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A novel photocatalyst and improvement of photocatalytic properties by Cu doping

Jingxue Sun, Gang Chen*,[1], Yingxuan Li, Chao Zhou, Hongjie Zhang

Department of Chemistry, Harbin Institute of Technology, Harbin 150001, People's Republic of China

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ABSTRACT

A new series of photocatalysts, $Bi_2Zn_{2/3-x}Cu_xTa_{4/3}O_7$ (Cu-β-BZT) crystals with pyrochlore structure were synthesized by the method of solid-state reaction (SSR). With small amount of Cu doped ($0.01 \leq x \leq 0.04$), the phase structure was kept to be monoclinic pyrochlore as pure β-BZT. The diffuse reflectance spectrum of Cu-β-BZT samples showed a red shift. The method of Cu doping enhanced the photocatalytic activity, and when the value of x is 0.03, the sample showed the highest activity, which is about 10 times higher than that of pure β-BZT under UV light. Especially, the samples of Cu-β-BZT showed photocatalytic activities under visible light irradiation ($\lambda > 400$ nm). Effects of the Cu doped on the photocatalytic activities of the catalysts were also discussed.

1. Introduction

Recently, the method of photocatalytic splitting water which can combine heterogeneous catalysts with solar technology has attracted much interest [1]. During this process, hydrogen, a clean-energy, can be obtained from water using solar light, which is also a kind of clean-energy. This is a renewable process which is one of the ways to solve both the environment and energy problems in the future [2–7]. Till now, semiconductor photocatalysts, such as TiO_2, have been widely applied to the problems of environment pollution. During the past decades since TiO_2 was reported, many metal oxides consisting of TiO_6, NbO_6 or TaO_6 octahedral units, such as $SrTiO_3$ [8], $BaTi_4O_9$ [9], $K_4Nb_6O_{17}$ [10], and $InTaO_4$ [11], have been extensively studied as new series of photocatalysts.

It is known that lots of compounds with $A_2^{3+}B_2^{4+}O_7$ pyrochlore structure exhibit antiferroelectric phases or dielectric anomalies [12,13], and series of photocatalysts with pyrochlore have been reported, such as Bi_2MNbO_7 (M = Al, Ga, In and Fe), Bi_2RNbO_7 (R = Y, rare earth elements) and Bi_2MTaO_7 (M = In, Ga, Fe, La and Y). Recently, pyrochlore compounds that belong to ternary system Bi_2O_3–ZnO–Me_2O_5 (Me = Nb and Ta) [14–16], which contain octahedral units, have been recognized as potential candidates for capacitor and high-frequency filter applications [17–20]. But the photocatalytic activity of this system has not been reported. Bi_2O_3–ZnO–Me_2O_5 belongs to the family of $A_2B_2O_7$ compounds with $A_2^{3+}B_2^{4+}O_7$ pyrochlore structure. The crystal structure of these compounds is comprised of B–O octahedra units and A–O tetrahedral units. In the system of Bi_2O_3–ZnO–Ta_2O_5, it can be predicated that the Bi^{3+} tends to occupy the A site because of its large ion radius, the Ta^{5+} tends to occupy B site for its smaller ion radius, and the Zn^{2+} will occupy both site of A and B for its medium radius. Due to the pyrochlore structure, the sample of this system may show photocatalytic activity. On the other hand, it is well known that the method of transition ions doping into catalysts can increase the QE (quantum efficiency) of the photocatalyst. In this method, the ions, act as electron/hole traps and reduce the rate of electron/hole pair recombination [21]. Copper is a good choice of dopant and it has been reported that the results indicated that doping of copper increased the photocatalytic activity of the samples [22].

In this paper, we found that the Cu-doped $Bi_2Zn_{2/3}Ta_{4/3}O_7$ samples, which belong to the system above, showed a desirable photocatalytic activity under both ultraviolet and visible light irradiation. The process, structure and shape of the samples were investigated. Also, effects of CuO and the photocatalytic properties of the samples were carefully discussed in this paper.

