

SYNTHESIS OF BiVO_4 BY MECHANOCHEMICAL REACTION BETWEEN Bi_2O_3 AND V_2O_5

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ABSTRACT

Bismuth vanadate (BiVO_4) based compounds have many fascinating and multifunctional properties for potential applications in a wide variety of areas. The different properties exhibited by this material depend strongly on the crystalline form and microstructure. In this work we report the selective synthesis of nanocrystalline bismuth vanadate powders of monoclinic phase through a mechanochemically assisted metathesis route. The metathesis pathway of forming the desired product is confirmed by the presence of NaNO_3 after milling the mixtures for different time periods of 15, 30 and 60 min. The crystallization process and thermal behavior of the BiVO_4 phase obtained at different milling times were studied by both differential thermal analysis (DTA) and thermo gravimetric analysis (TGA), and X-ray powder diffraction (XRD) methods. XRD patterns of the product after washing showed the formation of the BiVO_4 phase with monoclinic structure for different milling times, the structure which exhibit higher photocatalytic activity under visible light irradiation and superior coloristic properties over the other forms.

Keywords: Bismuth vanadate, Mechanical milling, Metathesis, monoclinic

1. INTRODUCTION

Bismuth vanadate (BiVO_4) and its relative oxides have been extensively investigated in the recent years because of their interesting properties like photocatalytic activity, ferroelasticity and conductivity etc. [1,2]. Another important application of BiVO_4 as yellow pigments and it is a

potential substitute for lead and cadmium based paints, due to their high performance and being free from ecotoxicological problems. These properties depend strongly on crystalline form and microstructure. BiVO_4 appears in three main crystalline forms: tetragonal zircon, monoclinic scheelite and tetragonal scheelite structures. Out of these, monoclinic BiVO_4 exhibits higher visible light photocatalytic activity, the oxygen vacancies intrinsically presenting in this crystal structure contribute to its high ionic conductivity, making it suitable to be used as solid electrolyte for application in a variety of solid state ionic devices [3]. The crystal structure formation and the shape of BiVO_4 can be controlled by the synthesis condition. Various synthesis methods have been employed for the preparation of BiVO_4 with different crystal structures, such as conventional solid state reaction, solution coprecipitation, metal organic decomposition, sol-gel process, hydrothermal, sonochemical methods etc [4-7]. These synthesis procedure involved complex steps, longer reaction times, large consumption of organic agents and the use of expensive equipment etc. Thus new synthesis methods were developed in order to prevent changes in stoichiometry, as well as to facilitate the reactions, by lowering the reaction temperatures and times.

The idea of inducing chemical reactions between precursor powders by mechanochemical activation has emerged as an attractive method to synthesize novel materials. It has been applied for the synthesis of ceramic materials with perovskite, fluorite, pyrochlore structures and also to obtain superconductor oxides, amorphous materials etc. Mechanochemical route of synthesis has also been applied to the synthesis of nanocrystalline bismuth vanadate powders [8,9]. However, in the present study we have employed the mechanochemical synthesis involving metathesis reaction driven by high energy ball milling as a simple and cost-effective method for the synthesis of nanostructured BiVO_4 system. Metathesis (double exchange) reactions taking place in solid state are extremely fast, self-energetic and yield crystalline materials in very short time intervals with unusual microstructures. It involves the exchange of reacting partners and is largely driven by the lattice energy of the co-produced salt [10]. As far as we know, there is no report on the mechanochemically assisted solid state metathesis route for the synthesis of BiVO_4 powders. By controlling the synthetic procedure, time and the molar ratio of Bi to V in the

starting materials, BiVO_4 samples with tetragonal scheelite, monoclinic scheelite, or tetragonal zircon structure can be prepared. The aim of the present work is to synthesize monoclinic BiVO_4 phase through mechanochemically assisted metathesis route at room temperature with different milling times.

2. EXPERIMENTAL TECHNIQUES

BiVO_4 samples with monoclinic crystal structure were synthesized by mechanochemically assisted solid state metathesis route at room temperature using high purity ammonium vanadate (NH_4VO_3), bismuth nitrate pentahydrate $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and sodium hydroxide (NaOH) (Aldrich >99+%). Stoichiometric mixtures of the above chemicals were placed in zirconia containers together with 20mm diameter zirconia balls as grinding media (ball to powder mass ratio 10:1). Dry mechanical milling was carried out in air at room temperature, in a Restch PM/400 planetary ball mill by using a rotating disc speed of 350rpm for 15, 30 and 60min. To eliminate the presence of the byproduct obtained during milling and to obtain the desired phase of interest, the milled powders were subjected to washing with distilled water, because NaNO_3 is highly soluble in water. The milled powders dissolved in distilled water and the solution was mixed by constant stirring in a magnetic agitator at room temperature for 1 hr to obtain a precipitate. After washing four times, the solution is centrifuged to separate water from the compound, speed and time kept for centrifuge is 300 rpm for 20 min. The washed precipitates were dried at 100°C for 2 hrs in air atmosphere and when the material is completely dry, it was mixed again in an agate mortar to obtain a homogeneous product. The X-ray diffraction measurements were carried out by using Philips X'Pert diffractometer using Ni filtered $\text{CuK}\alpha$ radiation ($\lambda=1.5418 \text{ \AA}$) before and after washing the milled product. Thermal analysis of the milled mixture before and after washing was carried out using a TG/DTA Perkin Elmer model Pyris. The mixture was heated at 5°C min^{-1} from room temperature to 600°C .

