

Characterization supported improved method for the synthesis of bismuth vanadate and its assessment with conventional synthetic route

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Abstract: The objective of present research work was to develop simplest synthetic route for BiVO_4 pigment. The economical synthetic route was planned to put forward a time efficient reaction. The challenge here was to reduce complexity of the conditions like high temperature and pH, use of multiple chemical reagents and catalyst/s.

Proposed synthetic route involves calcination of bismuth salt and vanadium pentoxide admixture without the addition of any alkaline metals or alkaline earth metals and in absence of any organic and/or inorganic compound as a reagent or as a catalyst nor even as a solvent. The said synthesis produces monoclinic BiVO_4 phase in single step, which is more stable than tetragonal BiVO_4 , a less stable intermediate product of conventional wet chemical co-precipitation (WCCP) reaction processes.

BiVO_4 prepared by proposed synthetic route has been checked for its purity, thermal stability and other physicochemical properties including colour analysis. The research article provides comparative results for conventional WCCP reaction and improved solid state reaction.

Keywords: Synthesis of BiVO_4 , Structural, Thermal and Colour analysis.

I. Introduction

The pigment industry strive hard on finding new products that meet the need of the market, but further improvements of existing and already commercialized pigment plays an important role as well [1].

Bismuth vanadate (BiVO_4) is a representative of "complex inorganic coloured pigments" or CICP. More specifically bismuth vanadate is a mixed-metal oxide pigment. It is used as a pigment since the 1970s but was first synthesised in 1924 for pharmaceutical purposes which has been reported in patent DE 422947 [2].

In nature it exists in three crystal structures viz, orthorhombic, monoclinic and tetragonal which are mineralogical named as Pucherite, Clinobisvanite and Deyerite respectively [3]. The natural deposits of BiVO_4 are not of significant importance to pigment industry. So in industry BiVO_4 is manufactured by co-precipitation reaction followed by calcination or by solid state process using appropriate starting materials [4].

Synthetically reported BiVO_4 are of three different types– tetragonal zircon-type structure, tetragonal scheelite structure (high-temperature phase) and monoclinic distorted scheelite structure or fergusonite structure. The phase transition between monoclinic scheelite structure and tetragonal scheelite structure of BiVO_4 reversibly occurs at about 255 °C (ferroelastic to paraelastic transition), whereas the irreversible transition from tetragonal zircon type structure to monoclinic BiVO_4 occurs after heat treatment at 400–500 °C and cooling to room temperature [5].

Synthetically prepared BiVO_4 pigment has brilliant greenish yellow colour. Due to its nontoxic nature and photochromic property [1,6] it is considered to be a promising alternative to toxic lead chromate and cadmium sulphide pigments in automobile and paint industry. Thermally stable, nontoxic BiVO_4 has gained a market value as a colourant of choice for food contact plastics [7].

According to patent literature, a preliminary patent about the method for the preparation of pure bismuth vanadate particularly for therapeutic purposes was reported in 1924 [2]. But, the fact that bismuth vanadate is a thermally stable and acid resistant pigment was discovered by E. I. Du Pont de Nemours and company in 1977 [8,9]. Monoclinic phase bismuth vanadate was discovered in 1978 [10,11].

In consideration of available literature, synthesis process of bismuth vanadate can be divided into two categories wet chemical co-precipitation (WCCP) reaction and solid state reaction.

The category of wet chemical co-precipitation (WCCP) reaction includes simple wet chemical co-precipitation (WCCP) method, combination of calcination and WCCP, hydrothermal method using autoclave, pyrolysis method and combination of microwave assisted WCCP method. Whereas the category of solid state reaction includes combination of calcination and/ or mechanical treatment (ball milling), catalysts assisted solid state reaction, microwave based solid state reaction.

WCCP method is a precipitation process which occurs as a reaction between bismuth nitrate and ammonium vanadate, solutions of which are prepared in acidic and alkaline medium respectively [12-17]. This

method has a drawback of synthesising tetragonal phase BiVO_4 instead of stable monoclinic compound. To produce monoclinic BiVO_4 , it needs to be processed further through annealing (calcinations) or ball milling process. Hydrothermal method in combination with WCCP method is a temperature and pressure dependent process [5,17-28]. Pyrolysis involves different stages of reactions along with WCCP method at different temperature and concentration of respective chemicals and organic reagents, making the process complex and cumbersome [29-31]. The phase transition of tetragonal to monoclinic BiVO_4 may be obtained by microwave irradiation of wet chemical co-precipitated solution [32]. BiVO_4 synthesised by sonochemical route involves the exposure of co-precipitated mixture to high-intensity ultrasound radiations [33]. A new technological route (low-temperature molten salt method) has been reported for the preparation of BiVO_4 . In this process the product obtained by co-precipitation route was mixed with a complex-salt $\text{LiNO}_3\text{-NaNO}_3$ by ball milling which is followed by calcinations of the product. Finally, the product is washed by hot water and filtered [34].

In solid state reaction, homogeneous mixing of stoichiometric quantities of bismuth oxide and vanadium pentoxide is carried out followed by a mechanical treatment particularly ball milling and/ or calcination. It yields a stable monoclinic compound [17,29,35-37]. Metal vanadate prepared by using a domestic microwave oven is reported to be a rapid time scale method than the conventional solid state procedure [38,39].

The significant drawback of WCCP method in combination to any other foresaid related process for the synthesis of BiVO_4 is multi-parameter dependent. However, it produces hazardous products causing damage to environment and needs to be treated further to neutralize prior to release and/or reuse. Another limitation of the reaction is that it involves multiple steps and processes to obtain a highly stable monoclinic bismuth vanadate with lesser yield.

Major limitations of WCCP method have been overridden by solid state reaction with regards to number of steps, chemical compositions, but the method is still not that rapid in respect of the duration required for synthesis of BiVO_4 . Nevertheless, the present research work makes use of a solid state synthetic route which is found to be efficient with regards to temperature, time and steps involved.

II. Experimental

2.1 Chemicals

All the chemicals used were of AR grade and used as received from Merck India, without further purification. Deionised water was used for wet chemical synthesis.

