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Synthesis and characterization of vanadium doped $Bi_4Ti_3O_{12}$ as photocatalyst material

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Abstract. One of interesting properties of $Bi_4Ti_3O_{12}$ is photocatalyst. The band gap of $Bi_4Ti_3O_{12}$ is 2.9 eV as results only work at ultraviolet wavelength range. Metal doped to $Bi_4Ti_3O_{12}$ can reduce band gap energy. In this work, $Bi_4Ti_3O_{12}$ was doped vanadium ($Bi_4Ti_{3-x}V_xO_{12}$ with x= 0.05; 0.1; 0.15; 0.2) using solid state reaction method. X-ray diffraction data show that $Bi_4Ti_{3-x}V_xO_{12}$ (x= 0.05; 0.1; 0.15; 0.2) were successfully formed with space group B2cb, however there is small impurities of VO_2 phase. Scanning electron microscopy (SEM) images showed that the particle of all obtained $Bi_4Ti_{3-x}VxO_{12}$ (x= 0.05; 0.1; 0.15; 0.2) have shape platelet-like. Diffuse Reflectance Spectroscopy data showed that the energy band gap of $Bi_4Ti_{3-x}V_xO_{12}$ decreased by increasing vanadium dopant.

1. Introduction

Aurivillius compound has widely studied due to the interesting properties of ferroelectric [1]. Aurivillius compound have general formula: $A_{n-1}Bi_2B_nO_{3n+3}$ (n= 1, 2, 3, 4,…) with cations A = Ca^{2+}, Sr^{2+}, Ba^{2+}, Pb^{2+}, Bi^{+3}, Na^{+1}, and cations B = Ti^{4+}, Nb^{5+}, Ta^{5+}, W^{6+} or Mo^{6+}. n is an integer that representing the amount of BO_6 layers perovskite blocks [2,3]. Recently, many researchers explored to properties of aurivillius compound besides ferroelectric such as photocatalyst, luminescence, and thermoelectric properties [4,5]. As well known that photocatalyst technology have potentially can be applied in many fields such as (a) waste treatment technology especially for organic dye waste, (b) to produce hydrogen gas by water splitting process technology. The photocatalyst properties of Aurivillius compound was reported by many researchers such as $Bi_4V_2O_{11}$, Bi_2WO_6, $Bi_4Ti_3O_{12}$ [6-8].

$Bi_4Ti_3O_{12}$ (BIT) is well known as three layered Aurivillius compound family and reported potentially applied as photocatalyst material. The band gap energy of BIT 3.1 eV which indicates that the work function of $Bi_4Ti_3O_{12}$ at ultra violet (UV) light range [9]. To applied it in tropical country like Indonesia area, this fact is not good, because mostly sun light in visible light range therefore need the technique as purpose to reduce the band gap energy. Metal doped to photocatalyst material is technique was used to reduce band gap energy. There are many metal can be used as dopant material photocatalyst such as, V, Mn, Fe, Cr. Chen, et al (2016) synthesized chromium doped BIT and reported the enhancing of photocatalytic activity as well as the photoabsorption in visible light range [8]. Meanwhile, Dumrongrojthanath, et al (2017) reported that Br doped $BiWO_6$ have higher photocatalytic activity and can work in visible light range [10]. It indicates that the metal doped to Aurivillius compound can solve the high band gap energy problem. Previous researches reported that vanadium metal can be used to improve the photocatalytic activity and optical properties of TiO_2 [11]. Hence, in this research, we synthesized vanadium doped the BIT to improve the optical properties using solid state reaction.

2. Experimental

Bismuth Oxide (Bi_2O_3), Titanium (IV) Oxide (TiO_2), Vanadium (V) Oxide (V_2O_5) were grinded for 1 hour in acetone and was calcined at 700 °C for 24 hours. The sample was put from furnace and then regrind for 1 hour and was calcined at 800 °C for 24 hours. The similar method have conducted for calcined at 850, 900, 900 and 1000 °C. Sample product was characterized using (a) powder X-ray diffraction (XRD) to identity the phase of sample, (b) scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS) to identify the morphology as well as element of sample, and (c) diffuse spectroscopy reflectance to identify the band gap energy of sample.

