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Room Temperature Solid-State Metathetic Synthesis of Photocatalytically Active Monoclinic $BiVO_4$ and Tetragonal $LaVO_4$.

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ABSTRACT

A facile room temperature solid state metathetic synthesis has been developed for the otherwise difficult to synthesize phases by solid-state methods namely monoclinic $BiVO_4$ and tetragonal $LaVO_4$ using Na_3VO_4 and $BiCl_3$/ $LaCl_3$ as reactants. Stoichiometric quantities of respective reactants were mixed and ground in an agate mortar for 2 hours. The grinding induced solid state metathetic reaction between the reactants and the reaction proceeded to completion. The resultant mixtures after being washed with distilled water to remove NaCl bye product showed XRD patterns characteristic of respective vanadates and are in good agreement with the corresponding JCPDS data. These are further characterised by FT-IR and SEM. The visible light photocatalytic activity of $BiVO_4$ towards degradation of methylene blue is also studied.

Keywords: Bismuth vanadate; lanthanum vanadate; solid state metathetic synthesis; photocatalyst.

INTRODUCTION

Bismuth vanadate, $BiVO_4$ exhibits unique ferroelastic, acoustic-optical and ion-conductive properties. Owing to its good performance and less ecotoxicological nature $BiVO_4$ is a potential substitute for lead and cadmium as pigment. $BiVO_4$ exists in three crystalline structures- tetragonal zircon, monoclinic (m) scheelite and tetragonal (t) scheelite forms [1] of which only $BiVO_4$ of monoclinic scheelite structure with a band gap of 2.4ev was reported to exhibit visible light photocatalytic activity. Several synthesis methods have been reported for $BiVO_4$ in terms of mechanochemical assisted solid-state [2], precipitation [3], solvothermal [4], sonochemical [5], hydrothermal [6], spray pyrolysis [7], combustion [8] etc. Generally, m-$BiVO_4$ is obtained by high temperature processes [9] while t-$BiVO_4$ is prepared in aqueous media by low-temperature processes.

Lanathanide orthovanadates, $LnVO_4$ crystallise in two polymorphic forms namely tetragonal (t) phase with zircon structure and monoclinic (m) phase with monazite structure. With increase in ionic radius there is a strong tendency for lanathanide ions to prefer monoclinic structure due to its higher oxygen coordination number 9 compared to 8 of tetragonal form [10]. Since La^{3+} has the highest ionic radius among the tripositive lanthanide ions, m-$LaVO_4$ exists as thermodynamically more stable state while t-$LaVO_4$ exists as metastable state. Consequently, of the two forms m-$LaVO_4$ can be easily prepared by conventional solid-state reactions [11] where as t-$LaVO_4$ can only be prepared by soft chemical routes under specified reaction conditions [12-14]. Of the two forms m-$LaVO_4$ has been reported to be neither a suitable host for luminescent activators nor a good catalyst compared to t-$LaVO_4$. It is therefore a challenge to synthesize the metastable zircon type t-$LaVO_4$ by solid-state synthesis.In view of the importance of $BiVO_4$ and $LaVO_4$ and also since the authors have succeeded in preparing tungstates of alkaline earth metals at room temperature and transition metal tungstates at 400^0C by solid-state metathetic reactions [15-16], the synthesis of $BiVO_4$ and $LaVO_4$ has been undertaken by solid-state metathesis. Metathetic reactions involve exchange of reaction partners and are driven by the high lattice energy of the co-product. Such reactions are extremely fast, self energetic and yield crystalline products with unusual microstructures.

MATERIALS AND METHODS

Sample Preparation: A.R.grade $BiCl_3$ and $LaCl_3.7H_2O$ (Loba) were used as precursors along with Na_3VO_4 (Aldrich). Stoichiometric quantities of reactants in 1:1 molar ratio as per the following reaction were weighed and ground thoroughly in an agate mortar for 2hrs in presence of ethanol.

$$MCl_3.nH_2O + Na_3VO_4 \rightarrow MVO_4 + 3NaCl + nH_2O$$

In the case of $BiVO_4$, the mixture immediately turned to canary yellow in colour. The homogenized mixture was washed with distilled water to remove NaCl bye product and dried at room temperature. The dried sample was used for phase identification.

