

## Synthesis of $\text{BiAO}_4$ by Mechanochemical Solid State Reaction between $\text{Bi}_2\text{O}_3$ and $\text{A}_2\text{O}_5$ (A = V, P, Nb and Sb)

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### Abstract

Bismuth vanadate ( $\text{BiVO}_4$ ) can be synthesized by mechanochemical reaction between bismuth oxide ( $\text{Bi}_2\text{O}_3$ ) and vanadium oxide ( $\text{V}_2\text{O}_5$ ) 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  $\text{Bi}_2\text{O}_3$  and  $\text{V}_2\text{O}_5$  is saturated around 90 %. Heating treatment above 300 °C leads to the formation of homogeneous  $\text{BiVO}_4$  with an increase in reaction ratio up to about 99.4 %. The mechanochemical method enables us to synthesize other bismuth complex oxides ( $\text{BiAO}_4$ ; A = P, Nb and Sb).

### INTRODUCTION

Bismuth vanadate ( $\text{BiVO}_4$ ) 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  $\text{BiVO}_4$ . 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  $\text{Bi}_2\text{VO}_5$ , aiming at utilization for BIMEVOX [24, 25]. Zyryanov [26] investigated the composition of crystalline products in  $\text{Bi}_2\text{O}_3$ – $\text{V}_2\text{O}_5$  system by mechanochemical method. We were studying the mechanochemical solid state reactions between binary oxides to form complex oxides with  $\text{ABO}_4$  composition [20, 21]. The mechanochemical reaction has a potential to synthesize the compounds from a mixture of  $\text{Bi}_2\text{O}_3$  and pentavalent oxide such as  $\text{V}_2\text{O}_5$  and  $\text{Sb}_2\text{O}_5$ .

The main purpose of this paper is to provide fundamental information mainly on the synthesis of  $\text{BiVO}_4$  by a mechanochemical method. In addition, the possibility of the synthesis of other bismuth complex oxides, which are  $\text{BiPO}_4$ ,  $\text{BiNbO}_4$  and  $\text{BiSbO}_4$ , is discussed.

## EXPERIMENTAL

### Sample preparation and milling the mixture

Five kinds of starting materials were used for the experiment. These are bismuth oxide ( $\text{Bi}_2\text{O}_3$ ), vanadium oxide ( $\text{V}_2\text{O}_5$ ), phosphorus oxide ( $\text{P}_2\text{O}_5$ ), niobium oxide ( $\text{Nb}_2\text{O}_5$ ) from Wako Pure Chemical Industries Ltd. (Japan) and antimony oxide ( $\text{Sb}_2\text{O}_5$ ) from Sigma-Aldrich (USA).  $\text{Bi}_2\text{O}_3$  was mixed with one of the pentavalent oxides described above ( $\text{V}_2\text{O}_5$ ,  $\text{P}_2\text{O}_5$ ,  $\text{Nb}_2\text{O}_5$  and  $\text{Sb}_2\text{O}_5$ ) 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 cm<sup>3</sup> 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  $\text{V}_2\text{O}_5$  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 $\text{BiVO}_4$ by milling the $\text{Bi}_2\text{O}_3$ and $\text{V}_2\text{O}_5$ mixture

Figure 1 shows the XRD patterns of the mixture of  $\text{Bi}_2\text{O}_3$  and  $\text{V}_2\text{O}_5$  milled for different periods of time. The pattern of the mixture milled for 1 min shows the peak intensity of  $\text{V}_2\text{O}_5$  being much lower than that of  $\text{Bi}_2\text{O}_3$ . This

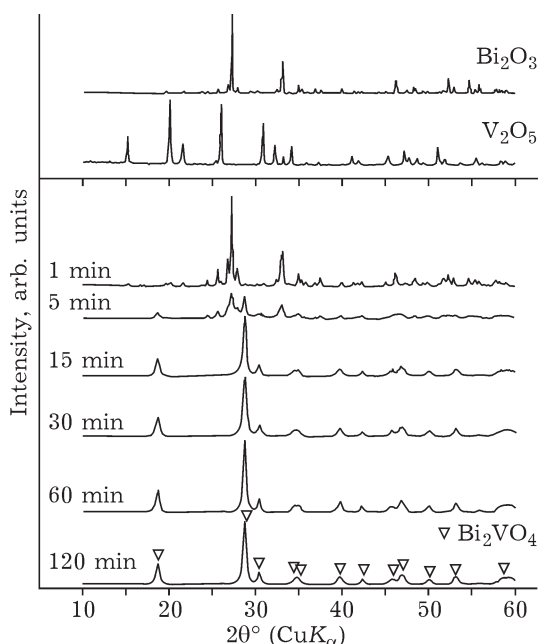


Fig. 1. XRD patterns of the  $\text{Bi}_2\text{O}_3$  and  $\text{V}_2\text{O}_5$  mixture milled for different periods of time.

