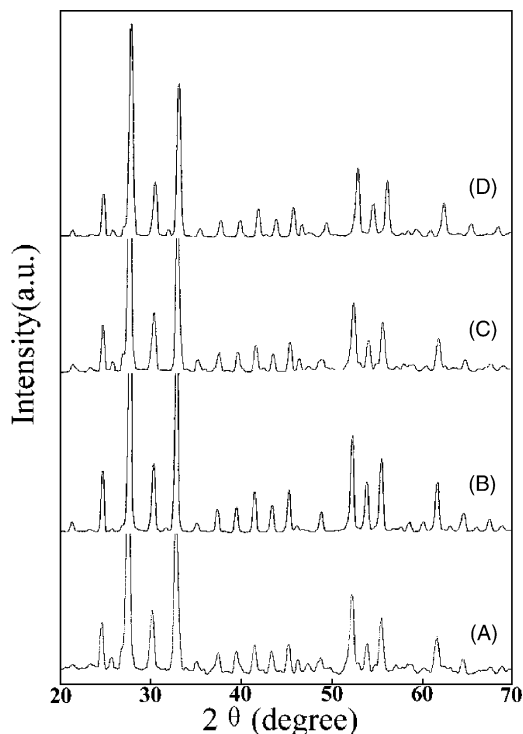


Fig. 2. XRD patterns of the prepared samples doped with different concentrations of Ba ions: (A) 0.1 at.%; (B) 1 at.%; (C) 5 at.%; (D) 10 at.%.

tra of the prepared 1 at.% Ba doped bismuth titanate with different treating temperature. Assignment of the infrared spectra of  $\text{Bi}_{12}\text{TiO}_{20}$  single crystals and nanocrystals has been reported previously [10,12,13]. The major lines associated to  $\text{Bi}_{12}\text{TiO}_{20}$  crystals that, as shown in our results in Fig. 3, is easily detected by the intense IR lines at 460, 527, 589, 665 and 819  $\text{cm}^{-1}$  and is in good agreement with previous manuscripts. The only sillenite bismuth titanate bands found in the IR spectra also suggested the Ba dopant bismuth titanate maintains a cubic structure similar to the sillenite bismuth titanate even under extensive modification by Ba ions.

### 3.2. Photocatalytic activity of the prepared samples

The UV-Vis spectra for methyl orange solution show two absorption maxima, as shown in Fig. 4, the first band observed at 270 nm and the second band at 464 nm. The band at 464 nm was used to monitor

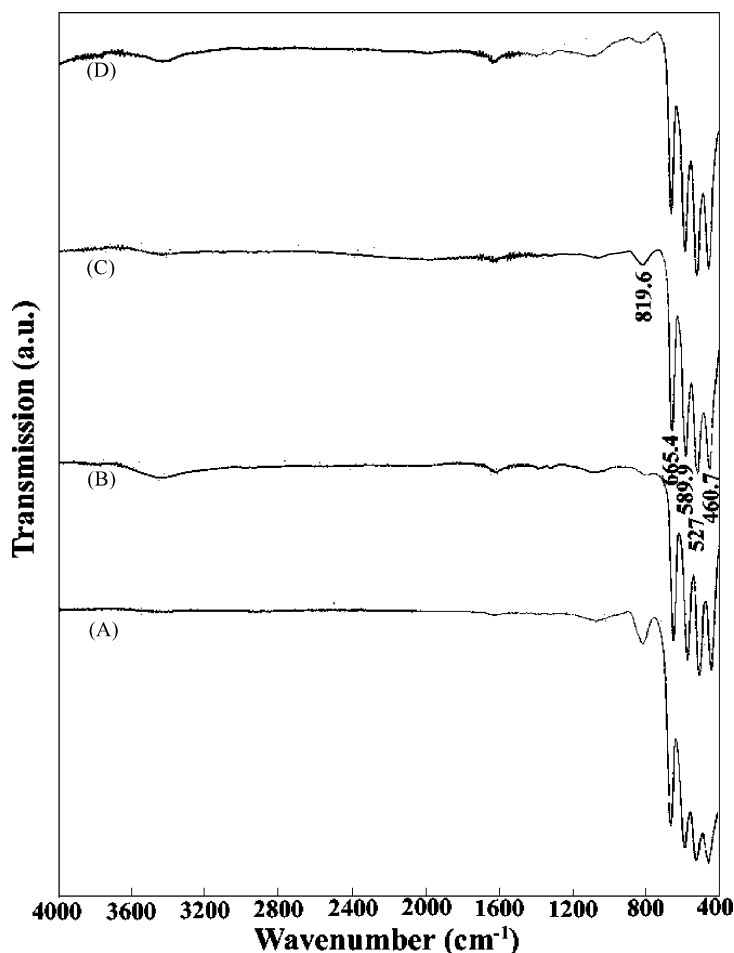


Fig. 3. Infrared spectra of Ba dopant Bi<sub>12</sub>Ti<sub>20</sub> crystals doped with different concentrations of Ba ions: (A) 0.1 at.%; (B) 1 at.%; (C) 5 at.%; (D) 10 at.%.

the effect of the photocatalysis on the degradation of methyl orange. Methyl orange can be absorbed onto catalysts from its aqueous solution. Hachem et al. [14] pointed out that the absorption was quite fast and the equilibrium concentration could be reached within about 45 min. In this paper, the absorption/degradation equilibrium of the suspensions was established by ultrasonically sonicated for 10 min and then magnetically stirred in a dark condition for 10 min. The magnetically stirred was carried out up to 6 h, no significant change in the concentration was found.

