Research Article

Rare Earth Free $\text{Zn}_3\text{V}_2\text{O}_8$ Phosphor with Controlled Microstructure and Its Photocatalytic Activity

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Microsphere of rare earth free phosphor, $\text{Zn}_3\text{V}_2\text{O}_8$, with broadband yellowish white emission was synthesized by combustion route and compared with the hydrothermal, sol-gel, and solid state reaction methods. The phosphor samples were characterized by X-ray diffraction and scanning electron microscopy. UV-visible absorption and photoluminescence (PL) emission and excitation spectra were investigated for these phosphors. $\text{Zn}_3\text{V}_2\text{O}_8$ phosphor containing 10 mol% of H_3BO_3 flux exhibited enhanced PL emission showing broadband from 450 nm to 750 nm. Effect of stoichiometry of Zn and V on the host lattice and its effect on the PL emission spectra were studied. Series of $\text{Mg}_3\text{V}_2\text{O}_8$, $\text{Ca}_3\text{V}_2\text{O}_8$, and $\text{Sr}_3\text{V}_2\text{O}_8$ phosphors were also synthesized and compared to the $\text{Zn}_3\text{V}_2\text{O}_8$ phosphor in terms of PL emission and internal quantum yield, and it was found that $\text{Zn}_3\text{V}_2\text{O}_8$ is the most efficient phosphor among the other phosphors studied with quantum yield of 60%. The visible light irradiated photocatalytic activity of these phosphors was investigated and it was found that the hydrothermal $\text{Zn}_3\text{V}_2\text{O}_8$ exhibited enhanced activity.

1. Introduction

Recently vanadates have attracted much attention because of their rich structural chemistry which easily adapts to various structural forms like tetrahedral, square-pyramidal, and octahedral coordination environments in various oxidation states. Due to structural variations, they have wide applications which are mainly focused in two directions: one as a photocatalyst and the other as optoelectronic materials [1–5]. According to the previous theoretical studies, the V-3d orbital is located below the analogous d orbitals of other transition metals and lowers the bottom conduction band narrowing the band gap of the semiconductor [6]. Accordingly, vanadates are considered as an effective visible light driven photocatalyst. Many vanadates such as YVO_4 , InVO_4 , and BiVO_4 have been already developed as visible light driven photocatalyst [7–9]. Recently, Shi et al. [10] and Wang et al. [11] found that $\text{Zn}_3(\text{VO}_4)_2$ and its hydrates could work as effective photocatalyst and solar energy transfer material.

There are several reports on vanadium oxide compounds being widely used as multifunctional optical materials: phosphors, luminescent indicators, thermoluminescent detectors, lasing media, scintillators, and so forth. [12]. Meta-, pyro-, and orthovanadates including those containing two constituent cations offer efficient intrinsic luminescence due to the vanadium-oxygen groups in their crystal structure [13]. The potential use of vanadates in phosphor application can be understood as due to their long-wavelength excitation properties, broad emission band, and excellent chemical stabilities [14]. Among other vanadates, $\text{Zn}_3(\text{VO}_4)_2$ has an interesting crystal structure that is of porous framework. The lattice is assembled from layers of Zn octahedra connected by vanadium groups [15]. Nakajima et al. [16] reported the luminescence and color properties of the AVO_3 ($A = \text{K}, \text{Rb}, \text{and Cs}$) and $\text{M}_3\text{V}_2\text{O}_8$ ($M = \text{Mg and Zn}$) prepared by solid state reaction method. Ni et al. reported preparation of $\text{Zn}_3(\text{VO}_4)_2$ microparticles using intermediate $\text{Zn}_3(\text{OH})_2\text{V}_2\text{O}_7 \cdot n\text{H}_2\text{O}$ nanosheets as a precursor prepared by hydrothermal method and investigated their optical properties [17]. 1D and 2D