2. Experimental

2.1. Preparation of samples

Polycrystalline samples of $Bi_2Zn_{2/3}Ta_{4/3}O_7$ were synthesized by a solid-state reaction method. The pre-dried oxides (Bi_2O_3, ZnO, Ta_2O_5) with high purity (above 99.9%) were used as starting materials. Stoichiometric mixtures were mixed and grinded for 30 min in an agate mortar. The mixture was then dried and pressed into small columns having a diameter of 10 mm and thickness of 2–3 mm under a pressure of 8 MPa. The columns were pre-heated at 800 °C in the air for 15 h and then grinded and pressed into columns again just like above. Specimens were

* Corresponding author. Tel.: +86 451 86413753; fax: +86 451 86413753.
E-mail address: gchen@hit.edu.cn (G. Chen).
[1] Permanent address.

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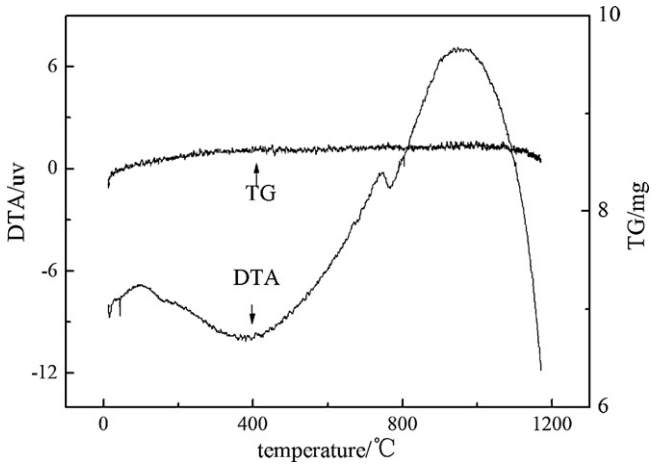

Fig. 1. TG–DTA patterns of the starting mixed materials.

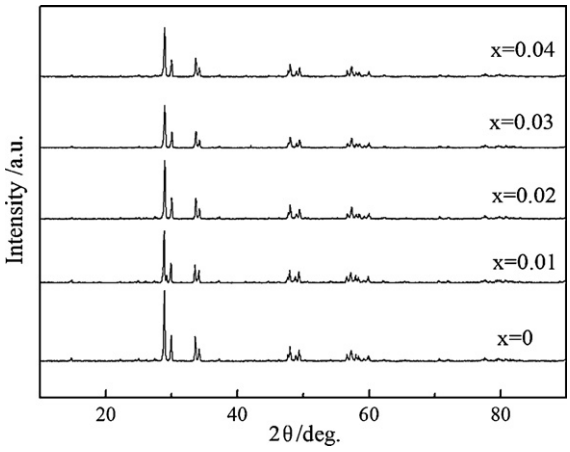

Fig. 3. X-ray diffraction of $Bi_2Zn_{2/3-x}Cu_xTa_{4/3}O_7$ with different values of *x*.

obtained when the columns were finally heated at 1000 °C, which was according to the TG–DTA analysis (as shown in Fig. 1), for 24 h in the air.

The samples of Cu-doped $Bi_2Zn_{2/3}Ta_{4/3}O_7$ were also prepared by solid-state reactions, mixtures of Bi_2O_3, ZnO, Ta_2O_5 and CuO were sintered under the same condition except that the temperature of final heating was chosen to be 850 °C.

2.2. Characterization

Structure of the sintered powders was confirmed by X-ray diffraction (XRD) on ractometer with Cu Kα radiation (λ = 1.5418 Å). The XRD patterns were recorded from 10° to 90° (2*θ*). Morphologies and particle sizes of the specimens were analyzed by scanning electron microscope (SEM) (Hitachi-4700). Diffuse reflection spectra of the powders were measured by ultraviolet–visible light diffusion spectrometry (UV–vis) (PG, TU-1900) to estimate the band gaps (*Eg*) of the obtained photocatalysts. Also, BET measurement (BF, ST2000) was used to determine the surface areas of the samples.

2.3. Photocatalytic reactions

For the photocatalytic reaction under UV irradiation, it was carried out at room temperature in a closed gas circulation system using a high-pressure Hg lamp (350 W) placed in an out-irradiation quartz cell. 0.1 g of powder was dispersed in an aqueous methanol solution (400 ml of distilled water and 20 ml of methanol) and then reacted for 2 h. For the photocatalytic reaction under visible light, Xe lamp (300 W) with a UV-cut filter (λ > 400 nm) was used as the light source instead of Hg lamp. At the same time, the sacrificial electron donor was changed to be a Na_2S–Na_2SO_3 solution (0.25 mol/L and 0.35 mol/L). Amount of H_2 evolved was determined by a gas chromatography (Agilent, GC-6820, TCD, molecular sieve 5 Å column, Ar carrier). The model of the devices was shown in Fig. 2.