The effect of heat-treating temperature on the photocatalytic activity of Ba doped bismuth titanate was examined. It can be seen that the degradation rate of

methyl orange is decreased with the increasing annealing temperature of the prepared powders. When using the 1 at.% Ba doped catalysts calcined at 400 °C for 10 min, the decolorization process of methyl orange was found completed in 1.5 h. Wang et al. [15] found that some long-lived by-products, which have low rate constants of reactions with hydroxyl radicals, were formed after the decolorization process of methyl orange solution. Yet these long-lived by-products are generally less harmful or harmless to environment and can be further treated by biological methods [15,16]. So the photocatalysts can be applied to photocatalytically treating some persistent organic pollutants. The significant decrease in the photocatalytic activity of Ba

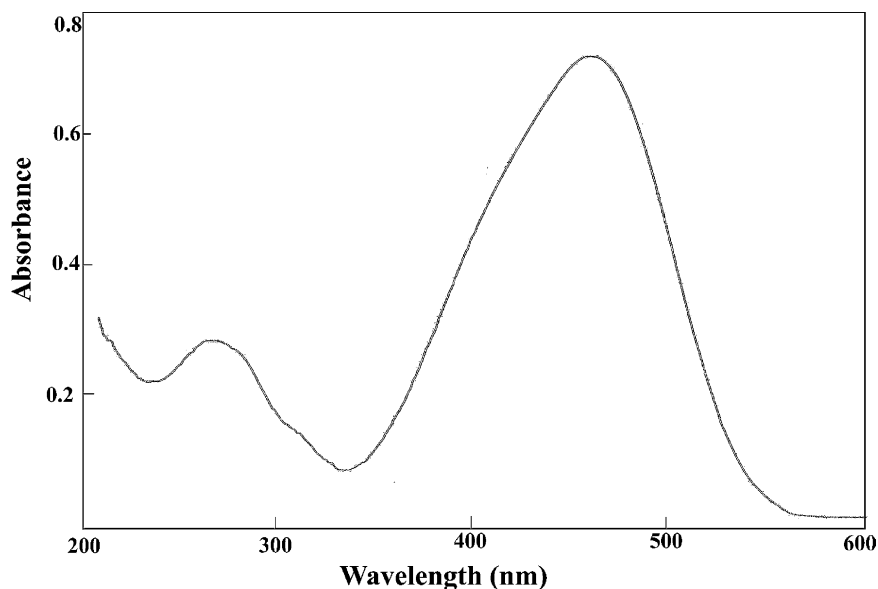


Fig. 4. The UV-Vis spectrum of methyl orange.

doped  $\text{Bi}_{12}\text{TiO}_{20}$  is probably due to the variation in particle size with the increasing calcination temperature. Because in large particles the dopants are always isolated far from the surface with a low chance of transferring trapped charge carriers to the interface and therefore the metal ions act more likely as recombination centers than as trap sites [17,18]. The decreased activity of Ba doped  $\text{Bi}_{12}\text{TiO}_{20}$  can also be attributed to the bismuth oxide that is easily volatilized at high temperatures and resulting in the formation of defects.

Fig. 5 shows the effect of the dopant concentration on the photocatalytic activity of Ba doped bismuth titanate. As shown in the figure, the dopant concentration of Ba ions in the prepared samples has a great effect upon its ability to decolorize methyl orange solution. When using the catalysts doped with 0.5 at.% Ba ions, the decolorization process can be completed in 1 h. As a comparison, pure phase of anatase  $\text{TiO}_2$  nanocrystals and  $\text{Bi}_{12}\text{TiO}_{20}$  prepared by us need 2.5 and 1.5 h, respectively, to photodegrade the methyl orange solution completely under similar conditions [5]. The photocatalytic decolorization of methyl orange solution is a pseudo-first-order reaction and its kinetics may be expressed as  $\ln(A_0/A) = kt$  [9]. The calculated apparent reaction rate constants ( $k$ ) of each catalyst from Fig. 5 are listed in Table 1. Yet as shown

in Fig. 5 and Table 1, when calcined at  $600^\circ\text{C}$  for 10 min, the 0.5 at.% Ba ions doped bismuth titanate show a highest activity and the degradation rate of methyl orange was found decreased with the increase of the dopant concentration. Metal ion dopants influence the photoreactivity of catalysts by acting as electron (or hole) traps and by altering the  $e^-/h^+$  pair recombination rate [19–21]. Although it is widely accepted that the photoreactivities of doped catalyst are