2.2 Material Synthesis

2.2.1 Synthesis of bismuth vanadate by conventional wet chemical method

Conventional method for the synthesis of monoclinic bismuth vanadate involves two consecutive steps. The preliminary step is to prepare tetragonal bismuth vanadate by wet chemical co-precipitation reaction. This tetragonal bismuth vanadate is less stable in comparison with monoclinic bismuth vanadate. To obtain monoclinic bismuth vanadate the dried tetragonal bismuth vanadate is to be calcined for longer period of time at high temperature.

Reagent preparation

Reagent A: Acidic solution of bismuth nitrate was prepared by dissolving 12.125 g of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (mol. weight 485.07) in 250 ml (1 M) HNO_3 solution.

Reagent B: Alkaline solution of ammonium vanadate was prepared by dissolving 2.922 g of NH_4VO_3 (mol. weight 116.98) in 250 ml (1 M) NaOH solution.

As the respective compounds are not readily soluble in corresponding medium they are vigorously shaken for several minutes for giving a clear solution.

Reagent B prepared by foresaid method was added drop wise to reagent A with constant stirring at a 60 °C. The resulting yellow precipitate containing solution was allowed to homogenise further for one hour. During the synthesis process pH of the solution was maintained neutral by suitable buffer solution.



The yellow pigment was filtered through sintered glass crucible. During filtration the residue was washed several times by hot deionised water to remove all the ions and salts formed during the process of co-precipitation reaction. The yellow pigment was dried in oven at 100 °C for about 24 hours. The dried pigment was characterised without further processing.

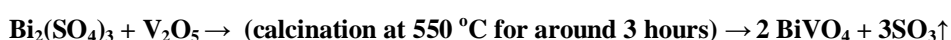
It was confirmed from the results of the characterisation that the yellow pigment synthesised by coprecipitation route is of tetragonal BiVO₄. To obtain monoclinic BiVO₄, the pigment was allowed to calcine at 550 °C in silica crucible for 12 hours.

2.2.2 Synthesis of bismuth vanadate by improved solid state route

Monoclinic bismuth vanadate was synthesised by single step solid state reaction. 7.06 g of anhydrous bismuth sulphate Bi₂(SO₄)₃ (mol. weight 706.14) was mixed with 1.81 g of vanadium pentoxide V₂O₅ (mol. weight 181.89). The mixture was triturated in an agate mortar-pestle for approximately 5 minutes which was followed by calcination at 550 °C for ~2 hours in a silica crucible. After 2 hours the crucible was removed from the furnace. The hot mass was immediately triturated in an agate mortar-pestle for another 5-10 minutes. The compound was calcined for additional one hour. At the end, the resulting compound was again triturated. In this process brownish white powder mixture got converted to greenish yellow pigment.

Important feature of this solid state reaction is that this reaction is carried out without the addition of any alkaline metal or alkaline earth metal and in absence of any organic and/or inorganic compound as a reagent or as a catalyst nor even as a solvent.

For the proposed synthetic route the reaction may be written as



2.3 Characterizations

2.3.1 FT-IR study

For the present research work FT-IR study was carried out on SHIMADZU FTIR-8101 in the range 4600 to 400 cm⁻¹.

2.3.2 Thermal analysis

Thermal study of synthesised pigments was carried out on Perkins Elmer Diamond TGA/DTA analyser at heating rate of 10 °C/min in argon environment up to 1000 °C using platinum foil crucible.

2.3.3 X-Ray diffraction (XRD) study

Synthesised pigments were subjected to XRD analysis in a PANalytical X'Pert PRO MPD - Multi Purpose X-Ray diffractometer and phase analysis was carried out using X'Pert Highscore.plus software.

2.3.4 Scanning Electron Microscopy (SEM)

For the synthesised pigments SEM images were scanned on JEOL JAPAN JXA-840A Electron probe Microanalyzer. Prior to loading the pigment sample to the microanalyzer it was coated with gold layer (Balzers Union SCD-040, Germany).

2.3.5 Visible reflectance spectra

Visible reflectance spectra were recorded using Cintra 10e (GBC, Australia) spectrophotometer. BaSO₄ was used as a reference and diluent. Samples were pressed in the form of disc. The sample to BaSO₄ ratio was 1:3. Mixing was done for several minutes with agate mortar-pestle. The spectrum was recorded in the wavelength range 420-720 nm at the data interval of 10 nm.

2.3.6 Colour analysis

In order to describe the degree of colour change due to illumination quantitatively, diffuse reflectance spectroscopy was used to characterise optical properties of pigments after illumination, qualitatively. In case of pigments, attention is primarily focused on colour sensation, which is restricted to the visible part of spectra (380–780 nm). It is accomplished by using diffused reflectance spectroscopy.

Nonprofit organization CIE (Commission Internationale de l'Eclairage) determined standard values that are used worldwide to measure colour. The values used by CIE are called L*, a* and b* and the colour measurement method is called CIELAB. L* represents the difference between light (where L*=100) and dark (where L*=0). A* represents the difference between green (-a*) and red (+a*), and B* represents the difference between yellow (+b*) and blue (-b*).

III. Results And Discussion

3.1 Analysis of FT-IR spectra

A broad but less intense band observed in the region 3000 – 3800 cm⁻¹ in all the three spectra (Fig.1. A, B and C) can be attributed to H₂O molecule assigning O–H stretching mode which is believed to contribute the broad band at around 3400 cm⁻¹.

The distinction between structural and absorbed water arises from the position of the O–H bend. For absorbed water, H–O–H bend typically occurs at $160 - 1600 \text{ cm}^{-1}$ whereas for structural water an M–O–H bend occurs below 1200 cm^{-1} , the exact position depending on the nature of the M species. Strong V–OH stretch absorptions in low frequency range prevent definite identification of possible V–OH and/or Bi–OH bends [13].

Fig.1(A) and (B) show a single broad band in the region $430 - 950 \text{ cm}^{-1}$ with a shoulder at 700 cm^{-1} merging all the possible V–O and/or Bi–O stretching frequencies. Comparing spectra (A) and (B), focus is only on the reduction of band intensity in the region $3000 - 3800 \text{ cm}^{-1}$ which is a possible result of calcination process but does not imply any change for V–O and/or Bi–O vibrations.