3. Results and Discussion

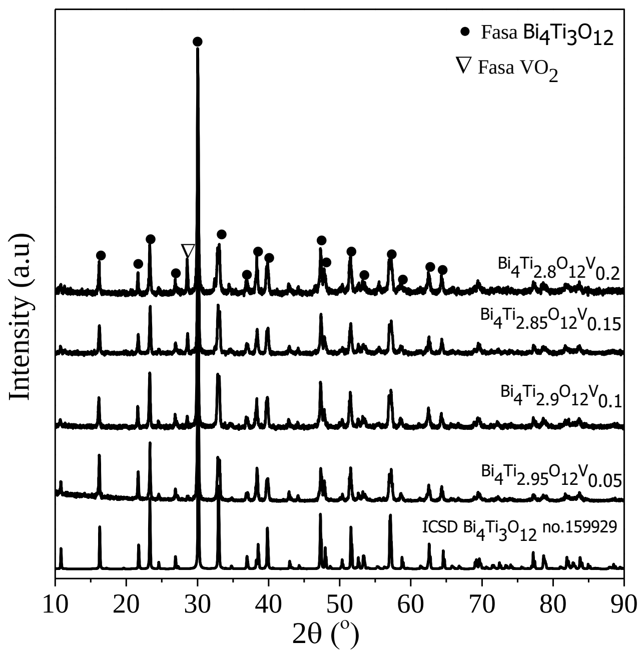

Figure 1. XRD data of $Bi_4Ti_{3-x}V_xO_{12}$ (x= 0.05; 0.1; 0.15; 0.2)

Figure 1 showed XRD pattern of $Bi_4Ti_{3-x}V_xO_{12}$ (x= 0.05; 0.1; 0.15; 0.2). All peaks of XRD indexed to International Crystallography Standard Data (ICSD) no 159929 with space group *B2cb* and as can be seen that compound $Bi_4Ti_{3-x}V_xO_{12}$ (x= 0.05; 0.1; 0.15; 0.2) was successfully synthesized but still found the impurities compound VO_2. The intensity of VO_2 peaks increases and it correspond to increases in %weight of vanadium. Figure 2 depicted the peak position of XRD data at around 2θ (°): 30 and it can been seen that the peak position is different which indicates the crystallite size of samples is different.

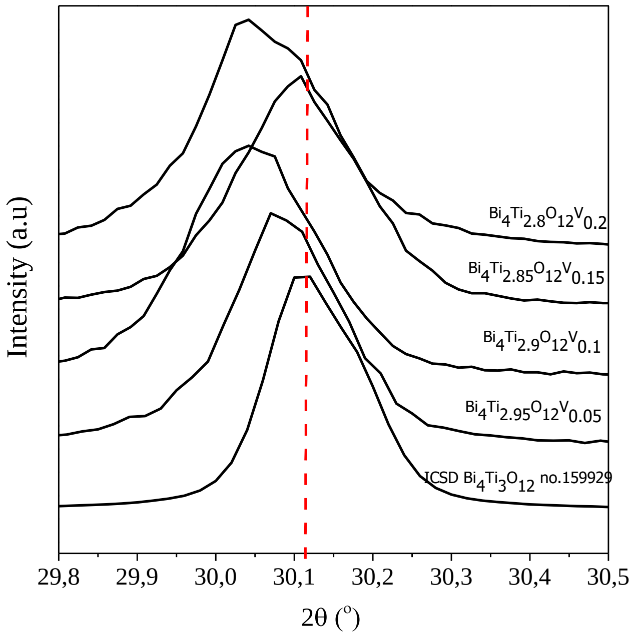

Figure 2. Peak position of XRD data of $Bi_4Ti_{3\text{-}x}V_xO_{12}$ (x= 0.05; 0.1; 0.15; 0.2) at around 2θ: 30°

