

Synthesis of BiAO_4 by Mechanochemical Solid State Reaction between Bi_2O_3 and A_2O_5 (A = V, P, Nb and Sb)

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Abstract

Bismuth vanadate (BiVO_4) can be synthesized by mechanochemical reaction between bismuth oxide (Bi_2O_3) and vanadium oxide (V_2O_5) by using a planetary ball mill at ambient temperature. The following solid state reaction takes place mechanochemically during the milling: $\text{Bi}_2\text{O}_3 + \text{V}_2\text{O}_5 \rightarrow 2\text{BiVO}_4$. The particles of the sample look like agglomerates of fine grains with sizes less than 200 nm, and the agglomerates seem to be consisting of primary particles with several microns. The mechanochemical reaction ratio between Bi_2O_3 and V_2O_5 is saturated around 90 %. Heating treatment above 300 °C leads to the formation of homogeneous BiVO_4 with an increase in reaction ratio up to about 99.4 %. The mechanochemical method enables us to synthesize other bismuth complex oxides (BiAO_4 ; A = P, Nb and Sb).

INTRODUCTION

Bismuth vanadate (BiVO_4) and its related materials were studied for use as ferroelastic [1–3], ion conductive materials [4–6], cadmium-free non-toxic yellow pigments [7–10] and oxidation catalysts [11, 12]. Furthermore, much attention has been recently paid to the photocatalytic property of these compounds [13–16].

The compounds were synthesized by a solid state reaction method conducted at high temperature [14, 15] and wet processes including hydrothermal method [17, 18]. The former is simple to operate, however, it requires high reaction temperature, and it has a limit in the degree of chemical homogeneity. On the contrary, the latter can provide products of fine and homogeneous particles with large specific surface area. However, they are complex processes with considerable reaction time, and the reagents used as starting materials are usually expensive. There has been growing demand to develop simple methods for synthesizing homo-

geneous BiVO_4 . One of the candidates for synthesizing these compounds may be a mechanochemical method, and it has a potential to form fine complex oxides in a single step milling operation [19–21], which enables us to synthesize the compounds at ambient condition [22, 23]. Shantha's group mainly reported on the mechanochemical synthesis of Bi_2VO_5 , aiming at utilization for BIMEVOX [24, 25]. Zyryanov [26] investigated the composition of crystalline products in Bi_2O_3 – V_2O_5 system by mechanochemical method. We were studying the mechanochemical solid state reactions between binary oxides to form complex oxides with ABO_4 composition [20, 21]. The mechanochemical reaction has a potential to synthesize the compounds from a mixture of Bi_2O_3 and pentavalent oxide such as V_2O_5 and Sb_2O_5 .

The main purpose of this paper is to provide fundamental information mainly on the synthesis of BiVO_4 by a mechanochemical method. In addition, the possibility of the synthesis of other bismuth complex oxides, which are BiPO_4 , BiNbO_4 and BiSbO_4 , is discussed.

EXPERIMENTAL

Sample preparation and milling the mixture

Five kinds of starting materials were used for the experiment. These are bismuth oxide (Bi_2O_3), vanadium oxide (V_2O_5), phosphorus oxide (P_2O_5), niobium oxide (Nb_2O_5) from Wako Pure Chemical Industries Ltd. (Japan) and antimony oxide (Sb_2O_5) from Sigma-Aldrich (USA). Bi_2O_3 was mixed with one of the pentavalent oxides described above (V_2O_5 , P_2O_5 , Nb_2O_5 and Sb_2O_5) at equimolar ratio to prepare starting mixtures for milling. 2 g of the mixture were subjected to milling in a planetary ball mill (Fritsch Pulverisette 7, Germany), so that the mixture was put into a zirconia pot of 45 cm³ inner volume with 7 zirconia balls of 15.7 mm diameter. Milling was carried out in air at 700 rpm.