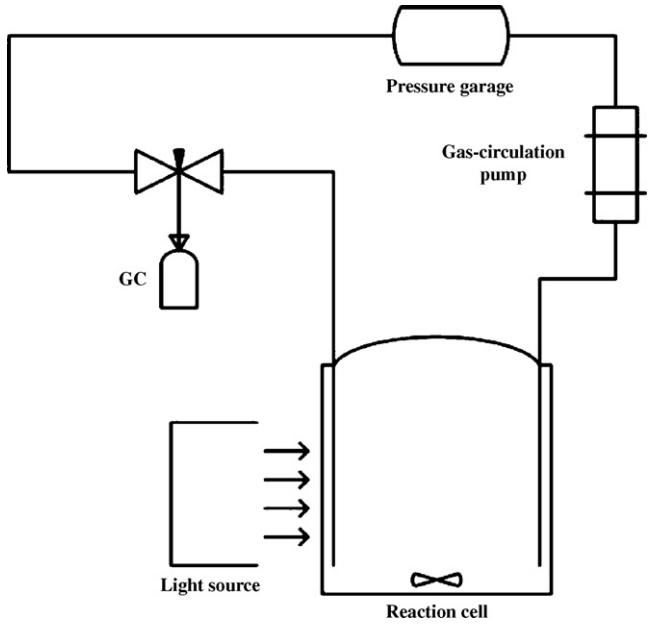

Fig. 2. Model of the photocatalytic activity testing device.

3. Results and discussion

3.1. Structure, and morphology

Because the ionic radius of Cu^{2+} cation (0.072 nm) is almost as same as that of Zn^{2+} cation (0.074 nm), it is reasonable that the movable Cu^{2+} is inclined to occupy B site first and then enter into A site after the B site was stuffed. Here the Cu-doped β-BZT was written as $Bi_2Zn_{2/3-x}Cu_xTa_{4/3}O_7$ with different amount of copper.

X-ray diffraction patterns of $Bi_2Zn_{2/3-x}Cu_xTa_{4/3}O_7$ ceramics are shown in Fig. 3. Value of *x* was chosen to be 0.01, 0.02, 0.03 and 0.04, respectively. It can be seen that the crystal structures of all Cu doped samples were characterized as monoclinic zirconolite as that of pure β-BZT [23], and no secondary phase was observed using X-ray diffraction. Also FT-IR spectra of the samples are shown in Fig. 4. The band at about 750 cm^{-1} responds to the Ta–O stretching modes while the band at about 1000 cm^{-1} is related to the Zn–O stretching modes.

The particle morphologies of as-prepared powders were not very regular, as shown by SEM (Fig. 5). The particle size of both the pure and Cu doped β-BZT is about 0.5 μm which is due to the method of solid-state reaction. It can be also seen that the sample of Cu-β-BZT shows a melting edge (Fig. 5b). As reported, specimens

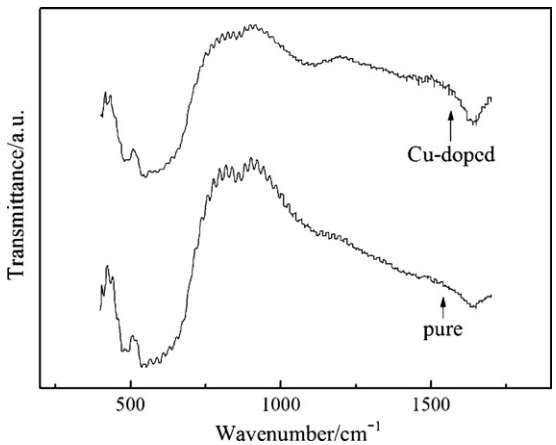

Fig. 4. FT-IR spectra of β-BZT and 0.03Cu-β-BZT.