FT-IR spectrum Fig.1(C), recorded for BiVO_4 synthesised by improved solid state route shows distinct V–O stretching frequencies in the range $430 - 950 \text{ cm}^{-1}$ assigning vibrations $\nu_1 \text{VO}_4^{3-}$ around 870 cm^{-1} , $\nu_3 \text{VO}_4^{3-}$ around 820 cm^{-1} , $\nu_4 \text{VO}_4^{3-}$ at 430 cm^{-1} and resultant $\nu_2 \text{VO}_4^{3-}$ is expected to be at around 350 cm^{-1} in accordance with the previous literature [5]. Furthermore, in agreement with prior reports [40] a band at 520 cm^{-1} shows the existence of stretching symmetrical vibrations for Bi–O bond. The band at 1025 cm^{-1} is due to the V–O stretching of V_2O_5 or lower valent vanadium oxide [41]. S=O stretching is generally found in the region $1300 - 1400 \text{ cm}^{-1}$. Absence of any peak in this particular region implies that the pigment BiVO_4 is free from sulphur impurity.

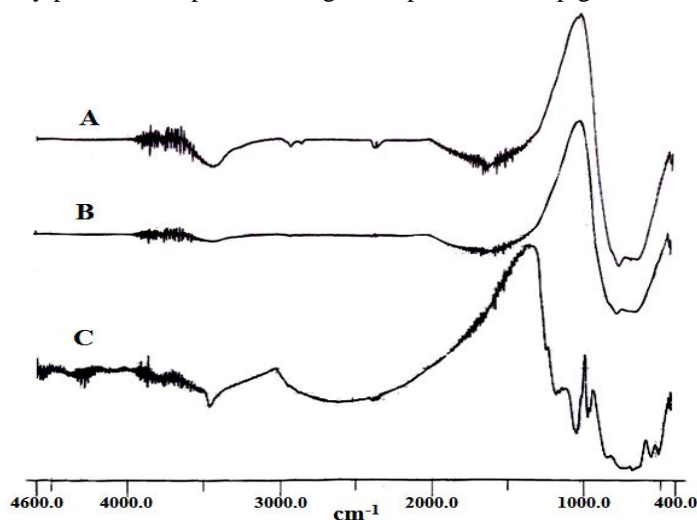


Figure 1. FT-IR spectra for synthesised BiVO_4 (A) by WCCP method (B) by WCCP + calcinations. (C) by improved solid state route.

3.2 Thermal analysis

The TGA curve in Fig.2 displays the mass loss of 0.80% in the interval of $316.36 \text{ }^\circ\text{C}$ and $348.85 \text{ }^\circ\text{C}$. The weight loss may be featured by the presence of structural water, analogous with FT-IR spectra recorded for BiVO_4 synthesised by co-precipitation route (Fig.1.(A)), which admits the presence of structural water molecule, but contradicts any chemical impurity or presence of any unreacted agent. It can be confirmed by Fig.3 which skips the mass loss plateau, as an effect of calcination, resulting in a steady TGA curve.

Considering the thermal behaviour of bismuth vanadate, no significant decomposition of its own structure should be expected [17]. Evidence to this no exothermic or endothermic peak were observed in case of DTA curve in Fig.2 and 3.

Fig. 4 provides important information to establish the conditions for solid state synthesis process. The TGA curve in the initial event shows the mass loss of 3.95% in the interval of $196.56 \text{ }^\circ\text{C}$ to $212.52 \text{ }^\circ\text{C}$ and in the other event, mass loss of 10.13% in the interval of $551.70 \text{ }^\circ\text{C}$ to $582.88 \text{ }^\circ\text{C}$ is observed. The data roughly supports the prediction of synthesis (calcination) temperature to be in the range of 500 to $550 \text{ }^\circ\text{C}$. A single endothermic peak observed in DTA curve in Fig. 4 gives the peak area of 499.37 mJ with heat of reaction i.e. enthalpy change, $\Delta H = 66.811 \text{ J/g}$.

In support of the data obtained from Fig. 4, the decomposition of precursor for the formation of BiVO_4 , is an evidence to Fig. 5. Furthermore, in Fig. 5, the TGA curve has no kind of elevation and even the DTA curve displays no exothermic or endothermic peak which is the similar case as in Fig. 3. Thus, the TGA and DTA study is in good agreement with the formation of BiVO_4 by new route discussed in present context.

Additional finding can be drawn for the similar format of curve in Fig. 3 and 5 that there is steady decrease in weight upto $\sim 900 \text{ }^\circ\text{C}$ but afterwards there is a gradual weight loss. This change may refer to melting point of $\text{BiVO}_4 \sim 900 \text{ }^\circ\text{C}$. For our findings no reference is available in support of melting point of BiVO_4 .

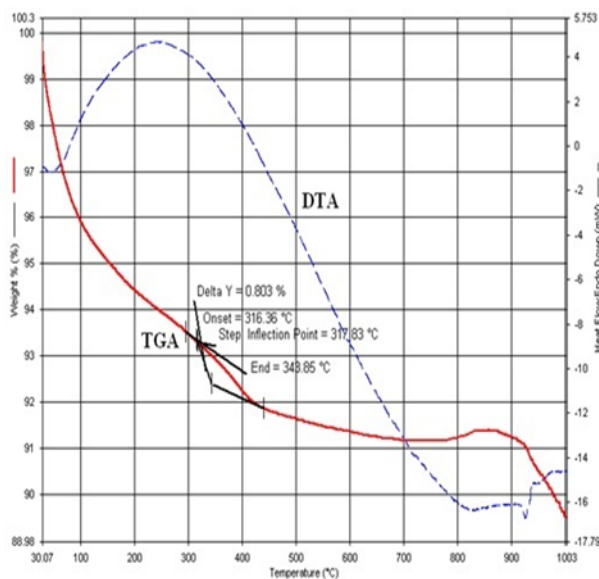


Figure 2. TGA and DTA curve for BiVO_4 synthesised by WCCP route

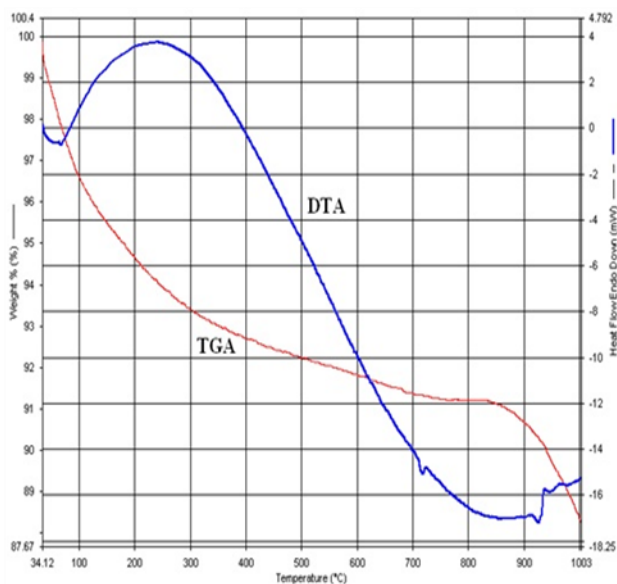


Figure 3. TGA and DTA curve for BiVO_4 synthesised by WCCP + calcinations.