Characterization

The milled samples were characterized by X-ray diffraction (XRD, RINT-2200, Rigaku, Japan) using $\text{CuK}\alpha$ radiation. Morphology of the milled sample was observed by a scanning electron microscope (SEM, S4100-L, Hitachi,

Japan). The leaching test of the milled samples was conducted at room temperature to determine the amount of V_2O_5 which remains in the milled mixture, as follows: 0.25 g of the sample was dispersed in 50 ml of 1N NaOH solution and agitated for 60 min. Subsequently, the suspension was filtered to take the filtrate. The concentration of V in the filtrate was measured by inductively coupled plasma-atomic emission spectrometry (ICP-AES, Optima 3300SYS, Perkin Elmer, USA).

RESULTS AND DISCUSSION

Synthesis of BiVO_4 by milling the Bi_2O_3 and V_2O_5 mixture

Figure 1 shows the XRD patterns of the mixture of Bi_2O_3 and V_2O_5 milled for different periods of time. The pattern of the mixture milled for 1 min shows the peak intensity of V_2O_5 being much lower than that of Bi_2O_3 . This

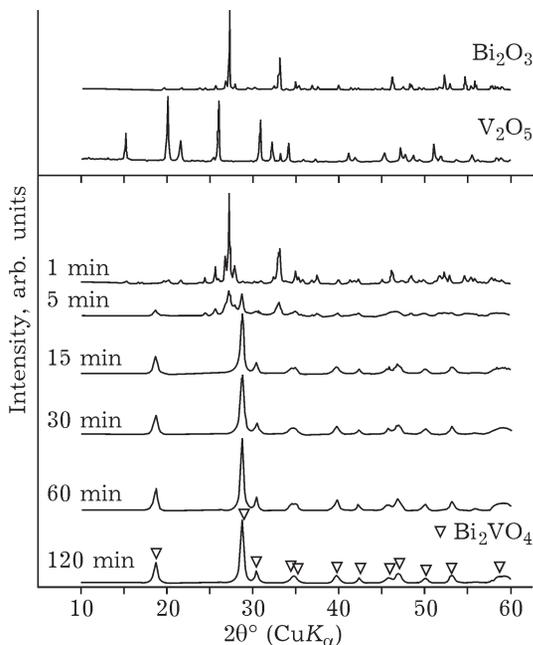


Fig. 1. XRD patterns of the Bi_2O_3 and V_2O_5 mixture milled for different periods of time.

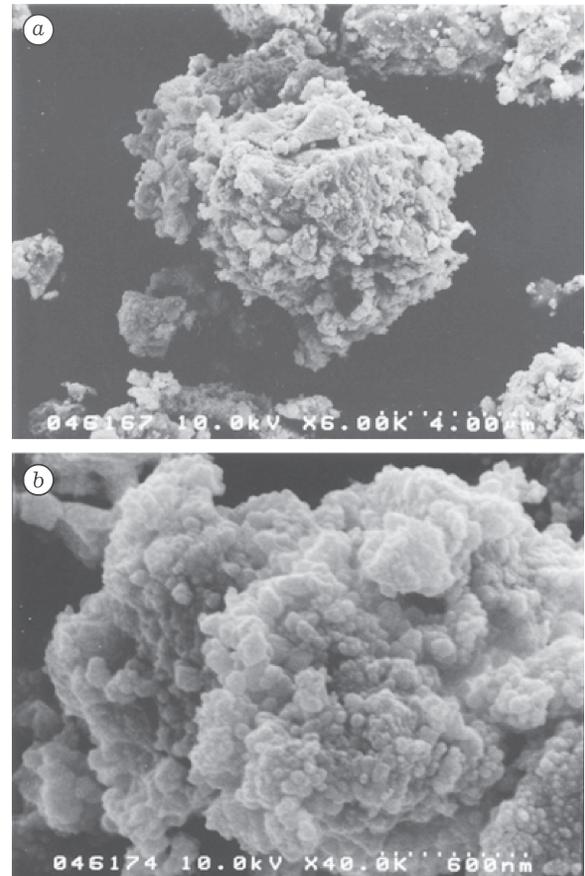


Fig. 2. SEM images of the Bi_2O_3 and V_2O_5 mixture milled for 60 min.