Characterization Techniques: Phase identification of the powders was investigated with X-ray diffractometer (PANalytical- X' Pert PRO, Japan) at room temperature, using Nickel filtered Cu-K_α radiation (λ= 1.54059 Å), over a range of $10^o \leq 2\theta \leq 80^o$ with a scan rate of 2^o min^{-1}. IR spectra were recorded using Shimadzu, model IR prestige-21 and range from 400-4000 cm^{-1}. Diffuse reflectance UV–vis spectra of the samples were measured for the dry pressed disk samples using Shimadzu UV-VIS spectrophotometer (UV-3600) between 200 and 800 nm range. Spectral grade $BaSO_4$ was taken as reference for the reflectance spectra. Microstructural investigations of the samples were performed on the powders of the samples using SEM (JEOL-JSM-6610LV, Tokyo, Japan).

RESULTS AND DISCUSSION

In recent years much attention is being paid to the synthesis of nanomaterials because of their interesting properties and potential applications. Most of these techniques are based on bottom up approach. However, if the required phase can be synthesized by solid-state reactions at ambient temperatures, it will be cost effective to obtain the same phase in nanoform by top-down approach as well.

Fig 1 depicts the XRD patterns of homogenised mixture of $BiCl_3$/$LaCl_3$ with Na_3VO_4 after grinding for 2 hours in an agate mortar at room temperature followed by washing with water until free from chloride and dried. In Fig.1(a), all the observed peaks could be indexed due to monoclinic $BiVO_4$ of JCPDS card no. 83-1698. Since all the observed diffraction peaks are in good agreement with that of m-$BiVO_4$ and since there are no extra peaks either due to contamination or due to unreacted precursors, the formation of phase pure $BiVO_4$ is confirmed. Fernandez-Osorio et al [17] reported the synthesis of monoclinic form of $BiVO_4$ by simple coprecipitaion reaction from aqueous solution of $Bi(NO_3)_3.5H_2O$ and $NaVO_3$ at room temperature and calcining the resultant precipitate at 500^0C for 2hrs. The same phase was obtained by solid-state metathesis reaction at room temperature in the present study. All the peaks in Fig 1(b) could be indexed to tetragonal zircon type $LaVO_4$ of space group $I4_1$/amd (JCPDS Card No: 32-0504). Absence of peaks due to either m- $LaVO_4$ phase or unreacted precursors indicates formation of phase pure t- $LaVO_4$.

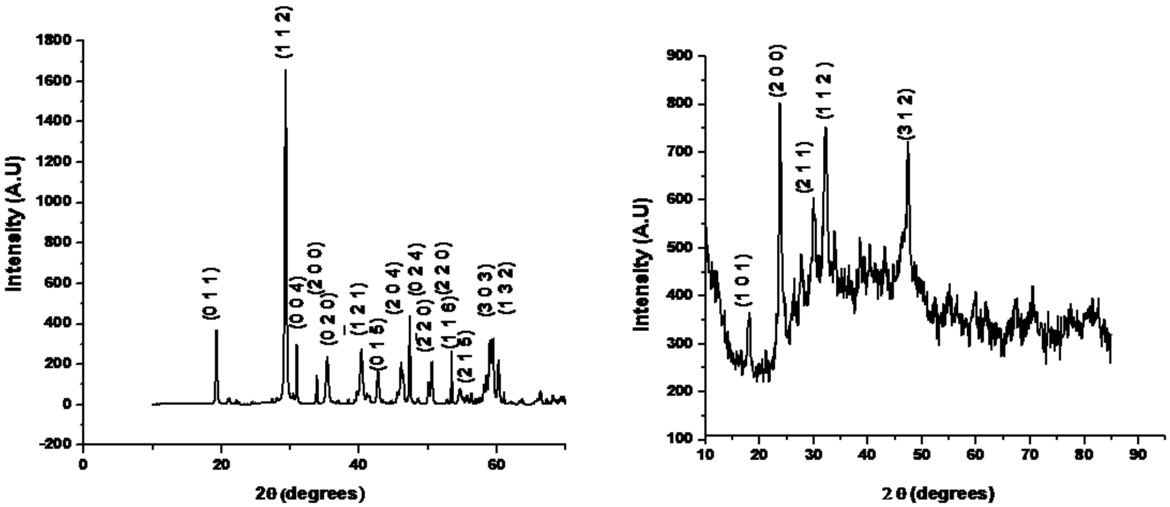

Fig. 1.XRD patterns of stoichiometric mixture of the reactants ground for 2hrs and washed free of chloride (a) $BiCl_3$ + Na_3VO_4 (b) $LaCl_3$ + Na_3VO_4.

