

# Optical, structural and photophysical properties of Ga<sub>2</sub>BiTaO<sub>7</sub> compound

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The Ga<sub>2</sub>BiTaO<sub>7</sub> compound was synthesized by solid-state reaction method and characterized by powder X-ray diffraction method and the Rietveld structure refinement. This compound crystallizes in the pyrochlore-type structure, cubic system with space group Fd3m and the lattice parameter  $a = 10.4544(2)$  Angstrom. The band gap of the Ga<sub>2</sub>BiTaO<sub>7</sub> compound was estimated to be about 2.47(1) eV. It shows strong optical absorption in the visible light region ( $\lambda > 420$  nm). This indicates that the Ga<sub>2</sub>BiTaO<sub>7</sub> compound has the ability to respond to wavelength of visible light region and has potential for splitting water into H<sub>2</sub> and O<sub>2</sub> under visible light irradiation. Photocatalytic degradation of methylene blue (MB) dye on the Ga<sub>2</sub>BiTaO<sub>7</sub> compound was first investigated under ultraviolet light and visible light irradiation. MB was obviously degraded after visible light irradiation for 140 min with the photocatalyst at room temperature in air. The high activity has potential to be kept in a wide range of wavelength up to 505 nm. © 2005 Springer Science + Business Media, Inc.

## 1. Introduction

Since photoinduced splitting of water on TiO<sub>2</sub> electrode was reported [1], semiconductor photocatalytic process has received much attention [2, 3]. It is well known that the clean and renewable source of hydrogen fuel can be produced by photocatalytic splitting of water with solar energy [2–4]. Especially, the scientific interests in the photocatalytic degradation of organic dyes have grown quickly in recent years [5, 6] because about 15% of the total world production of dyes is lost during the dyeing process and is released in the textile effluents, which pollute the groundwater heavily. Thus it is urgent to develop new light-driven photocatalysts with higher activity. It is generally agreed that countless compounds with the A<sub>2</sub><sup>3+</sup>B<sub>2</sub><sup>4+</sup>O<sub>7</sub> pyrochlore structure possess anti-ferroelectric phases or dielectric abnormality, and only a few compounds display ferroelectric property [7, 8]. The Ga<sub>2</sub>BiTaO<sub>7</sub> compound belongs to the family of the A<sub>2</sub>B<sub>2</sub>O<sub>7</sub> compounds, but space group and lattice constants are not yet clear. Moreover, no photophysical property of the Ga<sub>2</sub>BiTaO<sub>7</sub> compound has been investigated so far. Very recently, we have found that the In<sub>2</sub>BiTaO<sub>7</sub> compound crystallizes in the pyrochlore-type structure and acts as a photocatalyst under ultra-

violet light irradiation. We considered that Bi<sup>3+</sup> and Ta<sup>5+</sup> doping of B<sub>2</sub> site and Ga<sup>3+</sup> doping of A<sub>2</sub> site in the A<sub>2</sub><sup>3+</sup>B<sub>2</sub><sup>4+</sup>O<sub>7</sub> compound might lead to an increase in hole(carrier) concentration, and might offer a change in the magnetic, electrical transmission and photophysical properties. We also suggest that the Ga<sub>2</sub>BiTaO<sub>7</sub> compound might yield a slight modification of crystal structure and offer a change in photophysical properties. It is generally agreed that a slight modification of the structure of a semiconductor has a dramatic effect on the concentration and mobility of charge [6], which directly affect the photocatalytic and photophysical properties of the semiconductor. As a means to help understanding the origin of the photocatalysts, we report the optical, structural and photophysical properties of the Ga<sub>2</sub>BiTaO<sub>7</sub> compound.

## 2. Experimental procedure

The polycrystalline samples of the photocatalysts were synthesized by a solid-state reaction method. Ga<sub>2</sub>O<sub>3</sub>, Bi<sub>2</sub>O<sub>3</sub> and Ta<sub>2</sub>O<sub>5</sub> with purity of 99.99% were used as starting materials. The powders were dried at 200°C for 4 h. Then the stoichiometric amounts of precursors were