structures such as wires, fibers, rods, ribbons, or sheets of vanadate based compounds are typically attainable by a hydrothermal reaction of vanadium precursors in the presence of long chain alkylamines [10, 18]. Such reactions usually proceed for a prolonged duration (tens of hours to days). Therefore, a simple and economic process is required for the large scale production of such materials. Combustion synthesis is one of the simplest powder preparation processes in which chemical reaction between fuel and metal nitrates converts the metal ions to the target materials. Materials with high purity, better homogeneity, and high surface area are achieved by the combustion process [19]. Motivated by the broadband emission of $\text{Zn}_3(\text{VO}_4)_2$ phosphor, herein, the structural, morphological, and photoluminescence characterization of $\text{M}_3\text{V}_2\text{O}_8$ ($\text{M} = \text{Zn}, \text{Mg}, \text{Ca}, \text{and Sr}$) synthesized via the combustion method has been investigated, and comparison has been made to the hydrothermal, sol-gel, and solid state samples. Further, photocatalytic properties of these phosphors for the decomposition of organic pollution have been investigated and compared with each other.

2. Experimental

Polycrystalline vanadate $\text{M}_3\text{V}_2\text{O}_8$ ($\text{M} = \text{Zn}, \text{Mg}, \text{Ca}, \text{and Sr}$) was prepared by solution combustion method. Combustion method involves rapidly heating the aqueous solution containing stoichiometric amounts of corresponding metal nitrates, ammonium nitrate, and urea at relatively lower temperatures. Stoichiometric compositions of the redox mixture for solution combustion were calculated using total oxidizing and reducing valences of the species which serve as the numerical coefficients for the stoichiometric balance so that equivalence ratio of oxidant to reductant is equal to unity [20]. Thus the stoichiometry for the $\text{M}_3\text{V}_2\text{O}_8$ material becomes $3\text{M}(\text{NO}_3)_2 + 1(\text{NH}_4)_3\text{V} + 1\text{NH}_4\text{NO}_3 + 10\text{NH}_2\text{CONH}_2$. Appropriate weights of metal nitrates, ammonium nitrate, and urea were dissolved in minimum amount of distilled water at 80°C by stirring till a semitransparent yellowish sol is formed. Then the crucible containing the mixture was inserted inside a muffle furnace maintained at 530°C . Initially, the solution boiled, frothed, foamed, and caught fire. Then the fire propagates on its own, releasing excess amount of heat inside the furnace raising the furnace temperature to about 770°C , leading to the completion of reaction in less than ten minutes. The final foamy voluminous product was crushed and used for characterization such as phase analysis, crystallinity, morphology, and luminescence.

Hydrothermal sample of the $\text{M}_3\text{V}_2\text{O}_8$ phosphor was synthesized according to the previous report for metal vanadates [21]. Accordingly, 9 mmol $\text{Zn}(\text{NO}_3)_2$ was prepared followed by addition of ethyl amine and mixed drop by drop into the 6 mmol $(\text{NH}_4)_3\text{V}$ in hot water with constant stirring. The pH of the resulting solution was adjusted to 9 by nitric acid/ammonia water. Then the mixture was transferred into Teflon lined autoclave maintained at 150°C and kept for 24 h and naturally cooled to room temperature. The white precipitate was centrifuged and washed several times using

distilled water and dried at 120°C for 24 h. Finally, the powder was annealed at 775°C for 12 h.

Sol-gel sample of the $\text{M}_3\text{V}_2\text{O}_8$ phosphor was synthesized according to the previous report for metal vanadates [22]. Nine mmol $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 6 mmol $(\text{NH}_4)_3\text{V}$ solutions were prepared in distilled water and mixed with constant stirring. Citric acid (18 mmol) was added to the solution as chelating agent for the metal ions. The pH of the solution was adjusted to 1 by nitric acid/ammonia water. The resulted transparent solution was heated at 80°C to generate gel. The gel was further dried in oven at 120°C for 24 h to get dry gel. The dry gel was crushed and annealed at 775°C for 12 h. For comparison, samples of $\text{M}_3\text{V}_2\text{O}_8$ were also prepared by solid state reaction method where high purity oxides of the constituents (ZnO and V_2O_3) were mixed thoroughly in mortar and pestle with the help of ethanol and dried in air for 24 h. The mixture is then sintered at 775°C for 12 h unless otherwise specified according to a previous report [16].