Fig. 2 shows the FT-IR spectra of $BiVO_4$ and $LaVO_4$ at room temperature. As shown in Fig 2(a) the formation of $BiVO_4$ is characterized by a strong absorption band at 754cm^{-1} [18]. The obvious absorption at 1623 cm^{-1} is due to bending vibrations of the adsorbed H_2O molecules. The data is well in agreement with the literature data [19,6]. A broad absorption band in Fig 2(b) is observed at 786 cm^{-1}. Only t-$LaVO_4$ generates a broad band in the region of 730-980 cm^{-1}, while m- $LaVO_4$ gives several peaks at 783, 802, 821, 836 and 852 cm^{-1}[20]. The two weaker bands at 1635 and 1369 cm^{-1} can be assigned to the symmetric stretching vibration and bending vibration of the O-H groups, indicating that the as-prepared $LaVO_4$ contains some hydroxyl groups or H_2O on their surfaces.

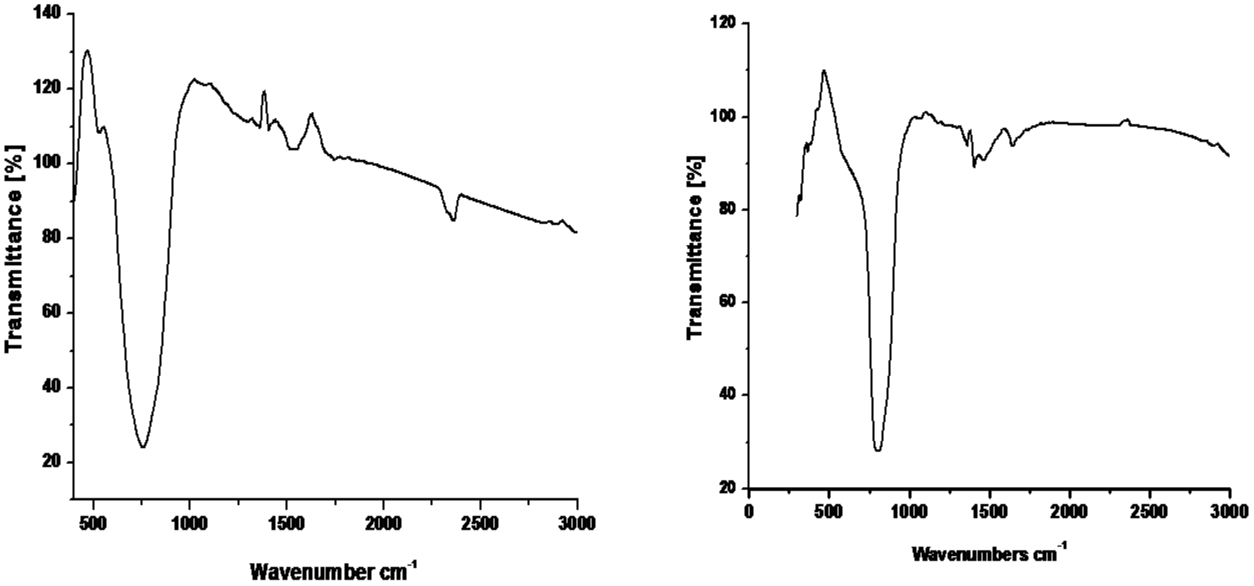

Fig. 2. Fourier Transform Infrared spectra of (a) $BiVO_4$ (b) $LaVO_4$.