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mixed and pressed into small columns. In order to study the best conditions of the reaction, the small columns were sintered at different temperatures for 52 h in an alumina crucible with an electric furnace. The sintered products were analyzed by powder X-ray diffraction method. The crystal structure of the  $\text{Ga}_2\text{BiTaO}_7$  compound was determined by the powder X-ray diffraction method with  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.54056$ ). The data were collected at 295 K with a step scan procedure in the range of  $2\theta = 5\text{--}100^\circ$ . The step interval was  $0.02^\circ$  and the scan speed was  $1^\circ \text{ min}^{-1}$ . The chemical composition of the compound was mensurated by scanning electron microscope-X-ray energy dispersion spectrum (SEM-EDS) and X-ray Fluorescence spectrometer (ARL-9800). The optical absorption of the  $\text{Ga}_2\text{BiTaO}_7$  compound was measured with an UV-visible spectrophotometer (Lambda35). The photocatalytic reaction was performed with 0.5 g powdered  $\text{Ga}_2\text{BiTaO}_7$  compound suspended in 100 ml methylene blue solution (MB solution concentration was  $0.0506 \text{ mol m}^{-3}$  and the initial pH value of the solution was 7) in a pyrex glass cell. The photocatalytic reaction system consisted of a 300 W Xe arc lamp, a 500 W high pressure Hg lamp and a cut-off filter ( $\lambda > 420 \text{ nm}$ ). The concentration of MB was determined with an UV-Vis spectrometer (Helios Beta) with the detecting wavelength at 670 nm. The ion chromatograph (DX-300) was used to confirm the production of MB degradation.

### 3. Results and discussion

#### 3.1. Structural properties

Fig. 1 shows X-ray diffraction patterns of the  $\text{Ga}_2\text{BiTaO}_7$  compound sintered at 1000, 1050 and  $1120^\circ\text{C}$  in air, respectively. It could be seen that the precursor phase of  $\text{Ga}_2\text{O}_3$  reduced rapidly with enhancing reaction temperature. The powder X-ray diffraction analysis showed that the  $\text{Ga}_2\text{BiTaO}_7$  compound is a single phase when the sintering temperature was  $1120^\circ\text{C}$ . This is consistent with the observation from SEM-EDS. The chemical composition of the  $\text{Ga}_2\text{BiTaO}_7$  com-

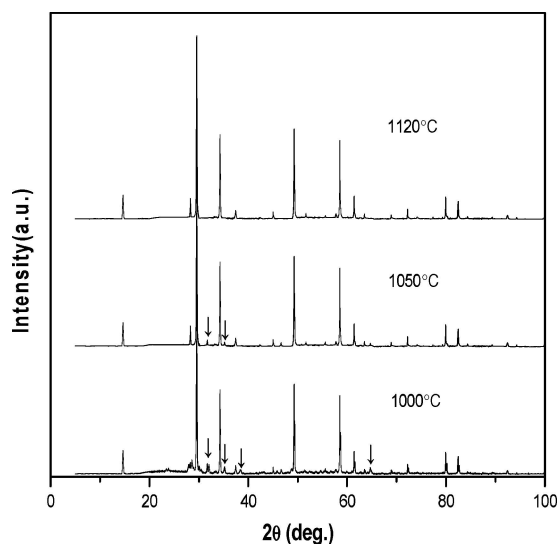


Figure 1 X-ray powder diffraction patterns of the  $\text{Ga}_2\text{BiTaO}_7$  compound at different synthetic temperatures. ↓: the patterns of  $\text{Ga}_2\text{O}_3$ .

pound was mensurated with characteristic X-rays of  $\text{Bi L}\alpha$ ,  $\text{Ga L}\alpha$ ,  $\text{Ta L}\alpha$ . The composition content was determined with the ZAF (element number, absorption and fluorescence corrections) quantification method. The SEM-EDS analysis revealed that the  $\text{Ga}_2\text{BiTaO}_7$  compound had a homogenous atomic distribution with no other impure elements. An average atomic rate of  $\text{Ga}:\text{Bi}:\text{Ta} = 2.00:1.98:1.02$  was obtained from measurements made at many different points. The atomic ratio of this compound was also confirmed by the measurement from X-ray Fluorescence spectrometer and the result was similar to above atomic rate. Based on above results, we may deduce that the purity of the prepared  $\text{Ga}_2\text{BiTaO}_7$  compound is almost 100%.