Phase identification was carried out using a Shimadzu XRD-6100 X-ray diffractometer with $\text{Cu K}\alpha$ radiation. The morphology of the phosphor particles was characterized by scanning electron microscopy (SEM). SEM measurements were conducted using Hitachi S-3000N SEM instrument. Elemental analysis and mass percentage of the constituent ions were estimated using energy dispersive spectroscopy X-ray mapping (EDX) coupled with SEM. Before SEM measurements, each sample was coated roughly 5 nm in thickness with platinum-palladium using Hitachi E-1030 ion sputter. Photoluminescence (PL) spectra (emission) were recorded using USB 4000-UV-VIS fiber optic spectrometer (Ocean optics). The photoluminescence excitation (PLE) spectra and absolute quantum yield were investigated using Hamamatsu absolute quantum yield measurement instrument with monochromatic xenon lamp and U6039-05 Ver3.4.2 for Quantaaurus-QY software. All the measurements were carried out at room temperature, unless mentioned otherwise.

Photocatalytic experiments were carried out in a 500 mL pyrex glass reactor with a magnetic stirrer as shown in supplementary Figure S8 (in Supplementary Material available online at <http://dx.doi.org/10.1155/2013/410613>). The reactor was kept inside SANYO incubator for temperature control and maintained at 30°C . Suspension of photocatalyst powder was prepared by dispersing 0.1 g photocatalyst in 400 mL aqueous Methylene Blue (MB) solution ($C_0 = 10 \text{ ppm}$, 400 mL) at a suitable height. Before starting the experiments, the photocatalyst suspension was equilibrated in MB solution by stirring for 60 min in the dark. An aliquot was drawn from the reactor, and the concentration of MB was analysed by UV/Visible spectrophotometer (Ultrospec 1100pro, Amersham Biosciences, $\lambda_{\text{max}} = 665 \text{ nm}$), which was treated as zero-time concentration in each experiment. Next, the reactor was exposed to 60 W halogen-tungsten lamp (Nakamura, Tokyo, Japan) having light output from about 400 nm to 900 nm, placed on the top of the reactor with about 5 cm spacing between the light bulb and the reactor. The degradation of MB during the reaction was monitored over time.

FIGURE 1: XRD patterns of series of $\text{Zn}_3\text{V}_2\text{O}_8$ phosphor prepared at different temperatures.

3. Results and Discussion

X-ray diffraction pattern of $\text{Zn}_3\text{V}_2\text{O}_8$ phosphor prepared at various temperatures is shown in Figure 1. At very low sintering temperatures of 500°C and 600°C, the $\text{Zn}_2\text{V}_2\text{O}_7$ phase predominated as indexed by the error bars. When temperature was increased to 750°C, pure $\text{Zn}_3\text{V}_2\text{O}_8$ phase well indexed with the JCPDS card number 73-0021 was observed (here shown only at 800°C) as indexed in Figure 1(d). The $\text{Zn}_3\text{V}_2\text{O}_8$ consists of orthorhombic crystal structure with Cmca space group. The crystal structure consists of isolated VO_4 tetrahedra [12]. Kurzawa and Bosacka also reported the existence of α and β forms of $\text{Zn}_3\text{V}_2\text{O}_8$, the former being the low temperature form and the latter the high temperature form and the transition temperature being 795°C [23]. Its lattice parameters observed from the XRD analysis are $a = 8.298 \text{ \AA}$, $b = 8.34 \text{ \AA}$, $c = 6.11 \text{ \AA}$, and $\beta = 111.5^\circ$, which is in accordance with a previous report [24]. According to Zhang et al., pure phase of $\text{Zn}_3\text{V}_2\text{O}_8$ is formed from the stoichiometric mixture of high purity ZnO and V_2O_5 heated above 700°C for 12 h.