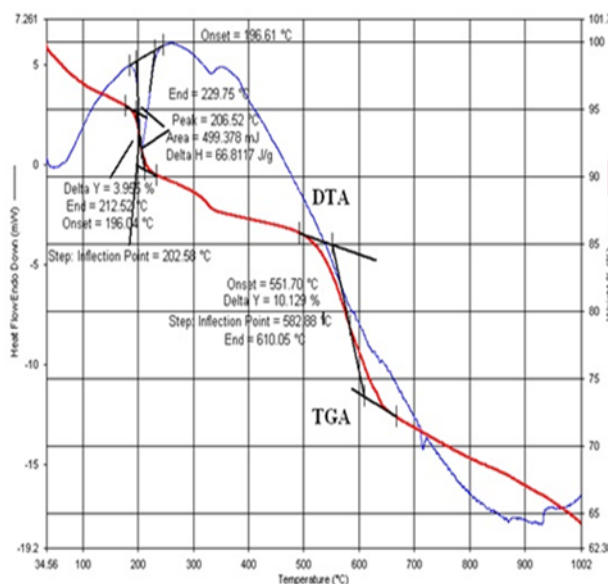


Figure 4. TGA and DTA curve for precursor ($\text{Bi}_2(\text{SO}_4)_3$ and V_2O_5) used for BiVO_4 synthesised by improved solid state route.

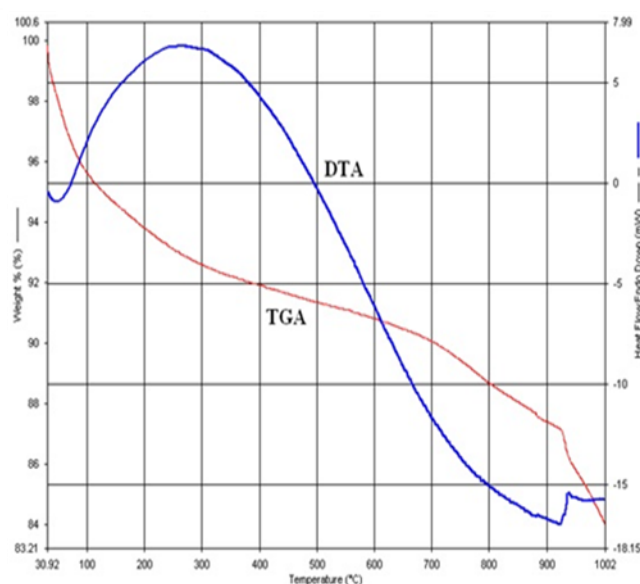


Figure 5. TGA and DTA curve for BiVO_4 synthesised by improved solid state route

3.3 X-Ray diffraction analysis

To investigate crystal structure of BiVO_4 synthesised by different routes, XRD pattern of prepared pigment was recorded. The XRD pattern recorded for the pigment synthesised by wet chemical co-precipitation route matches with the JCPDS data no. 00-014 133 which conforms the synthesis of BiVO_4 to be tetragonal. This is shown in Fig. 6. XRD pattern recorded for calcinated tetragonal BiVO_4 (shown in Fig. 7) is in good agreement with JCPDS data no. 01-083-1699 which attributes to monoclinic bismuth vanadate. The only drawback observed in Fig. 7, is with emerging impurity peaks which may be due to incomplete ferroelastic transition process from tetragonal to monoclinic BiVO_4 . This limitation can be overcome by increasing the calcination time period. XRD pattern recorded for the pigment synthesised by improved solid state reaction using $\text{Bi}_2(\text{SO}_4)_3$ and V_2O_5 (Fig. 8) is in good agreement with JCPDS no. 01-075-2480 which conforms the synthesis of monoclinic bismuth vanadate. No peak of impurity was observed in Fig. 8, which regulates the efficiency of synthesis process with geometry point of view.