indicates that the structure in V_2O_5 is easily disordered to form amorphous state by milling operation. In addition, the patterns of the mixtures milled over 15 min show no peaks of the starting materials, while the peaks of BiVO_4 (monoclinic, JCPDS No. 83-1700) were observed. This indicates that BiVO_4 can be synthesized by milling the Bi_2O_3 and V_2O_5 mixture. Thus, the following solid state reaction takes place mechanochemically during milling:



Figure 2 shows the SEM images of the sample milled for 60 min. The particles of the sample look like agglomerates of fine grains with sizes less than 200 nm, and the agglomerates seem to be consisting of primary particles with several microns.

Figure 3 shows the yield of vanadium (V_2O_5) remaining in the milled samples as a function of milling time. The yield rapidly decreases with an increase in milling time in the early stage of milling, and it reaches 12.4 % at 15 min of milling. However, there is no significant change in the yield in the range over 15 min. The reason for the saturation of the V yield around 12 % may be due to the dissolution of V from the surface of BiVO_4 particles formed by milling and the release of mechanical energy stored based on the events of ball-to-ball/ball-to-wall collisions. In addition, the colour of the sample milled for 2 h is greenish yellow. This suggests that the sample obtained may be in an inhomogeneous state.

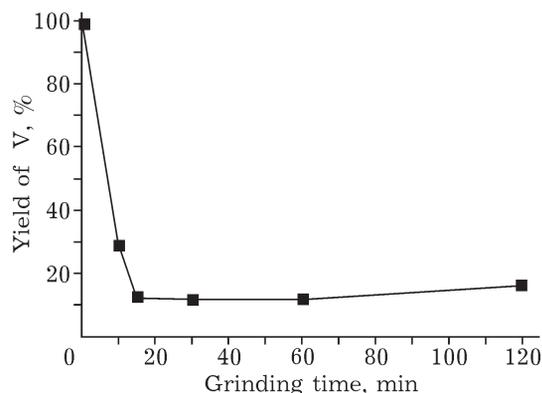


Fig. 3. Change in the yield of V_2O_5 with milling time.

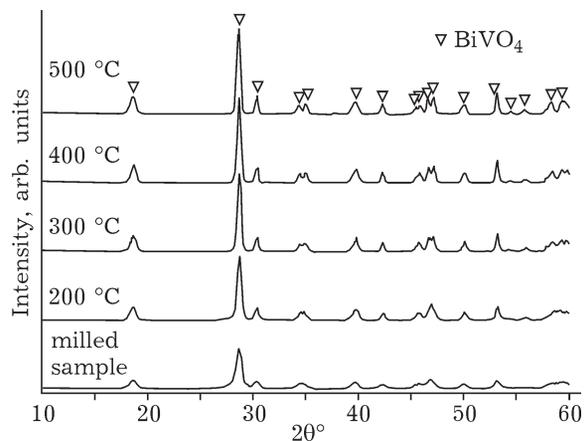


Fig. 4. XRD patterns of the 15-min milled sample heated at different temperatures.

Figure 4 shows the XRD patterns of the 15-min milled sample heated at different temperatures. Peak intensity of BiVO_4 increases and two peaks around 35 or 45° split further with an increase in heating temperature. This means that the crystallinity increases with an increase in heating temperature.

Figure 5 shows the yield of V (V_2O_5) remaining in the heated sample as a function of heating temperature. The yield of V decreases to 0.6 % at 300 °C and the value hardly changes over 300 °C. The colour of the sample mixture heated above 300 °C is bright yellow. From this result, the homogeneous BiVO_4 can be prepared by the heating treatment above 300 °C. The temperature is much lower than that required in the conventional ceramics powder

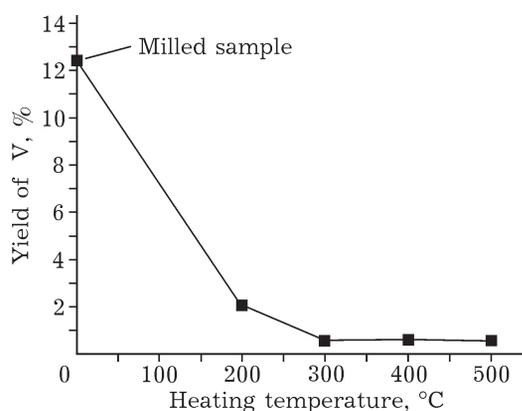


Fig. 5. Change in the yield of V_2O_5 with heating temperature.

elaboration at high temperature which is about 700–900 °C [14, 15].