The excitation and emission profiles of various $\text{M}_3\text{V}_2\text{O}_8$ ($\text{M} = \text{Zn, Mg, Ca, and Sr}$) were presented in Figure 2. The XRD patterns shown in Figure S1 indicated that the phases formed were $\text{M}_3\text{V}_2\text{O}_8$ for the corresponding metals. These phosphors can be excited by the light source from UV to visible light (260 nm to above 450 nm).

The absorption band in the PLE spectra of vanadate phosphors is due to the charge transfer (CT) of an electron from the oxygen 2p orbital to the vacant 3d orbital of V^{5+} ion in tetrahedral VO_4 with T_d symmetry [12, 16]. Distortion in crystal structure occurs due to variation of size of cations in various $\text{M}_3\text{V}_2\text{O}_8$, consequently changing the PLE excitation and PL emission bands. The $\text{Ca}_3\text{V}_2\text{O}_8$ has its main excitation spectrum in the UV region (below 330 nm), but Sr and Mg components showed red shift and extended up to 370, while Zn component extends further to 400 nm. In all four phosphors, the shoulder of the excitation spectrum extends up to 450 nm making them usable as visible light

FIGURE 2: PLE (dotted lines) and PL (solid lines) spectra of $\text{M}_3\text{V}_2\text{O}_8$ ($\text{M} = \text{Zn, Mg, Ca, and Sr}$). Inset shows the digital micrograph of corresponding phosphors in black light irradiation.

driven photocatalyst. Figure 2 also shows the PL emission profiles of these phosphors excited by 360 nm light. All the $\text{M}_3\text{V}_2\text{O}_8$ ($\text{M} = \text{Zn, Mg, Ca, and Sr}$) phosphors exhibited broadband visible luminescence; however, their luminescence intensity varied drastically according to the metal cations and their ionic size ($\text{Mg}^{2+} = 72$, $\text{Ca}^{2+} = 100$, $\text{Zn}^{2+} = 74$, and $\text{Sr}^{2+} = 118 \text{ pm}$ in octahedral sites). The broadband emission spectra of the $\text{M}_3\text{V}_2\text{O}_8$ phosphors consisted of two broad peaks corresponding to the emissions from excited $^3\text{T}_2$ and $^3\text{T}_1$ states to the $^1\text{A}_1$ ground state of V^{5+} ion in tetrahedral VO_4 with T_d symmetry, respectively [12, 16]. As depicted in the digital micrograph taken in black light irradiation (from 310 nm to 410 nm) in the inset figure (Figure 2), the Zn component is the brightest that decreased in the order $\text{Zn} \gg \text{Mg} \sim \text{Sr} > \text{Ca}$. Corresponding absolute quantum yield (QY) excited by 260 nm light was recorded which was 60%, 18%, 15%, and 2% for the Zn, Mg, Sr, and Ca components, respectively. The QY is defined as the ratio of numbers of photons emitted from a sample to those absorbed by the samples. The high value of quantum yield of $\text{Zn}_3\text{V}_2\text{O}_8$ with respect to the $\text{Mg}_3\text{V}_2\text{O}_8$, $\text{Sr}_3\text{V}_2\text{O}_8$, and $\text{Ca}_3\text{V}_2\text{O}_8$ is due to the increasing excitation diffusion assisted by the hybridization of the Zn 3d and O 2p orbitals for the valence band and Zn 4s and V 3d orbitals for the conduction band [16]. The CIE color coordinate of the $\text{M}_3\text{V}_2\text{O}_8$ ($\text{M} = \text{Zn, Mg, Ca and Sr}$) phosphors during black light irradiation is presented in Figure S2. The emission color of these phosphors slightly varied from each other as denoted by (x, y) values of (0.42, 0.49), (0.43, 0.46), (0.42, 0.42), and (0.34, 0.39) for Zn, Mg, Sr, and Ca components, respectively.