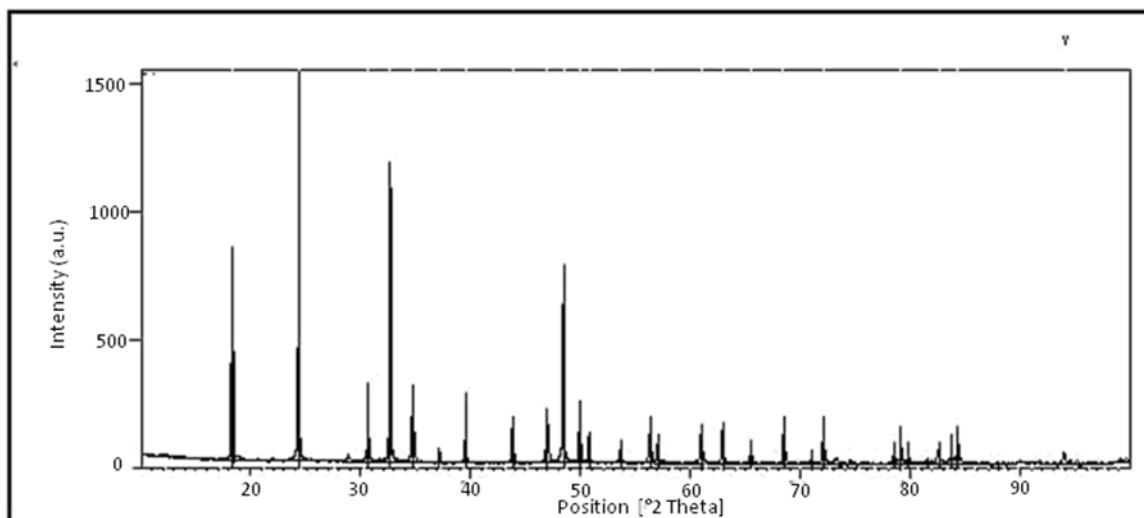


Figure 6. XRD of BiVO₄ synthesised by co-precipitation route

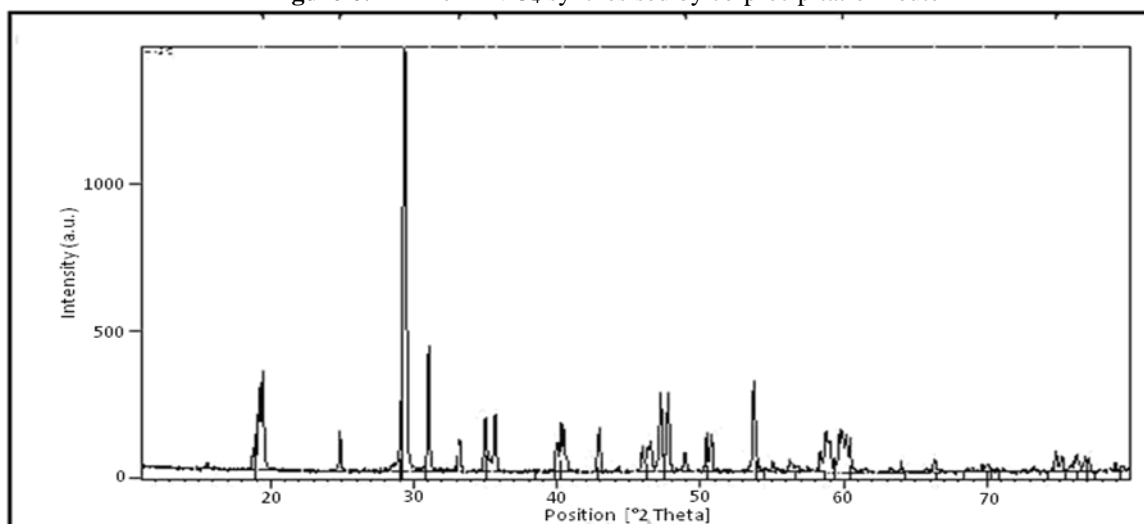


Figure 7. XRD of BiVO₄ synthesised by WCCP + calcinations

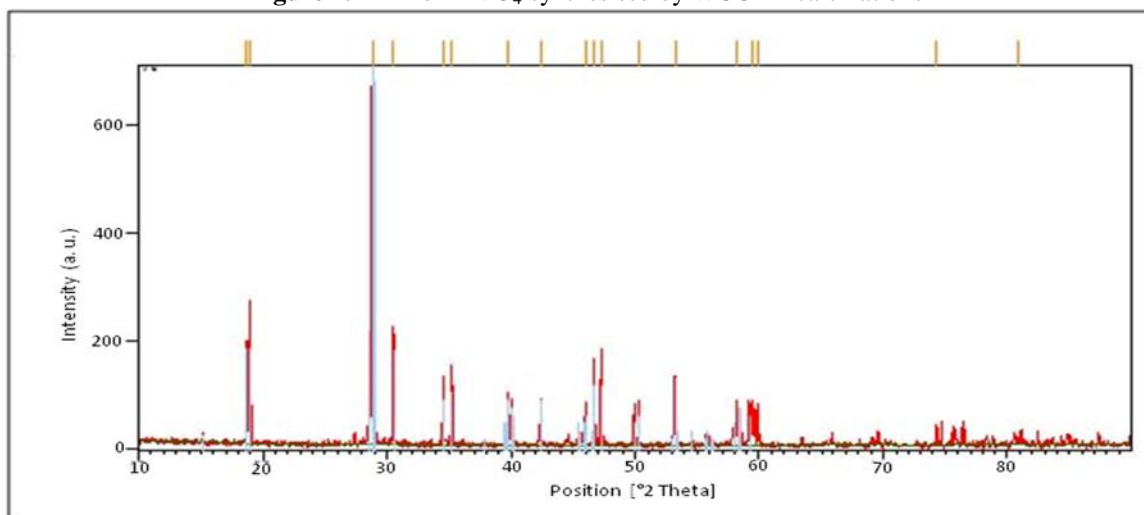


Figure 8. XRD of BiVO₄ synthesised by improved solid state route

Numerical data about crystallographic parameters (Table 1) has been given in support of the XRD Fig. 6, 7 and 8.

Table 1. Crystallographic parameters

Synthesis route	*WCCP	*WCCP + Calcination	*SSR
Crystal system	Tetragonal	Monoclinic	Monoclinic
a (Å)	7.2999	5.1956	5.1970
b (Å)	7.2999	5.0935	5.0960
c (Å)	6.4573	11.7045	11.7020
Alpha (°)	90.0000	90.0000	90.0000
Beta (°)	90.0000	90.0000	90.0000
Gamma (°)	90.0000	90.3830	90.4000
Calculated density(g/cm ³)	6.25	6.95	6.94
Volume of cell (10 ⁶ pm ³)	344.10	309.74	309.91

*WCCP: wet chemical co-precipitation method using precursors (Bi(NO₃)₃.5H₂O) and (NH₄VO₃)

*WCCP + Calcination: Calcination of dry powder synthesised by WCCP

*SSR: Solid state reaction involving calcination of Bi₂(SO₄)₃ and V₂O₅.

3.4 Morphological feature study

The synthesis condition and treatment process affects the morphological feature of the material. In case of wet chemical co-precipitation reaction, addition of reagents in proper manner and maintenance of appropriate physical conditions helps to maintain the uniformity of particle shape as well as size. Drop wise addition of an alkaline solution of NH₄VO₃ to acidic Bi(NO₃)₃ at controlled temperature and pressure along with maintenance of neutral pH resulted in globular shaped BiVO₄ pigment as captured in Fig. 9.(A) and (B). The average particle size of the pigment was in the range of 5 to 10 μm.

Manual grinding using agate mortar-pestle disturbed the spherical shape of pigment particle and even the size, which can be seen in case of SEM micrograph observed for BiVO₄ synthesised by co-precipitation followed by calcinations, as seen from Fig. 10. (A)–(B). Nevertheless, annealing showed significant effect to obtain needle shaped Fig. 10. (B) crystals of pigment.