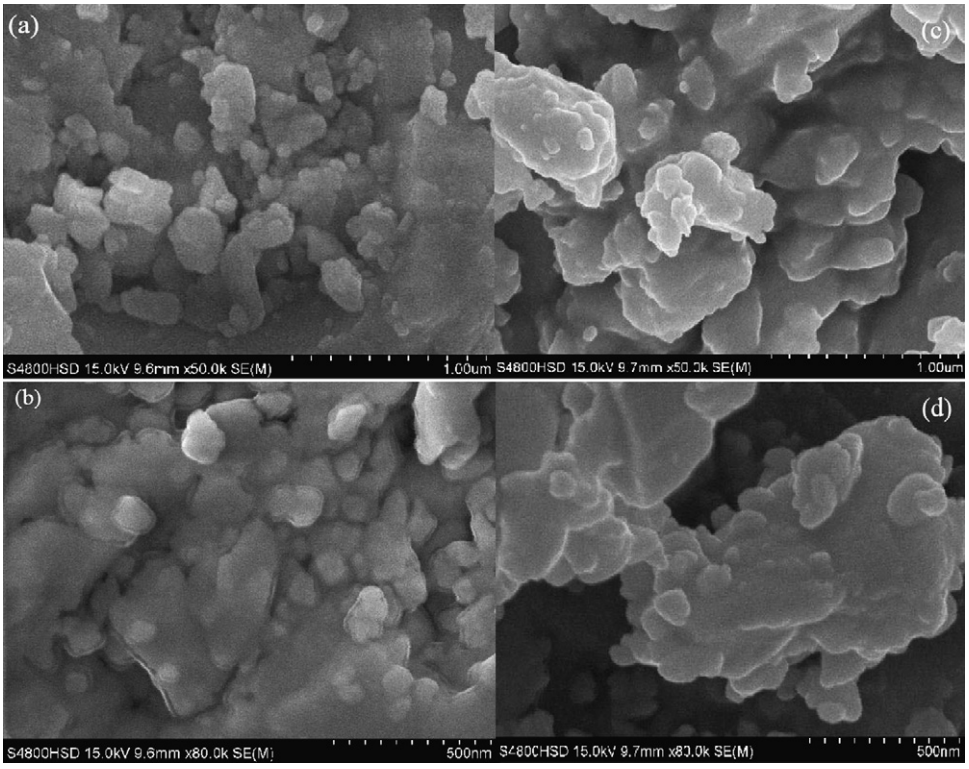

Fig. 5. SEM images of 0.03Cu-β-BZT (a), enlarged (b); pure β-BZT (c), enlarged (d).

based on composition of $Bi_2Zn_{2/3}Ta_{4/3}O_7$ were sintered at about 1000 °C. After doping Cu into the pure β-BZT, the temperature can be decreased to about 850 °C without changing the structure of powders. This could be attributed to the liquid-phase sintering that promoted the densification of β-BZT ceramics very effectively [24], as seen in Fig. 5b. Also, the liquid-phase caused by CuO decreased the surface areas of the samples, as shown in Table 1.

3.2. UV–vis diffuse reflectance spectra

It seems that CuO plays a disadvantageous factor in the samples from the results of SEM and BET analyses. On the other hand, the copper doped can change the character of absorption of the samples. As shown in Fig. 6, the Cu doped β-BZT specimens evidently improved the using of light, especially the visible light. It can be seen that the main absorption edge of pure β-BZT is about 417 nm. After Cu was doped, the main absorption edge was shifted to about 517 nm, and *Eg* of the samples is shown in Table 1. As shown, the band gap energy between the valence and conduction bands of 0.03Cu-β-BZT is 2.97 eV, while the partially filled Cu3d band is located 2.40 eV below the conduction band. When light with wavelengths longer than 417 nm is used for light source, the electrons in the Cu3d, are excited to the conduction band. In this process, Cu3d plays a role as donor band, which can shift the absorption edge.

Table 1
Eg and surface area of $Bi_2Zn_{2/3-x}Cu_xTa_{4/3}O_7$ with different values of *x*.

Value of *x*	*Eg* (eV)	Surface area ($m^2\ g^{-1}$)
0	2.97	2.09
0.01	2.51	1.33
0.02	2.48	1.24
0.03	2.40	1.19
0.04	2.45	1.45

3.3. Photocatalytic activities

Activities of $Bi_2Zn_{2/3-x}Cu_xTa_{4/3}O_7$ photocatalysts prepared by SSR with different values of *x* are shown in Fig. 7. When a UV-light source was used, the rate of hydrogen formation increased with the increase of the value of *x*, except for *x* = 0.04. It can be seen that the photocatalytic activity of 0.03Cu-β-BZT is about 10 times higher than that of pure β-BZT. The method of Cu-doping observably enhanced the activity, but when too much Cu was doped, the photocatalytic activity trend to decline. It may be because that Cu^{2+} acts as the center of combination of the electron–hole pairs. And the process of combining is also the main factor that restricts the rate of hydrogen production. It can be figured out that the optimized amount of Cu doped is 0.03 in molar ratio. The actual amount of copper is 0.027 in this sample which was decided by the test of Inductive Coupled Plasma Emission Spectrometer (ICP).