UV-Visible Diffuse reflectance spectra (UV-DRS) for $BiVO_4$ and $LaVO_4$ powders are shown in Fig 3. The spectra indicate maximum absorption for $LaVO_4$ in the UV region whereas for $BiVO_4$ the λ_{max} lies in the visible region. Hence photocatalytic activity of $LaVO_4$ is expected to be observed for irradiation with electromagnetic radiation of 270-280nm for a dye solution containing the photocatalyst. On the other hand, $BiVO_4$ with its highest absorption in the region of 400-450nm is clearly a visible light activated photocatalyst. This observation further confirms that the crystal structure of $BiVO_4$ is monoclinic and not tetragonal. The band gap of the synthesized samples was calculated by using this UV-vis DRS spectra using the equation, $E(eV)=hC/\lambda$ where E is the band gap energy (eV), h is Planck's constant, C is the velocity of light (m/s) and λ is the wavelength (nm) corresponding to the absorption edge. The synthesized $LaVO_4$ showed an absorption edge at 330 nm which corresponds to the band gap of 3.7 eV, while $BiVO_4$ showed absorption edge at 490 nm which corresponds to the band gap of 2.5 eV.

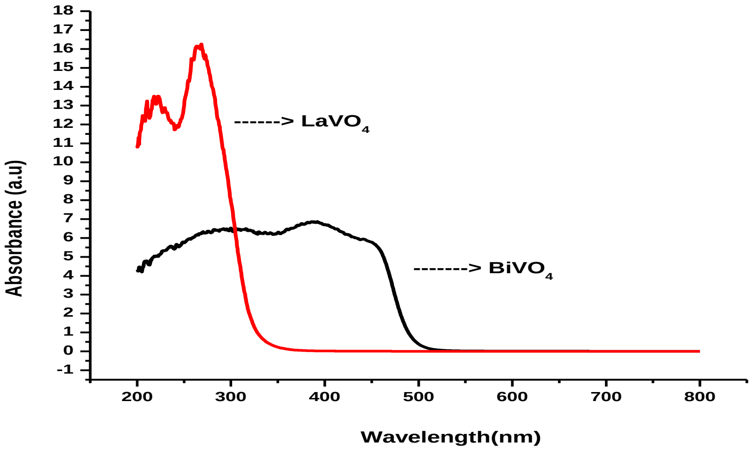

Fig. 3. UV-Vis diffuse reflectance spectrum of $BiVO_4$ and $LaVO_4$

SEM micrographs of the resultant $BiVO_4$ and $LaVO_4$ powders are depicted in Fig 4(a) and (b) respectively. Fig 4(a) shows that $BiVO_4$ sample to exist mostly in spherical particles of nearly uniform submicrometer size where as the micrograph in Fig. 4(b) shows no characteristic shape.