Aggregate as well as elongated fragments of BiVO₄, shown in Fig. 11.(A)–(B), are observed for pigments synthesised by improved solid state route, elongation of which is not more than 10 μm (1000 nm). A growth of dendrite type crystal is also indistinctly seen from Fig. 11. (B). Hypothetically, it can be predicted on the basis of previous literature that the fragments of BiVO₄ may get converted to discrete dendrites crystals, with some modification in annealing process.

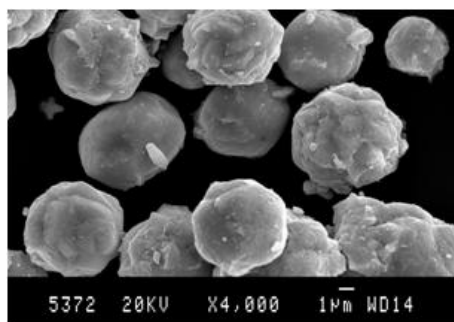


Fig. 9. A.

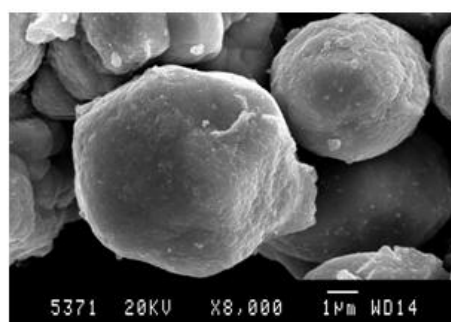


Fig. 9. B.

Figure 9. SEM micrograph of BiVO₄ synthesised by co-precipitation route

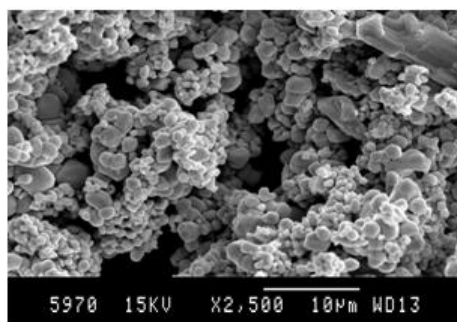


Fig. 10. A.

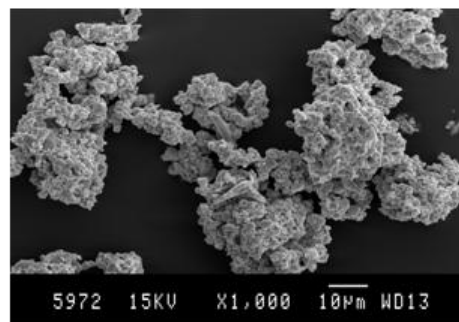


Fig. 10. B.

Figure 10. SEM micrograph for BiVO₄ synthesised by WCCP + calcinations

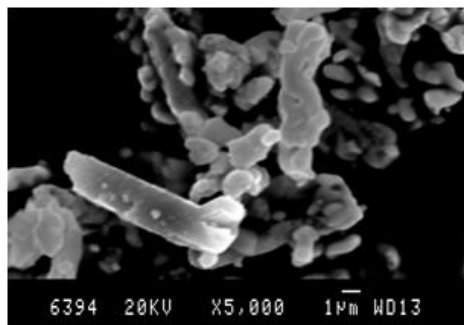


Fig. 11. A.

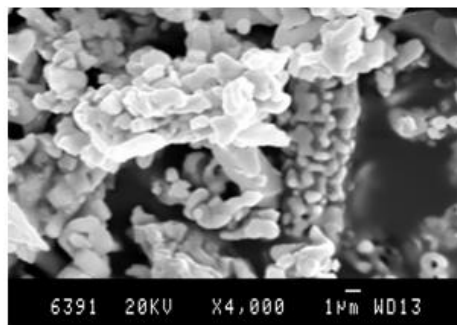


Fig. 11. B.

Figure 11. SEM micrograph for BiVO₄ synthesised by improved solid state route

3.5 Visible reflectance spectra

The visible reflectance spectra for all the three forms of BiVO₄ synthesised by different routes are recorded in the range 420 – 720 nm and are shown in Fig. 12. The tetragonal BiVO₄ which was prepared by co-precipitation route is murky yellow in colour, while the colour of monoclinic BiVO₄ synthesised by conventional WCCP route as well as by improved solid state route was vivid greenish yellow. It was found that the absorbance edges of the tetragonal BiVO₄ and the monoclinic BiVO₄ were quite different. The spectrum (Fig. 12. (A)) recorded for tetragonal BiVO₄ showed no prominent peak. This may be due to unstable nature of tetragonal BiVO₄. Both the spectra (Fig. 12. (B) and (C)) recorded for stable monoclinic BiVO₄ show inflection points at 500 nm.

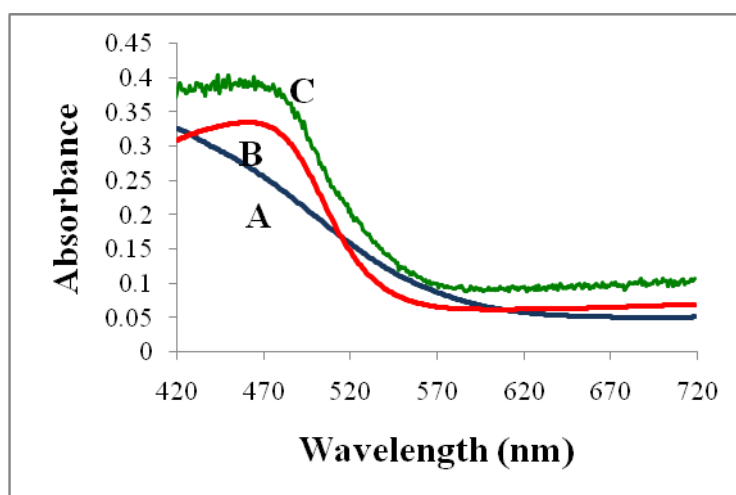


Figure 12. Visible reflectance spectra for synthesised BiVO₄
(A) by WCCP (B) by WCCP + calcination (C) by improved solid state route.

3.6 Colour analysis

Comparing conventional WCCP and improved solid state route for the synthesis of BiVO₄, in terms of colour parameters, the later one is found to be more superior than the previous, supporting data is available in Table 2. Results of colour characterisation prove that, the dominant wavelength is in range of 570–585 nm and also the hue angle is in the range of 60–120° for monoclinic BiVO₄ synthesised by either route. The ranges for dominant wavelength index to green colour shifting towards yellow whereas vice versa case for hue angle. Thus it can be concluded that the colour of the synthesised BiVO₄ is greenish yellow. Additionally the chromaticity value of the synthesised monoclinic BiVO₄ is more than 20, which means that it is a pigment having high chroma.