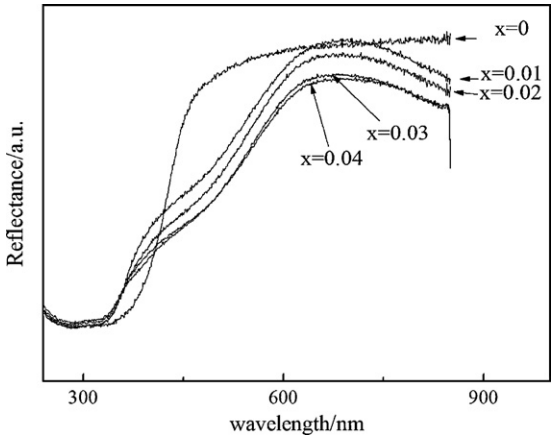

Fig. 6. Diffuse reflection spectra of $Bi_2Zn_{2/3-x}Cu_xTa_{4/3}O_7$.

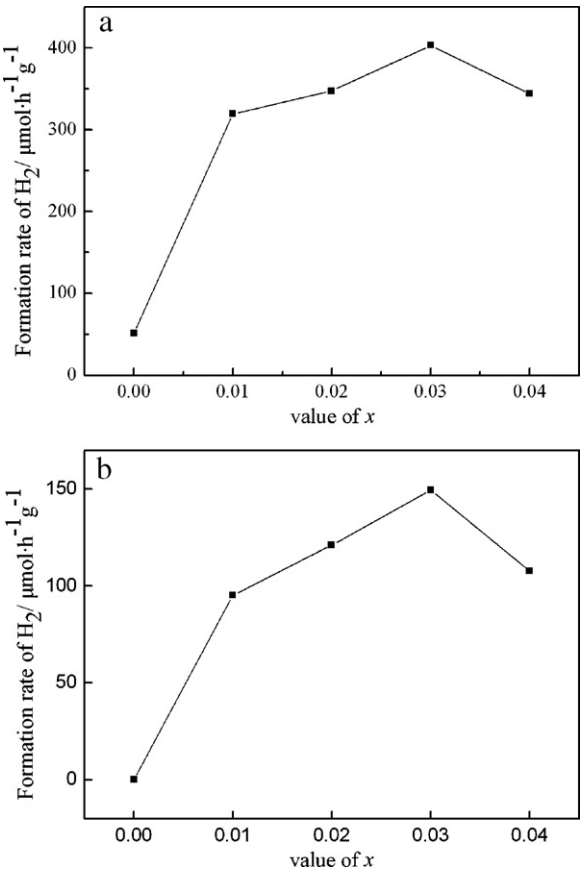

Fig. 7. Photocatalytic activity of $Bi_2Zn_{2/3-x}Cu_xTa_{4/3}O_7$ under UV light (a) and visible light (b).