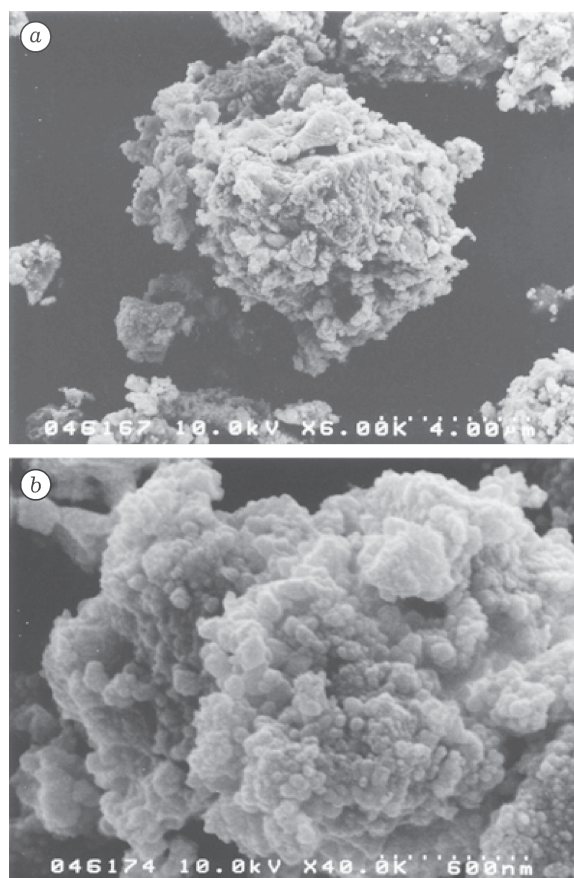


Fig. 2. SEM images of the  $\text{Bi}_2\text{O}_3$  and  $\text{V}_2\text{O}_5$  mixture milled for 60 min.

indicates that the structure in  $\text{V}_2\text{O}_5$  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  $\text{BiVO}_4$  (monoclinic, JCPDS No. 83-1700) were observed. This indicates that  $\text{BiVO}_4$  can be synthesized by milling the  $\text{Bi}_2\text{O}_3$  and  $\text{V}_2\text{O}_5$  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 ( $\text{V}_2\text{O}_5$ ) 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  $\text{BiVO}_4$  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.

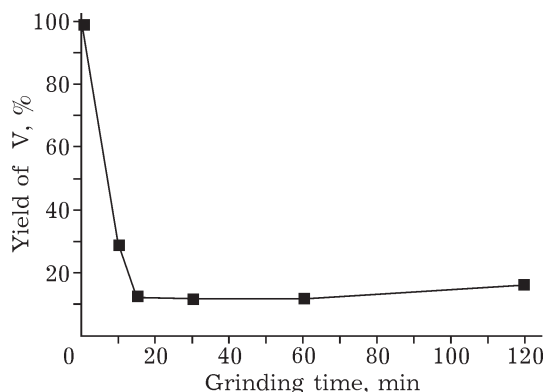


Fig. 3. Change in the yield of  $\text{V}_2\text{O}_5$  with milling time.

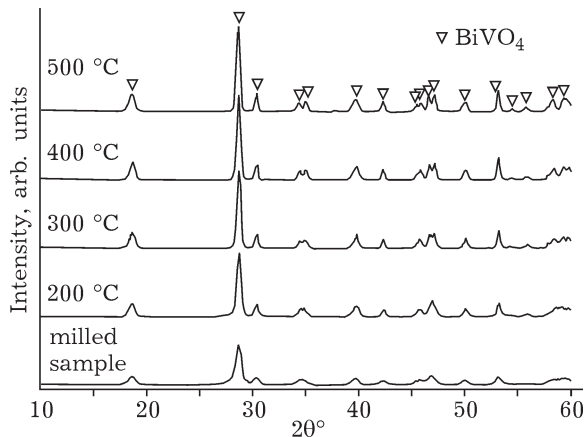


Fig. 4. XRD patterns of the 15-min milled sample heated at different temperatures.