Discussing about tetragonal BiVO₄, the colour values indicate the pigment with high chroma with the dominant wavelength in range of 570–585 nm which categorise the pigment to be of yellow colour, but the expected hue angle is not achieved by the pigment which may be due to unstable tetragonal phase of BiVO₄.

Table 2. Colour analysis of BiVO₄ pigment synthesized by different route

Synthesis route		*WCCP method	*WCCP + calcination	*SSR
Crystal system		Tetragonal	Monoclinic	Monoclinic
Colour parameters	Notation			
Tristimulus values	X	74.0795	66.2990	68.1119
	Y	77.2129	70.2201	72.0862
	Z	57.9454	44.3956	43.9718
Chromaticity coordinates	x	0.3540	0.3665	0.3698
	y	0.3690	0.3881	0.3914
	z	0.2769	0.2454	0.2388
CIE L*a*b* value	L*	90.4195	87.1047	88.0101
	a*	1.4302	-0.9904	-0.8874
	b*	21.4153	29.4691	31.5035
ab-Chromaticity	C _{ab} *	21.4630	29.4858	31.5160
Hue angle (ab)	h _{ab}	1.5041°	88.4628°	88.4574°
Dominant wavelength	WL	577.30 nm	575.60 nm	575.69 nm
Excitation purity	p _e	0.2277	0.3160	0.3346

3.7 Efficiency of improved solid state reaction

Related to synthesis technique, BiVO₄ synthesised by improved solid state route focused in present work has overcome the limitations of conventional route by providing distinctive, relevant and also well explanative results.

Stoichiometrically, for synthesis of BiVO₄ by conventional WCCP method it is observed that one mole of Bi(NO₃)₃ combines with one mole of NH₄VO₃ to give one mole of BiVO₄. On the other hand, the solid state reaction discussed here involves reaction of one mole of Bi₂(SO₄)₃ and one mole of V₂O₅ to form two moles of BiVO₄. Theoretically for conventional WCCP method the reactant to product ratio is 1:1 whereas for solid state reaction the ratio is 1:2. Thus the solid state reaction is product-yield efficient than the conventional WCCP method. It is true that in case of conventional solid state reaction where there is a reaction between Bi₂O₃ and V₂O₅ the reactant to product ratio is 1:2. But time factor does matter a lot which is around 14 hours and even the precursors need 24 hours activation prior to calcination [17]. In these respects the solid state reaction discussed in present exercise can thus be referred to be time efficient process.

In conventional WCCP synthetic route there are possibilities that by-product may interfere in final product, thus disturbing the purity profile of the material. This risk has been eliminated in solid state reaction wherein the by-products are liberated out, giving a high purity product.

Similar to BiVO₄ synthesised by other route, the pigment prepared by improved solid state reaction has the property of high range thermal stability. The pigment has high chroma value, possesses hue angle and dominant wavelength in the range which index its colour to be greenish yellow.

IV. Conclusion

An economically single step process for the synthesis of BiVO₄ has been achieved successfully. The new method overcomes the limitations of previously reported methods and at the same time maintaining the pigment quality.

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References

- [1]. Andreas Tücks and Horst P. Beck, The photochromic effect of bismuth vanadate pigment: Investigation on the photochromic mechanism, *Dyes and Pigment*, 72, 2007, 163-177.
- [2]. E. Zintl, L. Vanino, European Patent 422947, 1924.
- [3]. Hugh M. Smith (Ed.), *High Performance Pigments*, (Wiley-VCH, Germany, 2002).
- [4]. Gunter Buxbaum and Gerhard Pfaff (Eds.), *Industrial Inorganic Pigments*, (Wiley-VCH, Germany, 2005).
- [5]. M. Gotic', S. Music', M. Ivandaa, M. S'oufek and S. Popovic', Synthesis and characterisation of bismuth (III) vanadate, *J. Mol. Str.*, 744-747, 2005, 535-540.
- [6]. A. Tücks and H. P. Beck, The photochromic effect of bismuth vanadate pigments. Part I: Synthesis, characterisation and lightfastness of pigment coatings, *J. Solid State Chem.*, 178, 2005, 1145-1156.
- [7]. Colourants for food contact plastics, Eurocolour, ETAD, VdMi, 2002.
- [8]. R. W Hess, US Patent 4026722, 1977.