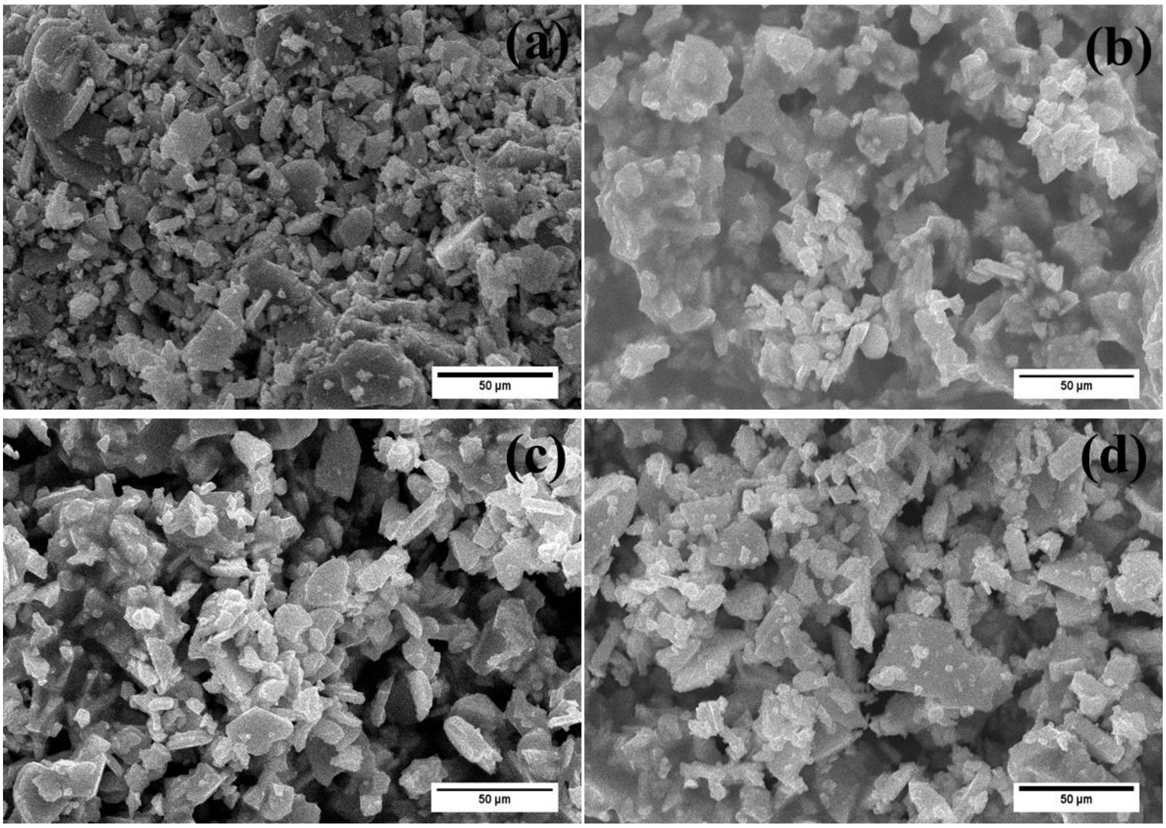

Figure 3. Image of $Bi_4Ti_{3\text{-}x}V_xO_{12}$ (x= 0.05; 0.1; 0.15; 0.2) particle: (a) x= 0.05, (b) x= 0.05, (c) x= 0.15, and (d) x= 0.2

Table 1. The results of EDS analysis

Compound	Weight (%)			
	Bi	Ti	V	O
$Bi_4Ti_{2.95}V_{0.05}O_{12}$	66.45	9.44	0,48	23.62
$Bi_4Ti_{2.9}V_{0.1}O_{12}$	66.74	9.42	1.27	22.56
$Bi_4Ti_{2.85}V_{0.15}O_{12}$	63.42	9.55	1.12	25.91
$Bi_4Ti_{2.8}V_{0.2}O_{12}$	65.62	9.59	0.56	24.23

As can be seen at figure 3, the particle shape of sample is platelet-like and it similar to previous report by other researchers about the particle shape of BIT [12]. The distribution size of particle is not uniform as caused the agglomeration and it will influence to photocatalytic activity because the shape as well as distribution size of particle plays important role in photocatalytic activity [13,14]. The result of elemental analysis was tabulated at Table 1 and shown that vanadium was succesfully introduced to sample. The weight of vanadium which obtained from EDS analysis is different to theoretical calculation and it indicates that the sample is not homogen especially for the impurities VO_2.