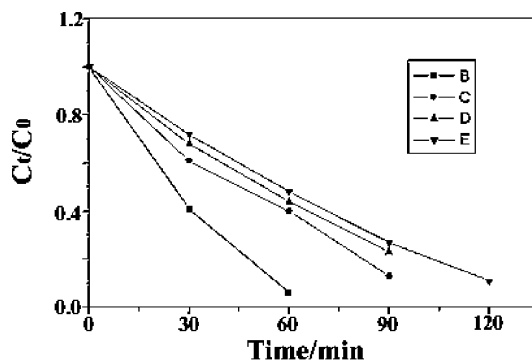


Fig. 5. The changes in concentrations of methyl orange solution at 464 nm by the prepared sample calcined at  $600^\circ\text{C}$  as a function of UV irradiation time. The dopant concentrations of the catalyst are (B) 0.5 at.%; (C) 1 at.%; (D) 5 at.%; (E) 10 at.%.

Table 1  
Comparison of the apparent reaction rate constants for several catalysts

Catalyst	Calcined temperature (°C)	Concentration of the catalysts (g/l)	Apparent reaction rate constants, $k$ ( $\times 10^{-3} \text{ min}^{-1}$ )	Aqueous methyl orange degradation, $t_{1/2}$ (min) <sup>a</sup>
1 at.% Ba doped bismuth titanate	400	5	15.5	19.4
1 at.% Ba doped bismuth titanate	500	5	10.2	29.5
1 at.% Ba doped bismuth titanate	600	5	9.8	30.7
0.5 at.% Ba doped bismuth titanate	600	5	20.4	14
5 at.% Ba doped bismuth titanate	600	5	7.1	42.4
10 at.% Ba doped bismuth titanate	600	5	6.3	47.8
Pure Bi <sub>12</sub> TiO <sub>20</sub> <sup>b</sup>	600	5	16.5	18
Anatase TiO <sub>2</sub> <sup>b</sup>	600	2	4.685	64

<sup>a</sup> Time required for 50% decolorization of 10 ppm methyl orange solution.

<sup>b</sup> In our experiment, 2 g/l anatase TiO<sub>2</sub> and 5 g/l Bi<sub>12</sub>TiO<sub>20</sub> show the highest activity to decolorize the methyl orange solution.

related to the dopant trap site, it is more important that the trapped charges should be transferred to the interface to initiate the photoreactions. The observed photoreactivity decrease in the prepared samples with increasing of the dopant concentration is probably due to the large dopant concentration of Ba ions which can lead to the dopants are more likely to serve as recombination centers than as trap sites for eventual charge transfer at the interface.

It is worth noting that doping with 0.5 at.% Ba ions can significantly increases the photocatalytic activity of Bi<sub>12</sub>TiO<sub>20</sub> crystals. As state previously, the increased activity of the catalysts should be attributed to the dopants, which can alter the e<sup>-</sup>/h<sup>+</sup> pair recombination rate. In the study of photo-degradation property of TiO<sub>2</sub> in aqueous environment, Gerisher [22] found that the rate of photooxidation is equal to and limited by the reduction rate of dissolved oxygen (O<sub>2</sub>) in the solution. Linsebigler et al. [3] pointed out that when O<sub>2</sub> is not reduced at a sufficiently high rate, electrons would accumulate on the photocatalyst particles and the recombination of electron/hole pair will be enhanced. So quick oxygen diffusion in catalyst crystals is also one important factor affecting the activity of the catalysts. Although there is no experimental evidence support, it is generally accepted that oxygen diffusion is based on rapid transport of vacancies, which migrate by a conventional hopping mechanism [23]. It has been widely documented that the incorporation of low-valent cations to the LaMO<sub>3</sub> oxides, which substituted La<sup>3+</sup>, is crucial for promoting catalytic activity and high ion conductivity [24,25]. Pena and Fierro [23] pointed out that the reduction

of the effective valence of A-site cations leads to the formation of a compensating population of oxygen vacancies at low oxygen partial pressure. The observed influence of the Ba ions on the activity of the Bi<sub>12</sub>TiO<sub>20</sub> crystals can be explained by the hypothesis that the substitution of Ti<sup>4+</sup> with low-valent cations Ba<sup>2+</sup> leads to the formation of a compensating population of oxygen vacancies, which help the oxygen diffusion in the catalytic crystals thus helping the separation of holes from electrons.

In summary, Ba ions were doped into sillenite bismuth titanates crystals by a CSD method. Photocatalytic activity of the prepared samples was evaluated by the photodecolorization of methyl orange solution. Result shows La<sup>3+</sup> dopant can significantly increases the photoactivity of Bi<sub>12</sub>TiO<sub>20</sub> crystals.

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