Effect of boric acid as a flux for the PL intensity of the $\text{Zn}_3\text{V}_2\text{O}_8$ phosphor was studied and presented in Figure 3. Slight red shift was observed in the emission peak position of the boric acid rich samples. Moreover, addition of small amount of boric acid fluxes ($\sim 10 \text{ mol\%}$) increased the PL intensity dramatically. However, further rise in the boric acid concentration decreased the PL intensity. The absolute quantum yields of the 0, 10, 40, and 80 mol% boric acid containing $\text{Zn}_3\text{V}_2\text{O}_8$ phosphors are 8.7%, 57%, 41.5%, and

FIGURE 3: Boric acid flux dependent PL emission spectra of $\text{Zn}_3\text{V}_2\text{O}_8$ phosphor.

13.9%, respectively. The excitation process ($^1\text{A}_1 \rightarrow ^1\text{T}_1, ^1\text{T}_2$) in the $\text{Zn}_3\text{V}_2\text{O}_8$ phosphor with ideal T_d symmetry is allowed, but intersystem crossing ($^1\text{T}_1, ^1\text{T}_2 \rightarrow ^3\text{T}_1, ^3\text{T}_2$) and luminescence process ($^3\text{T}_1, ^3\text{T}_2 \rightarrow ^1\text{A}_1$) are forbidden due to spin selection rule [25]. Addition of small amount of B^{3+} into the V^{5+} site is supposed to distort the VO_4 tetrahedron due to difference in size and thus the forbidden process is partially allowed due to spin-orbit interaction and increases the PL emission intensity and quantum yield [12]. Further, flux is the substance which facilitates the growth of crystals at relatively low sintering condition favorable for the PL emission. However, excess of H_3BO_3 flux actively participates in the reaction with the host composition, especially, vanadium, and generates $\text{Zn}_3\text{B}_2\text{O}_6$ and other Zn-borates [24]. These impurity phases lower the PL intensity of the $\text{Zn}_3\text{V}_2\text{O}_8$ phosphor.

Figure 4 shows the effect of stoichiometry of the starting materials on the PL emission intensity of the $\text{Zn}_3\text{V}_2\text{O}_8$ phosphor. Five different samples with various Zn and V moles proportions were prepared according to different R ($R = \text{Zn/V}$) values. R value of 1.58 (0.1 mole V-decreased), 1.55 (0.1 mole Zn-added), 1.5 (stoichiometric), 1.45 (0.1 mole Zn-decreased), and 1.42 (0.1 mole V-added) were prepared where former two are Zn excess while the latter two are V excess over stoichiometric compositions. It is found that Zn-excess or Zn-deficit (keeping V-stoichiometry) compositions do not favor the PL emission intensity. But V-excess composition with R value of 1.42 exhibited higher PL emission intensity over stoichiometric and other compositions. We have measured the XRD profiles of the $\text{Zn}_3\text{V}_2\text{O}_8$ phosphors prepared with various R values; however, there were no any other phases appearing under the present composition (Figure S3). Also the XRD peak positions and peak intensity were not much pronounced with small change in the composition of the starting materials. As already discussed, the broadband emission spectra of vanadate phosphors are due to the charge transfer (CT) of an electron from the oxygen

FIGURE 4: Effects of V and Zn stoichiometry on the PL emission intensity of $\text{Zn}_3\text{V}_2\text{O}_8$ phosphor.

FIGURE 5: Effects of synthesis temperature on the PL emission intensity of $\text{Zn}_3\text{V}_2\text{O}_8$ phosphor.

2p orbital to the vacant 3d orbital of V^{5+} in tetrahedral VO_4 . The luminescence is attributed to the $^3\text{T}_2, ^3\text{T}_1 \rightarrow ^1\text{A}_1$ transitions [12, 16]. The V-excess composition led to increasing the CT efficiency and increased the PL intensity. However, the factors that affect the luminescence efficiency of vanadate phosphors with a wide range of internal quantum efficiency (η) values are still unclear and have to be elucidated.