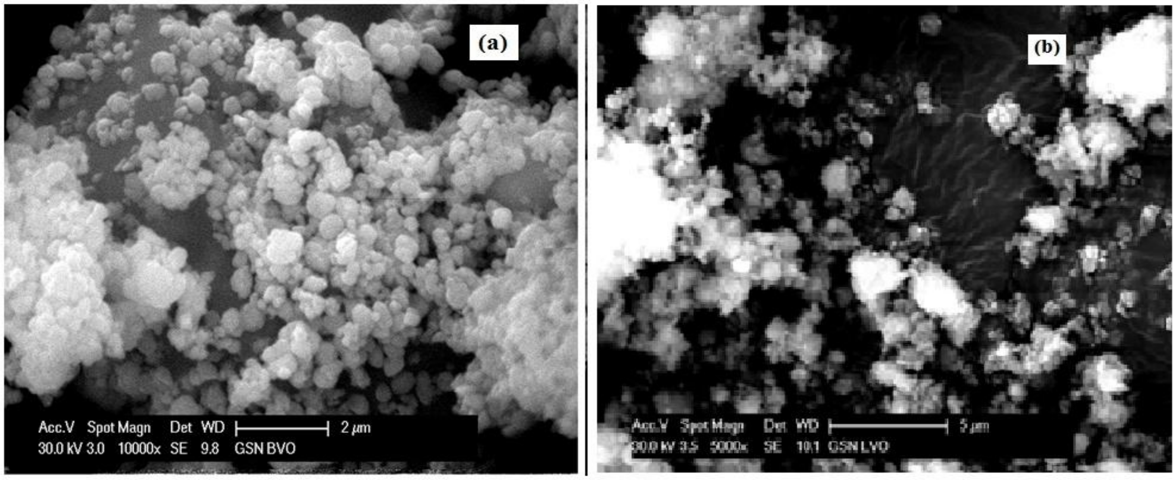

Fig. 4. SEM image of a) $BiVO_4$ powder and b) $LaVO_4$ powder

Photodegradation of methylene blue was used as probe reaction to evaluate the photocatalytic activity of $BiVO_4$ under visible light irradiation of 400W halogen lamp. Methylene blue solution (5ppm in 50ml) containing 100mg of $BiVO_4$ was used and the intial pH was adjusted to 8.5. The intial colour of the solution was blue and the solution was stirred in dark for 30 minutes to obtain equilibrium between the $BiVO_4$ powder and the dye solution. Then the solution was exposed to light from the halogen lamp under constant stirring, and the solution was collected at time intervals of 30 minutes. The supernatent solution after centrifugation was used to record the absorption spectra in the region of 400-800nm. After 30 minutes, the colour of the solution changed from blue to almost colourless. From the spectra as shown in the Fig 5, it can be noticed that degradation of methylene blue to an extent of 90-92% occured in 30 min. Further systematic studies on the effect of pH, amount of catalyst and concentration of dye are in progress. Since the absorption for $LaVO_4$ is in the U.V region, photocatalytic studies on $LaVO_4$ could not be investigated due to lack of U. V source.

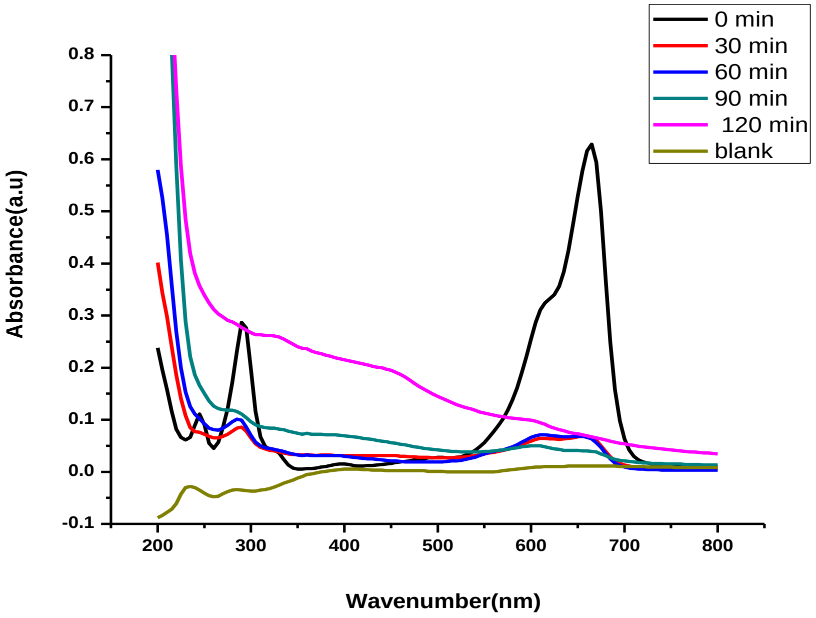

Fig.5 Absorption spectra at different time intervals for methylene blue solution containing $BiVO_4$ powder.

CONCLUSIONS

A simple room temperature solid state metathetic synthesis is reported for the preparation of MVO_4 (M=Bi and La) using respective metal chlorides and sodium orthovanadate as reactants. The metathetic reaction occurred at room temperature probably assisted by grinding and resulted in the formation of otherwise difficult to synthesize crystalline phases by solid-state method namely monoclinic-$BiVO_4$ and tetragonal-$LaVO_4$. XRD patterns of dried homogenised mixtures of $BiCl_3$/$LaCl_3$ and Na_3VO_4, washed free from chloride indicated formation of phase pure monoclinic $BiVO_4$ and tetragonal $LaVO_4$. The visible light photocatalytic activity of $BiVO_4$ towards degradation of methylene blue also confirmed that the $BiVO_4$ phase is monoclinic and not tetragonal.

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