- [9]. J. F Higgins, US Patent 4063956, 1977.
- [10]. D. H. Piltingsrud, US Patent 4115141, 1978.
- [11]. R. W.Hess, US Patent 4115142, 1978.
- [12]. A.K. Bhattacharya, K.K. Mallick and A. Hartridge, Phase transition in BiVO_4 , Mater. Letter, 30, 1997, 7–13.
- [13]. P. Wood and F.P. Glasser, Preparation and properties of pigmentary grade BiVO_4 precipitated from aqueous solution, Ceramics Intern., 30, 2004, 875–882.
- [14]. Abdul Halim Abdullah, Norsalinda Mohd Ali and Mohamed Ibrahim Mohamed Tahir, Synthesis of bismuth vanadate as visible-light photocatalyst, Malay. J. Anal. Sci., 13 (2), 2009, 151–157.
- [15]. A. Marti'nez-de la Cruz and U.M.G. Pe'rez, Photocatalytic properties of BiVO_4 prepared by the co-precipitation method: Degradation of rhodamine B and possible reaction mechanisms under visible irradiation, Mater. Res. Bull., 45, 2010, 135–141.
- [16]. Pusit Pookmanee, Sumintra Paosorn, and Sukon Phanichphant, Chemical synthesis and characterization of bismuth vanadate powder, Adv. Mater. Res., 93-94, 2010, 153-156.
- [17]. Elisabeth G. van der Linden, Luiz Fernando B. Malta and Marta Eloisa Medeiros, Evaluation of synthetic routes to pigmentary grade bismuth vanadate, Dyes and Pigments, 90, 2011, 36-40.
- [18]. Saimi Tokunaga, Hideki Kato and Akihiko Kudo, Selective preparation of monoclinic and tetragonal BiVO_4 with scheelite structure and their photocatalytic properties, Chem. Mater., 13, 2001, 4624-4628.
- [19]. JingBing Liu, Hao Wang, Shu Wang and Hui Yan, Hydrothermal preparation of BiVO_4 powders, Mater. Sci. Engg., B104, 2003, 36–39.
- [20]. Xi Zhang, Zhihui Ai, Falong Jia, Lizhi Zhang, Xiaoxing Fan and Zhigang Zou, Selective synthesis and visible-light photocatalytic activities of BiVO_4 with different crystalline phases, Mater. Chem. Phy., 103, 2007, 162–167.
- [21]. Pusit Pookmanee, Kanlaya Pingmuang, Sukon Phanichphant and Wiyong Kangwansupamonkon, Characterization of bismuth vanadate powder synthesized by a hydrothermal method, J. Micro. Soc. Thai., 23(1), 2009, 95-98.
- [22]. A. Zhang and J. Zhang, The effect of hydrothermal temperature on the synthesis of monoclinic bismuth vanadate powders, Mater. Sci-Poland, 27 (4/1), 2009, 1015–1023.
- [23]. A. Zhang, J. Zhang, N. Cui, X. Tie, Y. An and L. Li, Effects of pH on hydrothermal synthesis and characterization of visible-light-driven BiVO_4 photocatalyst, J. Mol. Catalysis A: Chem., 304, 2009, 28–32.
- [24]. Pusit Pookmanee, Kanlaya Pingmuang, Wiyong Kangwansupamonkon and Sukon Phanichphant, Methylene Blue Degradation over Photocatalyst Bismuth Vanadate Powder Synthesized by the Hydrothermal Method, Adv. Mater. Res., 93-94, 2010, 177–180.
- [25]. Yue Shen, Miaoliang Huang, Yi Huang, Jianming Lin and Jihuai Wu, The synthesis of bismuth vanadate powders and their photocatalytic properties under visible light irradiation, J. Alloy Compd, 496, 2010, 287–292.
- [26]. Haoyong Yin, Yongfei Sun, Dejun Shi, Xiaoxi Wang and Ling Wang, Controlling crystallization and morphologies of monoclinic bismuth vanadate (BiVO_4) dendrite with enhanced photocatalytic activities, Intern. J. Phy. Sci., 6 (17), 2011, 4287-4293.
- [27]. N. Kumada, T. Takei, R. Haramoto, Y. Yonesaki, Q. Dong, N. Kinomura, S. Nishimoto, Y. Kameshima, and M. Miyake, Preparation and crystal structure of a new bismuth vanadate, $\text{Bi}_{3.33}(\text{VO}_4)_2\text{O}_2$, Mater. Res. Bull., 46, 2011, 962–965.
- [28]. Haiyan Jiang, Hongxing Dai, Xue Meng, Lei Zhang, Jiguang Deng, Yuxi Liu and Chak Tong Au, Hydrothermal fabrication and visible-light-driven photocatalytic properties of bismuth vanadate with multiple morphologies and/or porous structures for Methyl Orange degradation, J. Environ. Sci., 24 (3), 2012, 449–457.
- [29]. I.C. Vinke, J. Diepgrond, B.A. Boukamp, K.J. de Vries and A.J. Burggraf, Bulk and electrochemical properties of BiVO_4 , Solid State Ionics, 57, 1992, 83–89.
- [30]. A. Galembeck and O. L. Alves, Bismuth vanadate synthesis by metallo-organic decomposition: thermal decomposition study and particle size control, J. Mater. Sci., 37, 2002, 1923 – 1927.
- [31]. Scott S. Dunkle, Richard J. Helmich, and Kenneth S. Suslick, BiVO_4 as a Visible-Light Photocatalyst Prepared by Ultrasonic Spray Pyrolysis, J. Phys. Chem. Letter, 113, 2009, 11980–11983.
- [32]. Hui Ming Zhang, Jing Bing Liu, Hao Wang, Wen Xiong Zhang and Hui Yan, Rapid microwave-assisted synthesis of phase controlled BiVO_4 nanocrystals and research on photocatalytic properties under visible light irradiation, J Nanopart. Res., 10, 2008, 767–774.
- [33]. Lin Zhou, Wenzhong Wang, Shengwei Liu, Lisha Zhang, Haolan Xu and Wei Zhu, A sonochemical route to visible-light-driven high-activity BiVO_4 photocatalyst, J. Mol. Catalysis A: Chem., 252, 2006, 120–124.
- [34]. Ye Liu, Junfeng Ma, Zhensen Liu, Changhong Dai, Zuwei Song, Yong Sun, Jingrui Fang and Jingang Zhao, Low-temperature synthesis of BiVO_4 crystallites in molten salt medium and their UV–Vis absorption, Ceramics Intern., 36, 2010, 2073–2077.
- [35]. K. Shantha and K.B.R. Varma, Fabrication and characterization of grain oriented bismuth vanadate ceramics, Mater. Res. Bull., 32 (11), 1997, 1581-1591.
- [36]. K. Shantha and K.B.R. Varma, Preparation and characterization of nanocrystalline powders of bismuth vanadate, Mater. Sci. and Engg., B56, 1999, 66–75.
- [37]. T. Tojo, Q.W. Zhang and F. Saito, Synthesis of BiAO_4 by mechanochemical solid state reaction between Bi_2O_3 and A_2O_5 (A = V, P, Nb and Sb), Chem. Sustainable Dev., 15, 2007, 243-247.
- [38]. B. Vaidhyanathan, Munia Ganguli and K.J. Rao, Fast Solid state synthesis of metal vanadates and chalcogenides using microwave irradiation, Mater. Res. Bull., 30 (9), 1995, 1173-1177.
- [39]. B. Vaidhyanathan, K. Balaji and K. J. Rao, Microwave-assisted solid-state synthesis of oxide ion conducting stabilized bismuth vanadate phases, Chem. Mater., 10, 1998, 3400-3404.
- [40]. L. I. Afonina, E. S. Naydenko, Yu. M. Yukhin and L. E. Danilova, Synthesis of high-pure bismuth citrate using the solid-liquid reactions, Chem. Sustainable Dev., 17, 2009, 235-241.
- [41]. P. K. Sinhamahapatra and S.K. Bhattacharyya, Studies on thermal properties of bismuth vanadate catalysts, J. Thermal Anal., 15, 1979, 233-249.