3. RESULTS AND DISCUSSION

Figure 1 shows the XRD spectrum of the mixture of NH_4VO_3 , $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and NaOH milled for 15min (a) and after washing off the byproduct (b). The reported XRD pattern of the NaNO_3 (PDF: 36-1474) and monoclinic (clinobisvanite) BiVO_4 (PDF: 75-1866) is shown at the bottom as a reference. The presence of NaNO_3 is clearly visible from the Figure 1(a). The presence of NaNO_3 after milling as a by-product strongly indicates that the reaction followed a metathetic pathway and acted as a driving force for the reaction to get a desired product. The metathesis reaction for the formation of the product is represented as follows

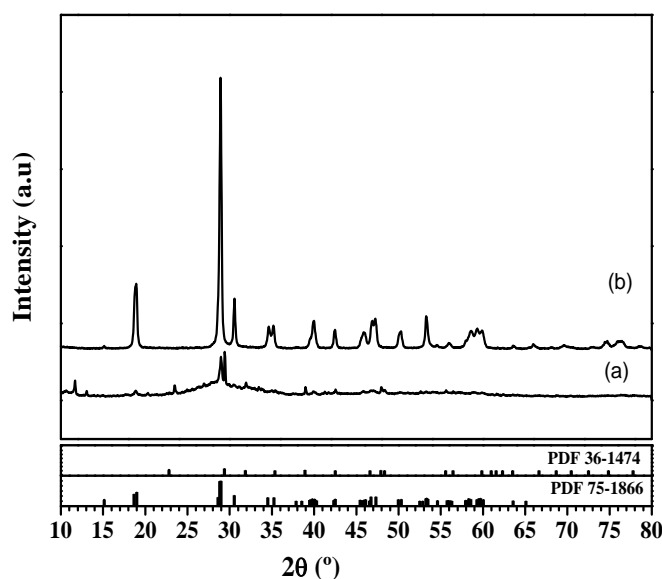
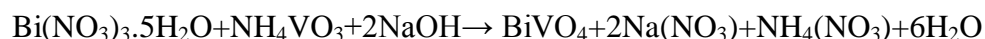


Figure1. XRD patterns of the NH_4VO_3 , $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and NaOH mixture after milling for 15 min (a) and after washing (b). The reported XRD pattern of NaNO_3 (PDF: 36-1474) and monoclinic BiVO_4 is shown at the bottom.

Due to the presence of NaNO_3 phase in the milled product, it is subjected to four washing operations. The amount of washing is determined as reported in the literature where it states that four washing operations are sufficient to dissolve the salt. The X-ray diffraction analysis was

done after the washing operations in order to determine the formation of possible phase after washing. The XRD pattern (Figure 1 (b)) showed the formation of single phase monoclinic bismuth vanadate, as the XRD pattern matches with the reported PDF file: 75-1866 for the monoclinic phase of BiVO_4 . Figure 2 shows the TGA-DTA curve for the sample powder (a) milled for 15 min and (b) after washing. DTA spectra of the milled powder show the presence of three endothermic peaks at 223°C , 270°C and 303°C . The endothermic peak at 223°C corresponds to loss of water, 270°C corresponds to the polymorphic change in NaNO_3 and 303°C corresponds to the melting point of NaNO_3 . TGA gives a weight loss of 17% as the temperature increases from room temperature to 500°C .