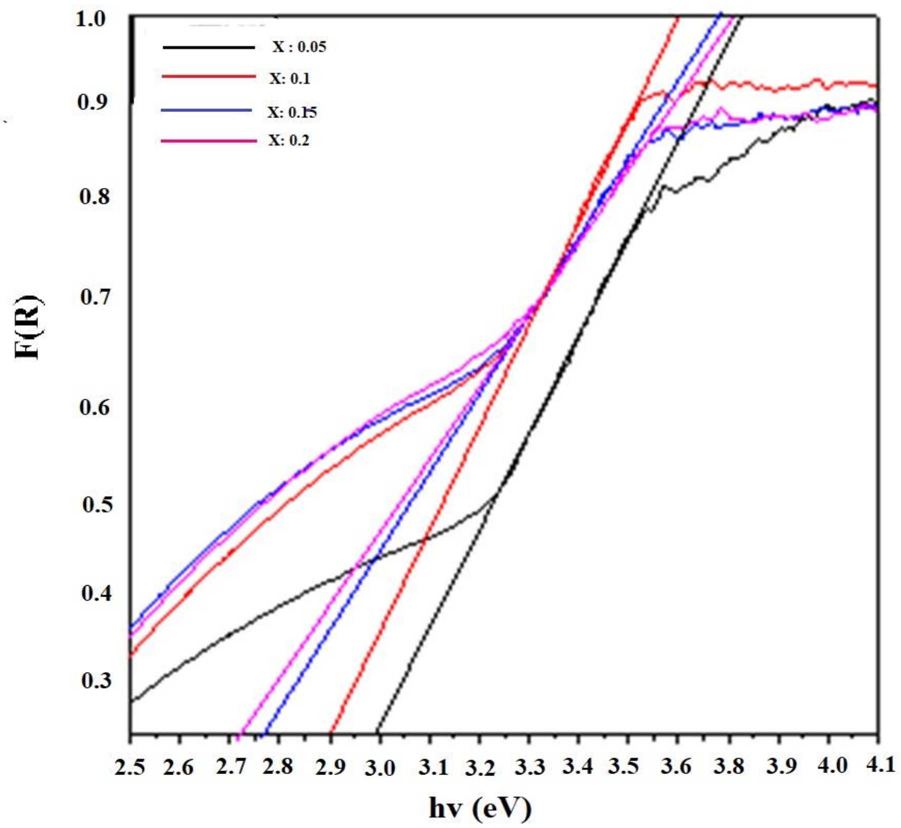

Figure 4. Diffuse reflectance spectroscopy of $Bi_4Ti_{3-x}V_xO_{12}$ (x= 0.05; 0.1; 0.15; 0.2)

Tabel 2. The band gap energy of Vanadium doped BIT

Compound	Band gap energy (eV)
$Bi_4Ti_{2.95}V_{0.05}O_{12}$	3.0
$Bi_4Ti_{2.9}V_{0.1}O_{12}$	2.9
$Bi_4Ti_{2.85}V_{0.15}O_{12}$	2.75
$Bi_4Ti_{2.8}V_{0.2}O_{12}$	2.71

Figure showed the DRS spectra of $Bi_4Ti_{3-x}V_xO_{12}$ (x= 0.05; 0.1; 0.15; 0.2) and was analyzed using Kubelka-Munk equation to calculate the band gap energy. The value of band gap energy $Bi_4Ti_{3-x}V_xO_{12}$ (x= 0.05; 0.1; 0.15; 0.2) as tabulated at Table 2. As can be seen that the band gap energy decreases and as consequence the work function of sample shifted to visible light range (at around 430 nm). The decreases of band gap energy was caused the new state between conduction band and valence band as result the band gap was formed is lower. As result, it give a advantage to BIT as photocatalytic material.

4. Conclusion

$Bi_4Ti_{3-x}V_xO_{12}$ (x= 0.05; 0.1; 0.15; 0.2) was synthesized using solid state reaction and found the impurities VO_2. The work function of $Bi_4Ti_{3-x}V_xO_{12}$ (x= 0.05; 0.1; 0.15; 0.2) is lower than $Bi_4Ti_3O_{12}$ as results the sampel product can work in visible light range.

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