Full-profile structure refinement of the collected powder diffraction data for the  $\text{Ga}_2\text{BiTaO}_7$  compound was performed using the Rietveld program REITAN [9]. The result of refinement is shown in Fig. 2. Positional parameters and isotropic thermal parameters of the  $\text{Ga}_2\text{BiTaO}_7$  compound were refined. The structure of the  $\text{Ga}_2\text{BiTaO}_7$  compound shown in Fig. 3, can be described as consisting of the three-dimensional network of  $\text{MO}_6$  ( $\text{M} = \text{Ta}, \text{Bi}$ ), stacked along  $[101]$  and separated by a unit cell translation ( $10.4544(2) \text{ \AA}$ ). The atomic coordinates and isotropic thermal parameters of the  $\text{Ga}_2\text{BiTaO}_7$  compound are listed in Table I. The result of the final refinement for the  $\text{Ga}_2\text{BiTaO}_7$  compound indicated a good agreement between the observed and calculated intensities in the pyrochlore type crystal structure, cubic system with space group  $\text{Fd}\bar{3}\text{m}$  when the O atoms are included in the model. The lattice parameter is  $a = 10.4544(2) \text{ \AA}$ . All the diffraction peaks for the  $\text{Ga}_2\text{BiTaO}_7$  compound could be successfully indexed based on the lattice constant and the space group mentioned above. Our X-ray diffraction results shows that the  $\text{Ga}_2\text{BiTaO}_7$  and  $\text{In}_2\text{BiTaO}_7$  compound crystallize in the same structure, and  $2\theta$  angles of each reflection of the  $\text{Ga}_2\text{BiTaO}_7$  compound change with

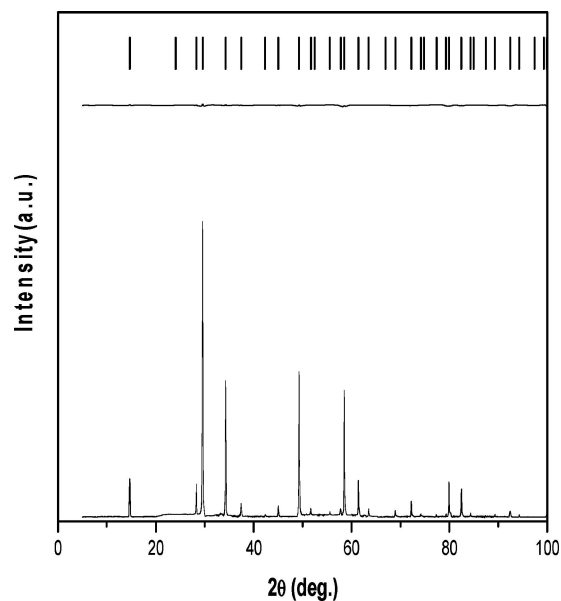


Figure 2 Rietveld refinement of XRD data for the cubic  $\text{Ga}_2\text{BiTaO}_7$  compound by a solid state reaction method at  $1120^\circ\text{C}$ . A difference (observed-calculated) profile is shown beneath. The tic marks represent reflection positions.

TABLE I Structural parameters for the cubic  $\text{Ga}_2\text{BiTaO}_7$  compound prepared by solid state reaction method

Atom	x	y	z	Beq	Occupation factor
Ga	0.0000	0.0000	0.0000	2.911	1.0
Bi	0.5000	0.5000	0.5000	0.458	0.5
Ta	0.5000	0.5000	0.5000	0.500	0.5
O(1)	-0.1860	0.1250	0.1250	1.000	1.0
O(2)	0.1250	0.1250	0.1250	1.000	1.0

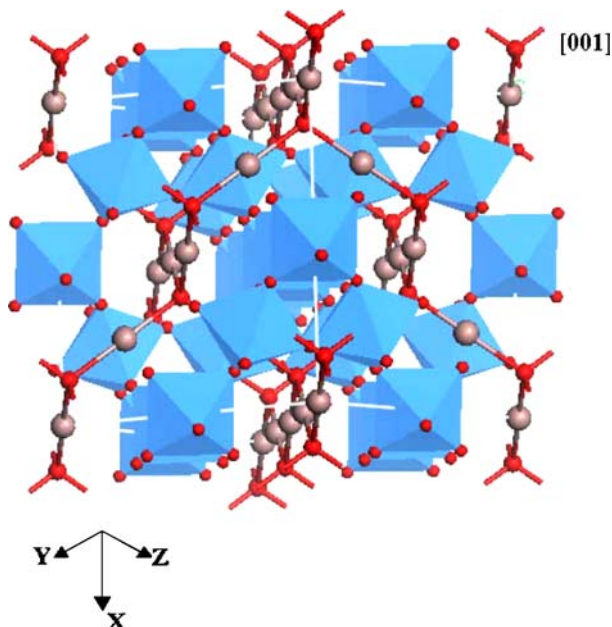


Figure 3 The schematic structural diagram of the cubic  $\text{Ga}_2\text{BiTaO}_7$  compound. Three-dimensional network of  $\text{MO}_6$  stacked along [101] and separated by a unit cell translation.