Figure 5 exhibits the effect of sintering temperature on the PL emission intensity of the $\text{Zn}_3\text{V}_2\text{O}_8$ phosphor. On increasing the sintering temperature, the PL emission intensity gradually increased and reached maximum at around 775°C and decreased slightly above it. It is noted that, at very low sintering temperatures (below 700°C), another phase $\text{Zn}_2\text{V}_2\text{O}_7$ predominated as shown in the XRD diagram in Figure 1.

FIGURE 6: Effects of synthesis methods on the PL emission intensity of $\text{Zn}_3\text{V}_2\text{O}_8$ phosphor.

Li et al. [26] reported that, at lower sintering temperatures, $\text{Zn}_2\text{V}_2\text{O}_7$ and ZnO phases dominated above $\text{Zn}_3\text{V}_2\text{O}_8$ phase while at higher temperatures $\text{Zn}_4\text{V}_2\text{O}_9$ phase appeared as the major phase. In our study, 775°C sintered product contained the minimum impurity phases. Thus, the highest PL intensity at 775°C might be due to the formation of the least impurity containing $\text{Zn}_3\text{V}_2\text{O}_8$ phase with higher crystallinity. Further, the $\text{Zn}_3\text{V}_2\text{O}_8$ phosphors with various RE^{3+} additives (where $\text{RE} = \text{Eu}, \text{Ce}, \text{Tb}, \text{and Bi}$; each being added 5 mol%) were prepared and their PL emission profiles were investigated. None of them are found to enhance the PL emission of the $\text{Zn}_3\text{V}_2\text{O}_8$ phosphor as depicted in Figure S4. Also effect of various transition metal ions, Tn^{n+} , substitution (where $\text{Tn} = \text{Ti}, \text{Cr}, \text{Mn}, \text{Co}, \text{Cu}$; each being added 10 mol%) on the PL emission brightness were investigated and presented in Figure S5. However, there is no increase in the PL intensity of the $\text{Zn}_3\text{V}_2\text{O}_8$ phosphor. On the contrary, all the transition ions replacements decreased the PL brightness in the order $\text{Cu} \approx \text{Co} > \text{Mn} > \text{Cr} \gg \text{Ti}$. Further, various ions substitutions starting from monovalent to tetravalent (Na^+ , Ag^+ , Mg^{2+} , Sr^{2+} , Al^{3+} , and Si^{4+} ; each being 5 mol%) were substituted to create defects on the $\text{Zn}_3\text{V}_2\text{O}_8$ host and presented in Figure S6, but none of them are effective for the improvement of PL brightness of $\text{Zn}_3\text{V}_2\text{O}_8$ phosphor, and rather they decreased the PL brightness of the $\text{Zn}_3\text{V}_2\text{O}_8$ phosphor in the order $\text{Ag} \gg \text{Si} > \text{Na} \approx \text{Mg} > \text{Al} > \text{Sr}$.

The $\text{Zn}_3\text{V}_2\text{O}_8$ phosphor was prepared by four different methods, namely, combustion, hydrothermal, modified sol-gel, and traditional solid state reactions. The corresponding PL emission spectra were recorded and presented in Figure 6. The highest PL intensity was found for the combustion synthesized samples and it was decreased in the order of combustion $>$ hydrothermal $\gg$ sol-gel $>$ solid state. From the XRD analysis (omitted here), the phase formation under all methods was the same. However, they have completely different morphologies. As shown in Figure 7(a), spherical particles with particles dimension between 1 and 3 μm were

formed when the samples were prepared by the combustion method. The combustion method is the rapid and economic method to produce large scale of phosphor particles with homogeneous particles distribution. Porous microstructure is the identity of this process which is useful for the catalytic and surface technology. Due to spherical particle shape and homogeneous size distribution, the PL emission intensity is better. The hydrothermally treated sample (at 150°C for 24 h and sintered at 775°C for 12 h) showed thin plate like particles which get connected with each other and formed flower like structure. During the hydrothermal treatment, $\text{Zn}_3\text{V}_2\text{O}_7(\text{OH})_2(\text{H}_2\text{O})_2$ was formed as reported by Shi et al. which exhibits flower like microstructures [10]. The flower like microstructure is composed of very thin (about few nanometers) but wide (1–5 μm) flakes as shown in Figures 8(a) and 8(b). The average size of the flowers is 3–5 μm which is comparable to the wideness of the flakes.