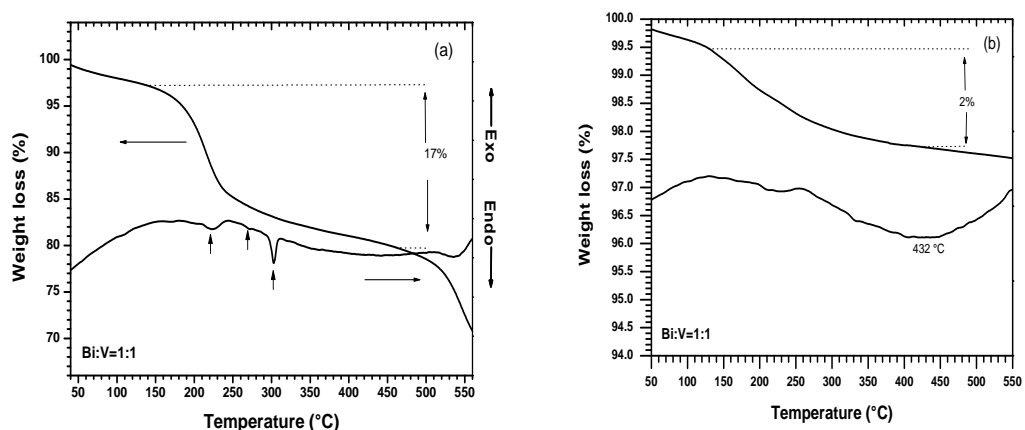


Figure 2. TGA/DTA curves for the sample (a) after milling for 15 min (b) after washing

Figure 3 shows the XRD pattern obtained for the starting reagent mixture milled for 30 min (a) and after washing (b). The reported XRD pattern of NaNO_3 with rhombohedral crystal system and monoclinic BiVO_4 crystal structure is shown as reference at the bottom. Figure 3 shows the samples milled for 30 min also shows the presence of NaNO_3 and after the four washing operation gives the monoclinic bismuth vanadate phase. The spectra obtained from the thermal analysis for the 30 min milled sample are shown in figure 4. DTA spectra show four endothermic peaks at 114°C , 226°C , 270°C and 301°C and an exothermic peak at 210°C and the

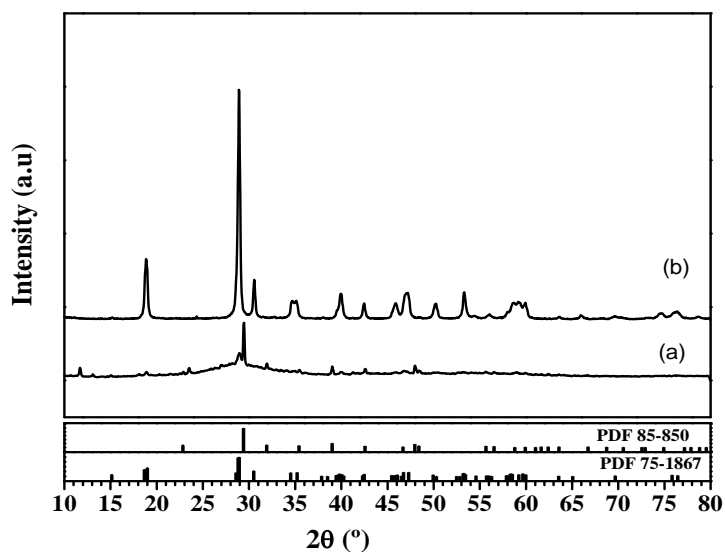


Figure 3. XRD patterns of the NH_4VO_3 , $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and NaOH mixture after milling for 30 min (a) and after washing (b). The reported XRD pattern of NaNO_3 (PDF: 85-850) and monoclinic BiVO_4 is shown at the bottom.

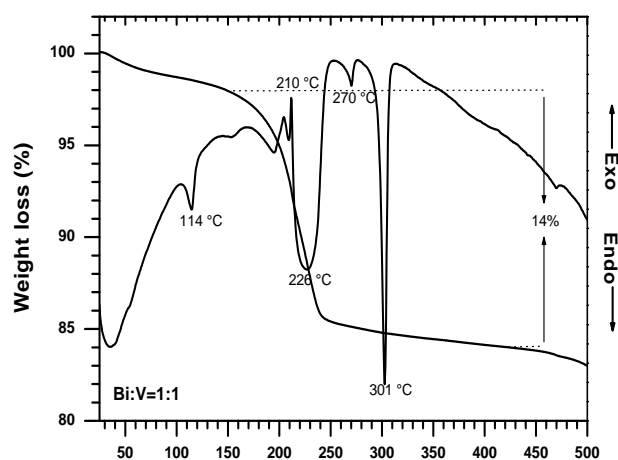


Figure 4. TGA/DTA curves for the sample (a) after milling for 30 min (b) after washing

weight loss corresponds to 14%. The endothermic peak at low temperature corresponds to the loss of water and temperature of 270°C corresponds to the polymorphic change in NaNO_3 and 301°C corresponds to melting point of NaNO_3 . Figure 5 shows the starting reagents milled for 60 min (a) and after washing (b). The reported XRD pattern of the NaNO_3 (PDF: 85-0850) and monoclinic clinobisvanite BiVO_4 (PDF: 83-1699) is shown at the bottom as reference.