$\text{In}^{3+}$  being substituted by  $\text{Ga}^{3+}$ , which indicates a decrease in lattice parameter of the photocatalysts with decrease of the M ionic radii,  $\text{Ga}^{3+}$  (0.62 Å) <  $\text{In}^{3+}$  (0.92 Å). The lattice parameter decrease from  $a = 10.692(1)$  Å for the  $\text{In}_2\text{BiTaO}_7$  compound to  $a = 10.4544(2)$  Å for the  $\text{Ga}_2\text{BiTaO}_7$  compound. The outcome of refinements generated the unweighted  $R$  factor,  $R_p = 9.24\%$  in space group  $\text{Fd}3\text{m}$  when the O atoms are included in the model. A possible origin for the large  $R$  factor might be due to minor impurities in the compound. However, powder diffraction pattern and SEM-EDS analysis do not show the presence of any other phases. It seems to be necessary to derive from a slightly modified structure model for the  $\text{Ga}_2\text{BiTaO}_7$  compound. It is generally agreed that the defects and the disorder/order of a fraction of the atoms can cause a change of structures, because they generate physically different bond-distance distributions, thermal displacement parameters and/or occupation factors for some of the atoms [10].

### 3.2. Photophysical properties

Fig. 4 shows the result of diffuse reflection spectrum of the cubic  $\text{Ga}_2\text{BiTaO}_7$  compound. An average absorption of less than 5% was obtained from 500 to 800 nm. In contrast to the well-known  $\text{TiO}_2$  whose absorption edge

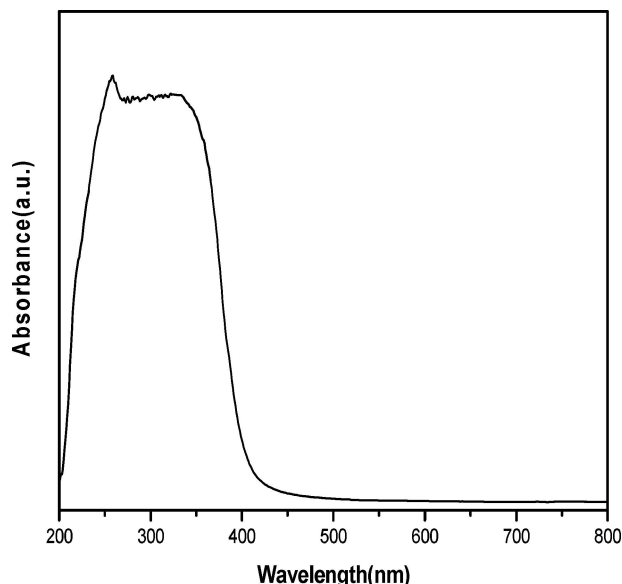


Figure 4 Diffuse reflection spectrum of the cubic  $\text{Ga}_2\text{BiTaO}_7$  compound prepared by a solid state reaction method.

is at about 400 nm, the newly developed  $\text{Ga}_2\text{BiTaO}_7$  compound showed obvious absorption in visible light region up to 505 nm. This new spectrum showed an obvious shift to longer wavelength compared with that of the  $\text{TiO}_2$  compound. This means that strong photoabsorption of the  $\text{Ga}_2\text{BiTaO}_7$  compound occurs at wavelengths shorter than 505 nm. The absorption edge of diffuse reflection spectrum shifted to longer wavelength. It means that the compound can utilize more irradiation light energy. The experiment result also proved that the photoabsorption was strong. In a word, the  $\text{Ga}_2\text{BiTaO}_7$  compound has the ability to respond to the wavelength of visible light region.