The interesting point is that the hydrothermal product even after thermal treatment at 700°C retained its original microstructure as shown in Figure 8(c); however, the particles thickness grew rapidly making a bit thicker plates. But, as thermal treatment temperature was increased to 800°C , the flake like particulates gradually destroyed that might be due to the melting of the flakes as seen in Figure 8(d). The detail of the morphology control during hydrothermally synthesized $\text{Zn}_3\text{V}_2\text{O}_8$ phosphor and its hydrates has been discussed earlier [10, 11, 17, 18]. Cylindrical particles of 10–12 μm long and 2–3 μm diameter were formed by the sol-gel method. However, much bigger and rough microstructure was observed in case of solid state samples. The typical EDX spectra of $\text{Zn}_3\text{V}_2\text{O}_8$ phosphor coupled with SEM were presented in Figure 7(e). The clear peaks of Zn, V, and O and their peak intensity are in accordance with the compound $\text{Zn}_3\text{V}_2\text{O}_8$. Thus, it is concluded that the morphology of the $\text{Zn}_3\text{V}_2\text{O}_8$ phosphor can be well controlled by the synthetic methods as well, and the photoluminescence characteristics depend on the morphology of the phosphor particles.

Figure 9 shows the thermal quenching behavior of the $\text{Zn}_3\text{V}_2\text{O}_8$ phosphor at different temperatures from room temperature to 500°C . The relative peak intensity of the $\text{Zn}_3\text{V}_2\text{O}_8$ phosphor decreased marginally with the raise of temperature as shown in the inset in Figure 9. It is believed that with the raise of temperature the PL intensity decreased due to vibrational loss of the excited electrons. This process limits the application of phosphors at relatively hot temperatures or if the device gets heated during operations. The $\text{Zn}_3\text{V}_2\text{O}_8$ phosphor showed good thermal stability and can be used up to 60°C with marginal loss of PL intensity.

Based on the absorption (not shown here) and excitation spectra (Figure 3), it is found that the $\text{M}_3\text{V}_2\text{O}_8$ phosphor exhibits photoabsorption ability from UV to visible light regions. Thus, it exhibits UV-Vis light driven photocatalysis. Methylene Blue (MB) degradation under visible light irradiation was carried out using various samples of $\text{M}_3\text{V}_2\text{O}_8$ phosphors ($\text{M} = \text{Ca}, \text{Sr}, \text{Mg}, \text{and Zn}$) prepared at 775°C for 12 h by hydrothermal method, and the results are presented in Figure 10. Under tungsten-halogen light

FIGURE 7: SEM micrographs of the $\text{Zn}_3\text{V}_2\text{O}_8$ phosphor synthesized at 775°C by different methods: (a) combustion, (b) hydrothermal, (c) gel-combustion, (d) solid state, and (e) typical EDX profile coupled with SEM.

irradiation (light of nearly 400 nm to 900 nm), MB degradation was achieved in all the samples; however, the rate of MB degradation was faster in the $\text{Zn}_3\text{V}_2\text{O}_8$ phosphor than in $\text{Mg}_3\text{V}_2\text{O}_8$, $\text{Sr}_3\text{V}_2\text{O}_8$, and $\text{Ca}_3\text{V}_2\text{O}_8$ phosphors. Further, the synthesis method of the $\text{Zn}_3\text{V}_2\text{O}_8$ phosphor has a significant effect on the MB degradation rate. The MB degradation rate was highest for the hydrothermally synthesized $\text{Zn}_3\text{V}_2\text{O}_8$ phosphor compared to the combustion and other methods which are the contrary to the PL emission efficiency.