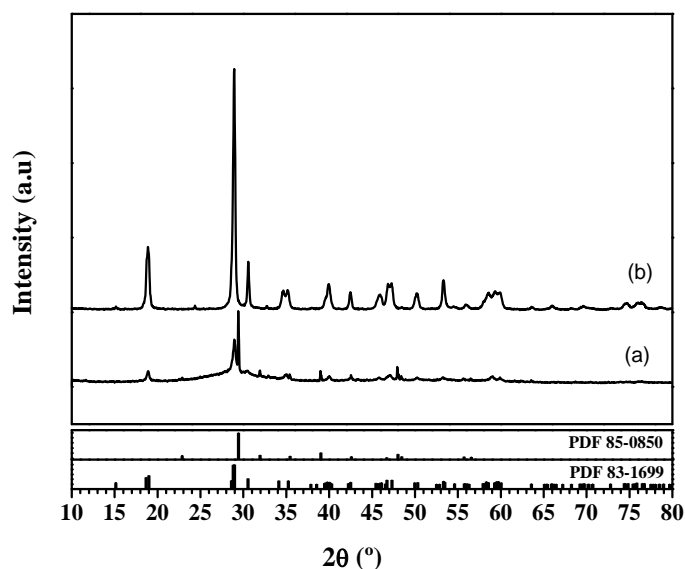


Figure 5. XRD patterns of the NH_4VO_3 , $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and NaOH mixture after milling for 60 min (a) and after washing (b). The reported XRD pattern of NaNO_3 (PDF: 36-1474) and monoclinic BiVO_4 is shown at the bottom.

As shown in the figure 5(b), the diffraction pattern of the mixture milled for 60 min and after washing operation well agrees with the standard monoclinic clinobisvanite crystalline structure. Figure 6 shows the thermal analysis curves of the milled sample. DTA spectra shows the presence of two peaks of endothermic behavior, the first one correspond to a temperature of 270°C is due to the polymorphic transition experienced by the rhombohedral structure of NaNO_3 , while the second peak located at 303°C corresponds to the melting point of the same. TGA shows a weight loss of 13% by weight as the temperature increases from 100-220° C and it can attribute to the loss of water.

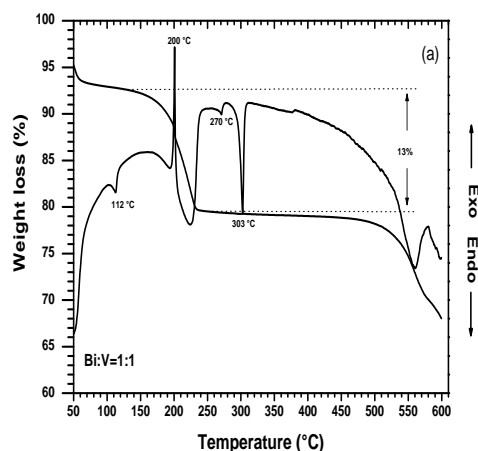


Figure 6. TGA-DTA graphs of the NH_4VO_3 , $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and NaOH mixture milling for 60 min

4. CONCLUSIONS

The milling induced solid state metathesis reaction have taken place in $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ - NH_4VO_3 -NaOH system, where the formation of a high lattice energy by product (NaNO_3) drives the reactions to produce the desired products. By controlling the synthesis condition including effective use of precursors, BiVO_4 monoclinic clinobisvanite crystal structure could be obtained, the crystalline phase which is of great interest to many applications. The milling induced solid state metathesis approach is very simple, environmentally friendly, and economic and reduces the time of preparation of the compound compared to other method of synthesis.

5. REFERENCES

- [1] S. Tokunaga, H. Kato and A. Kudo, *Chem. Mater.*, **13**, 4624-4628 (2001).
- [2] H. Li, G. Liu and X Duan, *Material Chemistry and Physics*, **115**, 9-13 (2009).
- [3] Y Sun, Y Xie, C. Wu, R. Long, *Crystal Growth Design*, **10**, 602-607 (2010).

- [4] Z. Zhang, W. Wang, M. Shang, W. Yin, *Catalysis Communications*, **11**, 982-986 (2010).
- [5] L. Zhang, D. Chen and X. Jiao, *J. Phys. Chem. B*, **110**, 2668-2673 (2006).
- [6] W Liu, L. Cao, G. Su, H. Liu, X. Wang, L. Zhang, *Ultrasonics Sonochemistry*, **17**, 669-674 (2010).
- [7] A. K. Bhattacharya, K. K. Mallick, A. Hartridge, *Materials Letters*, **30**, 7-13 (1997).
- [8] K Shantha, K.B.R. Varma, *J. Am. Ceram. Soc.*, **83**, 1122-1128 (2000).
- [9] T. Tojo, Q.W. Zhang, F. Saito, *Chemistry for Sustainable Development*, **15**, 243-247 (2007).
- [10] P. Parhi, S. S. Singh, A.R. Ray, A. Ramanan, *Bull. Mater. Sci.*, **29**, 115-118 (2006).