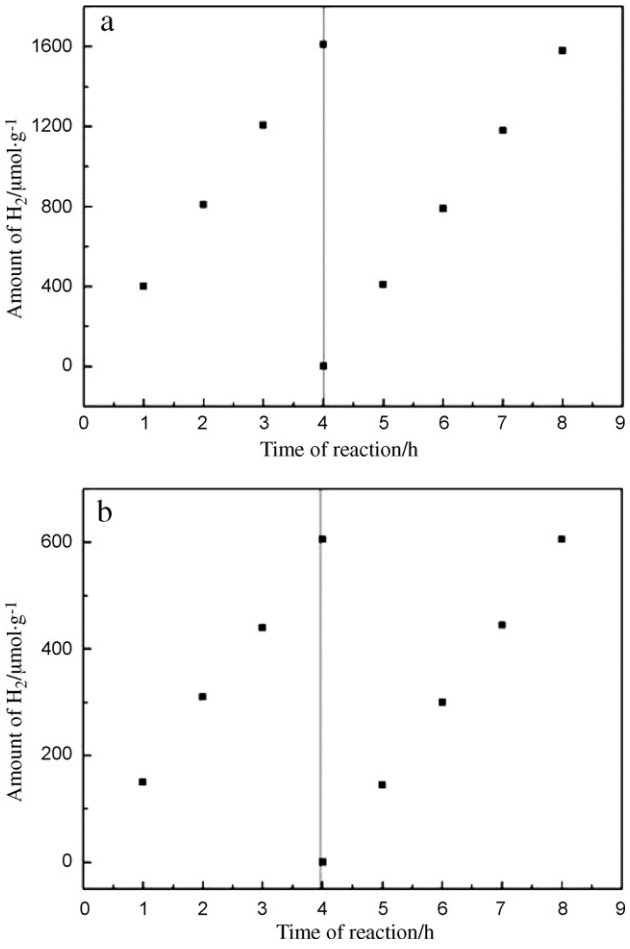

Fig. 8. Photocatalytic activity of 0.03Cu-β-BZT under UV light (a) and visible light (b).

When a visible-light source was used, the rate of hydrogen production presents the same trend as that of under UV light. It should be noted that pure β-BZT do not response to visible light due to its large band gap, but when Cu was doped, the donor band formed by Cu3d makes it possible to produce hydrogen under visible light. Same as above, when the amount of Cu is more than 0.03, the activity shows a trend to decline. And the apparent quantum yield (AQY%) of 0.03Cu-β-BZT is about 0.5% at $\lambda = 420$ nm. As shown in Fig. 8, the sample of 0.03Cu-β-BZT exhibits a stable activity under both UV and visible light. After a reaction of 8 h, the rate of hydrogen formation did not decline.

3.4. Effects of Cu doping

A significant change in photocatalytic activity of β-BZT towards hydrogen generation can be observed in the presence of transition metal (copper) as dopant. Effects of the Cu doped have been reported in some studies [25,26]. The enhancement of the photocatalytic activity was proposed to occur via the function of trapping photogenerated electrons by Cu ions, thereby reducing the rate of unexpected electron–hole recombination. The photocatalytic effect of copper-doped was reported to occur though the redox reaction of Cu^+/Cu^{2+}, which can inhibit the electron–hole recombination. There is Cu^{2+} which occupied the B site, and also Cu^+ can exist in this structure which may be to help the existence of Cu^+/Cu^{2+} potential. Also, the copper that doped into β-BZT can provide a shallow trap for the electron and hole that was generated by irradiation, as a result it can inhibit the recombination and extend the life of charge carrier. Therefore, the rate of hydrogen generation can be increased because there are more available electrons [27].

The result of UV–vis diffuse reflectance showed that the doping of copper changed the absorbance of light and absorption edges of the Cu-β-BZT showed a shift to longer wavelength. So it makes it possible to obtain the photocatalytic activity under visible light irradiation. A significant change in photocatalytic activity of β-BZT towards hydrogen generation under visible light can be observed in the presence of transition metal (copper) as dopant. Similar as reported, under visible light irradiation ($\lambda > 400$ nm), the electrons can be excited from the valence band of β-BZT, which is formed by the 2p orbitals of oxygen, to the conduction band formed by the 3d orbitals of copper which is lower than that of 4f of Ta. And then these excited electrons will be captured and transferred to H^+ ions. Therefore, the configuration of 3d orbitals actually predicts the electron captureability of a dopant [28,29].

However, the ideas above seem to explain the increase of photocatalytic activity at low concentrations of copper-doped ($x < 0.03$), but do not suitable for the negative effect at higher concentrations. One explanation is that this phenomenon may due to the short-circuiting mechanism of the coupled reaction, which occurs when Cu^{2+} is at a high concentration. And the Cu^{2+} might act as a recombination center and enhance the rate of recombination reaction [30].

4. Conclusions

In summary, it has been shown that a new series of Cu-β-BZT with a structure of pyrochlore were synthesized by solid-state reaction method in air. The method of Cu doping exhibited a positive

effect at low concentration ($x < 0.03$). The band gap of 0.03Cu-β-BZT was decreased to be about 2.40 eV compared with the 2.97 eV of pure β-BZT. Photocatalytic activity of 0.03Cu-β-BZT was dramatically enhanced than that of pure β-BZT under UV light. Especially, specimens of Cu-β-BZT also responded to visible light.

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