Synthesis of BiAO_4 ($A = \text{P}, \text{Nb}$ and Sb)

The synthesis of BiVO_4 by mechanochemical method suggests the feasibility for the synthesis of other bismuth complex oxides, such as BiPO_4 , BiNbO_4 and BiSbO_4 .

Figure 6 shows the XRD patterns of the Bi_2O_3 - P_2O_5 , Bi_2O_3 - Nb_2O_5 and Bi_2O_3 - Sb_2O_5 mixtures milled for 2 h. In each case, the appearance of new peaks of BiPO_4 (JCPDS No. 80-0209), BiNbO_4 (JCPDS No. 71-1518) or BiSbO_4 (JCPDS No. 82-1805) was observed. The XRD analysis was confirmed that Bi_2O_3 reacts with each of P_2O_5 , Nb_2O_5 and Sb_2O_5 powders to form BiPO_4 , BiNbO_4 and BiSbO_4 , respectively. In the similar manner as the case of V_2O_5 , the following reactions can take place by milling:

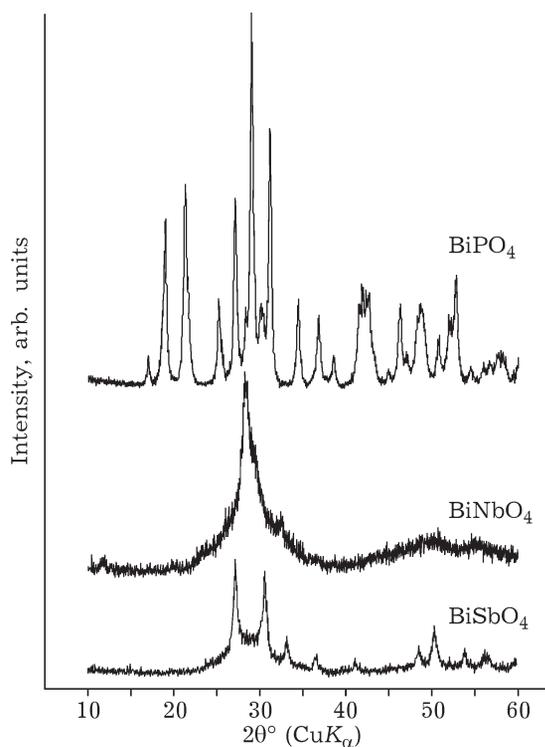


Fig. 6. XRD patterns of the Bi_2O_3 and pentavalent oxide (P_2O_5 , Nb_2O_5 or Sb_2O_5) mixture milled for 2 h.

Based on the mechanochemical synthesis of BiVO_4 , synthesis of BiPO_4 , BiNbO_4 and BiSbO_4 was also demonstrated. Further investigation of reaction between trivalent oxides and V_2O_5 is under consideration.

CONCLUSIONS

The following conclusions can be made based on the experimental results.

1. BiVO_4 can be synthesized by milling the Bi_2O_3 and V_2O_5 mixture at room temperature through mechanochemical solid state reaction.

2. The mechanochemical reaction ratio between Bi_2O_3 and V_2O_5 is saturated around 90 %. Heating treatment above 300 °C is necessary for the synthesis of homogeneous BiVO_4 with an increase in reaction ratio up to about 99.4 %. The temperature needed is much lower than that of conventional ceramics powder elaboration at high temperature.

3. The mechanochemical method is also applicable to the syntheses of BiPO_4 , BiNbO_4 and BiSbO_4 .

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