Figure 4 shows the XRD patterns of the 15-min milled sample heated at different temperatures. Peak intensity of  $\text{BiVO}_4$  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 ( $\text{V}_2\text{O}_5$ ) 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  $\text{BiVO}_4$  can be prepared by the heating treatment above 300 °C. The temperature is much lower than that required in the conventional ceramics powder

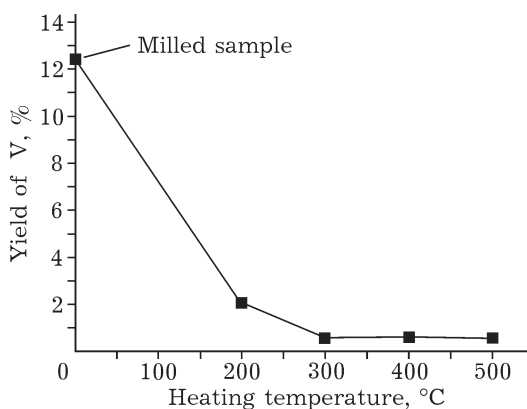


Fig. 5. Change in the yield of  $\text{V}_2\text{O}_5$  with heating temperature.

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

### Synthesis of $\text{BiAO}_4$ ( $A = \text{P, Nb and Sb}$ )

The synthesis of  $\text{BiVO}_4$  by mechanochemical method suggests the feasibility for the synthesis of other bismuth complex oxides, such as  $\text{BiPO}_4$ ,  $\text{BiNbO}_4$  and  $\text{BiSbO}_4$ .

Figure 6 shows the XRD patterns of the  $\text{Bi}_2\text{O}_3$ - $\text{P}_2\text{O}_5$ ,  $\text{Bi}_2\text{O}_3$ - $\text{Nb}_2\text{O}_5$  and  $\text{Bi}_2\text{O}_3$ - $\text{Sb}_2\text{O}_5$  mixtures milled for 2 h. In each case, the appearance of new peaks of  $\text{BiPO}_4$  (JCPDS No. 80-0209),  $\text{BiNbO}_4$  (JCPDS No. 71-1518) or  $\text{BiSbO}_4$  (JCPDS No. 82-1805) was observed. The XRD analysis was confirmed that  $\text{Bi}_2\text{O}_3$  reacts with each of  $\text{P}_2\text{O}_5$ ,  $\text{Nb}_2\text{O}_5$  and  $\text{Sb}_2\text{O}_5$  powders to form  $\text{BiPO}_4$ ,  $\text{BiNbO}_4$  and  $\text{BiSbO}_4$ , respectively. In the similar manner as the case of  $\text{V}_2\text{O}_5$ , the following reactions can take place by milling:

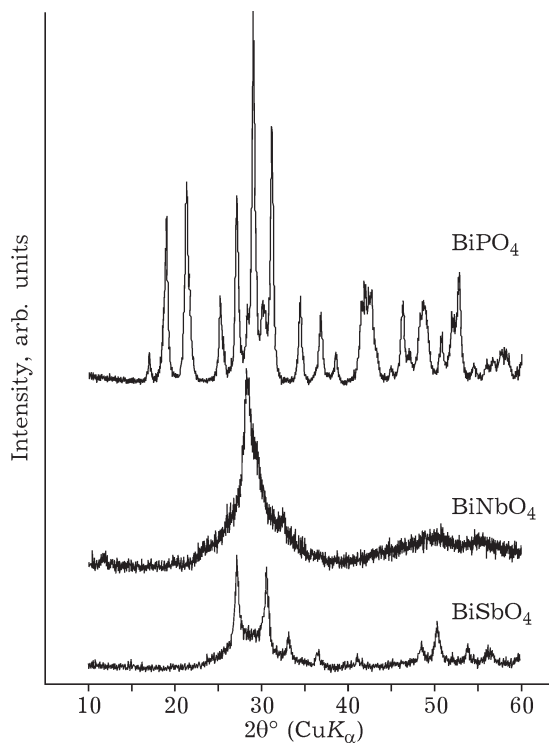


Fig. 6. XRD patterns of the  $\text{Bi}_2\text{O}_3$  and pentavalent oxide ( $\text{P}_2\text{O}_5$ ,  $\text{Nb}_2\text{O}_5$  or  $\text{Sb}_2\text{O}_5$ ) mixture milled for 2 h.

Based on the mechanochemical synthesis of  $\text{BiVO}_4$ , synthesis of  $\text{BiPO}_4$ ,  $\text{BiNbO}_4$  and  $\text{BiSbO}_4$  was also demonstrated. Further investigation of reaction between trivalent oxides and  $\text{V}_2\text{O}_5$  is under consideration.

### CONCLUSIONS

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

1.  $\text{BiVO}_4$  can be synthesized by milling the  $\text{Bi}_2\text{O}_3$  and  $\text{V}_2\text{O}_5$  mixture at room temperature through mechanochemical solid state reaction.

2. The mechanochemical reaction ratio between  $\text{Bi}_2\text{O}_3$  and  $\text{V}_2\text{O}_5$  is saturated around 90%. Heating treatment above 300 °C is necessary for the synthesis of homogeneous  $\text{BiVO}_4$  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  $\text{BiPO}_4$ ,  $\text{BiNbO}_4$  and  $\text{BiSbO}_4$ .

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