It is commonly accepted that the photocatalytic process of semiconductors is the direct photon absorption by band gap of the semiconductors and generates electron-hole pairs in the particles, and the excitation of an electron from the valence band to the conduction band is initiated by light absorption with energy equal to or greater than the band gap of the semiconductor. This suggests that the narrower the band gap is, the easier it is to excite an electron from the valence band to the conduction band. If the conduction band potential level of semiconductor is more negative than that of  $\text{H}_2$  evolution, and the valence band potential level is more positive than that of  $\text{O}_2$  evolution, decomposition of water can occur even without applying electric power [1]. The photoabsorption of the  $\text{Ga}_2\text{BiTaO}_7$  compound suggests that it has potential ability to generate  $\text{H}_2$  from water under visible light irradiation. The band gap of the  $\text{Ga}_2\text{BiTaO}_7$  compound was estimated by extrapolations of the straight regions of the absorption coefficient,  $\alpha^2$ , versus photon energy  $h\nu$ . The absorption coefficient was determined by the equation  $\alpha = \ln(1/T)/d$ , where  $T$  is the transmissivity and  $d$  is the thickness of the sample [11, 12]. The band gap of the  $\text{Ga}_2\text{BiTaO}_7$  compound was estimated to be 2.47(1) eV, which was much narrower compared with that of the  $\text{Bi}_2\text{InTaO}_7$  compound (2.9 eV). It means that the photoabsorption of the  $\text{Ga}_2\text{BiTaO}_7$  compound is more easier than that

of the  $\text{Bi}_2\text{InTaO}_7$  compound. It will result in higher photocatalytic activity for the  $\text{Ga}_2\text{BiTaO}_7$  compound compared with that of the  $\text{Bi}_2\text{InTaO}_7$  compound. The  $\text{Ga}_2\text{BiTaO}_7$  compound consists of the network of  $\text{MO}_6$  as shown in Fig. 3. The structure of the  $\text{Ga}_2\text{BiTaO}_7$  compound is built by forming infinite corner-sharing  $\text{MO}_6$  octahedra which formed the zigzag chains along  $[11\bar{1}]$ . This suggests that photogenerated electron-hole pairs in the  $\text{Ga}_2\text{BiTaO}_7$  compound can move easily in this direction. The mobility of electron-hole pairs affects the photoabsorption because it affects the probability of electrons and holes to reach reaction sites on the surface.

### 3.3. Photocatalytic degradation of methylene blue

Fig. 5 shows the MB degradation in the presence and absence of the  $\text{Ga}_2\text{BiTaO}_7$  compound under ultraviolet light irradiation. It could be seen that MB concentration in the solution varied only from 0.0506 to 0.0458  $\text{mol m}^{-3}$  after ultraviolet light irradiation for 65 min without the  $\text{Ga}_2\text{BiTaO}_7$  photocatalyst. The result also indicated that MB concentration in the solution decreased quickly to 0  $\text{mol m}^{-3}$  after ultraviolet light irradiation for 65 min with the  $\text{Ga}_2\text{BiTaO}_7$  photocatalyst. The solution color changed from deep blue to colorless. The results showed that MB was degraded easily with the  $\text{Ga}_2\text{BiTaO}_7$  compound under ultraviolet light irradiation. The anion of  $\text{SO}_4^{2-}$  is one of the main products of MB degradation. A  $\text{SO}_4^{2-}$  ion concentration of 0.0319  $\text{mol m}^{-3}$  was explored in the solution after the photocatalytic reaction over the  $\text{Ga}_2\text{BiTaO}_7$  compound under ultraviolet light irradiation, indicating that 63% of sulphur from MB was turned into sulphate. It was obvious that MB was mineralized rather than bleached at this study. The initial rates of MB degradation were about  $1.30 \times 10^{-5}$  and  $0.12 \times 10^{-5} \text{ mol s}^{-1} \text{ m}^{-3}$  respectively

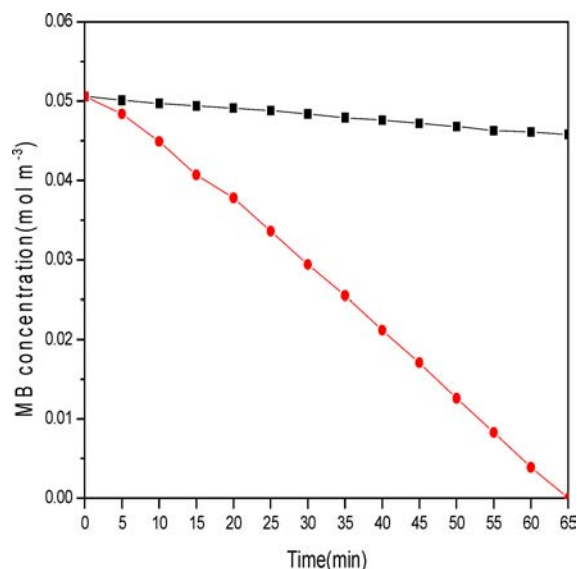


Figure 5 Photocatalytic methylene blue degradation under ultraviolet light irradiation at room temperature in air for 65 min in the presence of the  $\text{Ga}_2\text{BiTaO}_7$  compound (●) and in the absence of the  $\text{Ga}_2\text{BiTaO}_7$  compound (■).

in the presence and absence of the  $\text{Ga}_2\text{BiTaO}_7$  compound.