The rate constants determined for the MB degradation for the hydrothermal, combustion, sol-gel, and solid state samples are 0.0017, 0.0015, 0.0009, and 0.0007, respectively, as presented in Figure S7 and Table 1. The highest rate of MB degradation of the hydrothermal sample might be ascribed to a large surface area of the sample as shown in Table 1 which is very similar to the results described by Shi et al. [10]; however, they have carried out the photocatalytic experiments for the samples treated at low temperatures.

FIGURE 8: SEM micrographs of $\text{Zn}_3\text{V}_2\text{O}_8$ phosphor synthesized by hydrothermal methods: (a) hydrothermally treated at 150°C for 24 h, (b) image “a” at higher magnification, (c) hydrothermally treated at 150°C for 24 h and then treated at 700°C for 12 h, and (d) hydrothermally treated at 150°C for 24 h and then treated at 800°C for 12 h.

TABLE 1: Photophysical and photocatalytic activities of $\text{Zn}_3\text{V}_2\text{O}_8$ phosphor synthesized by different methods.

Preparation method	Annealing condition	Emission maxima (nm)	PL quantum yield (%)	Particle size (μm)	BET surface area (m^2/g)	Rate constant (min^{-1})
Hydrothermal	775°C 12 h	580	52	3–5	8.16	0.0017
Combustion	530°C 10 min ($\sim 770^\circ\text{C}$)	580	60	1–3	5.81	0.0015
Sol-gel	775°C 12 h	580	32	10–12	2.01	0.0009
Solid state	775°C 12 h	580	26	10–30	1.06	0.0007

The rate of MB degradation for the combustion sample is comparable to that for the hydrothermal samples owing to its better feasibility in the dual purpose of lighting as well as photocatalytic uses.

4. Conclusion

$\text{M}_3\text{V}_2\text{O}_8$ ($\text{M} = \text{Ca}, \text{Sr}, \text{Mg}, \text{and Zn}$) phosphors were successfully synthesized by chemical combustion method. These vanadate phosphors exhibited broadband emission from 440 nm to over 750 nm due to charge transfer transition

in the VO_4 tetrahedra, and colors of these luminescent materials are yellowish white with slight variation in CIE chromaticity. $\text{Zn}_3\text{V}_2\text{O}_8$ exhibited the brightest luminescence which goes in the decreasing order as $\text{Zn}_3\text{V}_2\text{O}_8 > \text{Mg}_3\text{V}_2\text{O}_8 \sim \text{Sr}_3\text{V}_2\text{O}_8 > \text{Ca}_3\text{V}_2\text{O}_8$ with corresponding quantum yields of 60%, 18%, 15%, and 2%, respectively. Addition of 10 mol% boric acid flux enhanced the PL intensity of $\text{Zn}_3\text{V}_2\text{O}_8$ phosphor by more than 6-fold with slight red shift of the emission peak position. V-excess composition favors the PL emission intensity over other compositions. The PL emission intensity of the $\text{Zn}_3\text{V}_2\text{O}_8$ phosphor synthesized by different methods

FIGURE 9: Temperature dependent relative PL emission intensity of $\text{Zn}_3\text{V}_2\text{O}_8$ phosphor. Inset shows the emission spectra of $\text{Zn}_3\text{V}_2\text{O}_8$ phosphor as a function of temperature.

FIGURE 10: Photocatalytic MB degradation under tungsten-halogen light irradiation over $\text{M}_3\text{V}_2\text{O}_8$ ($\text{M} = \text{Zn}, \text{Mg}, \text{Sr}, \text{and Ca}$) phosphors.

was in the order combustion > hydrothermal > sol-gel > solid state. These vanadate phosphors exhibited photocatalytic degradation of MB under visible light irradiation, and the rate of degradation of MB for the $\text{Zn}_3\text{V}_2\text{O}_8$ was in the order hydrothermal > combustion > sol-gel > solid state. Thus, the $\text{Zn}_3\text{V}_2\text{O}_8$ phosphor is a promising material for the dual application of lighting as well as photocatalyst.

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