MB degradation with the  $\text{Ga}_2\text{BiTaO}_7$  compound or the  $\text{TiO}_2(\text{P-25})$  compound was also carried out under visible light irradiation ( $\lambda > 420 \text{ nm}$ ). The results showed that MB concentration in the solution decreased to 0  $\text{mol m}^{-3}$  after visible light irradiation for 140 min with the  $\text{Ga}_2\text{BiTaO}_7$  compound, and the initial rate of MB degradation was about  $0.60 \times 10^{-5} \text{ mol s}^{-1} \text{ m}^{-3}$ , and a  $\text{SO}_4^{2-}$  ion concentration of 0.0246  $\text{mol m}^{-3}$  was explored in the solution after the photocatalytic reaction. The solution color also changed from deep blue to colorless. As a comparison, MB concentration in the solution changed only from 0.0506 to 0.0351  $\text{mol m}^{-3}$  after visible light irradiation for 140 min with the  $\text{TiO}_2$  compound, and the  $\text{SO}_4^{2-}$  ion concentration after the photocatalytic reaction was 0  $\text{mol m}^{-3}$ . Above results suggested that the  $\text{Ga}_2\text{BiTaO}_7$  compound was more active to MB photocatalytic degradation than the  $\text{TiO}_2$  compound under visible light irradiation. In addition, MB was not decomposed without light irradiation. In order to increase the activity of the catalyst, we should not only modify the electronic structure of the catalyst but also increase the surface area of the catalyst. The surface area was measured by BET method (Flow-Prep 060). BET measurement indicated that the surface area of the  $\text{Ga}_2\text{BiTaO}_7$  compound was  $0.88 \text{ m}^2 \text{ g}^{-1}$ . This is only about 1.8% of the  $\text{TiO}_2(\text{P-25})$  compound ( $49.23 \text{ m}^2 \text{ g}^{-1}$ ), indicating much higher efficiency of the new photocatalyst could be expected from increasing surface area. The particle distribution of the  $\text{Ga}_2\text{BiTaO}_7$  compound was homogeneous and the estimated average particle size was nearly  $1.4 \mu\text{m}$ . Studies are currently underway in our laboratory to investigate direct water splitting into  $\text{H}_2$  and  $\text{O}_2$  under visible light irradiation with the photocatalyst.

### 4. Conclusions

In conclusion, we prepared single phase of the  $\text{Ga}_2\text{BiTaO}_7$  compound by solid state reaction method and investigated the structural, optical absorption and photocatalytic degradation properties. The  $\text{Ga}_2\text{BiTaO}_7$  compound crystallizes in the pyrochlore-type structure, cubic system with space group  $\text{Fd}\bar{3}\text{m}$  and the lattice parameter  $a = 10.4544(2)$  Angstrom. The band gap of the  $\text{Ga}_2\text{BiTaO}_7$  compound was estimated to be about 2.47(1) eV. The  $\text{Ga}_2\text{BiTaO}_7$  compound shows strong optical absorption in the visible light region ( $\lambda > 420 \text{ nm}$ ). This indicates that the  $\text{Ga}_2\text{BiTaO}_7$  compound has the ability to respond to wavelength of visible light region and has potential for splitting water into  $\text{H}_2$  and  $\text{O}_2$  under visible light irradiation. Photocatalytic degradation of methylene blue dye on the  $\text{Ga}_2\text{BiTaO}_7$  compound was first investigated under ultraviolet light and visible light irradiation. MB was degraded largely after visible light irradiation for 140 min over the photocatalyst at room temperature in air. The high activity has potential to be kept in a wide range of wavelength up to 505 nm. The study of optical and structural properties of the  $\text{Ga}_2\text{BiTaO}_7$  compound will provide useful information on the physics of the photocatalyst and on the synthesis of visible light catalysts.

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