# Reactivity and Structural Properties of a Mechanochemically Treated Ag<sub>2</sub>O-V<sub>2</sub>O<sub>5</sub> System in Relation to AgVO<sub>3</sub> Polymorphs

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Formation and chemical properties of amorphous AgVO<sub>3</sub>, which was prepared by mechanochemical treatment of an Ag<sub>2</sub>O-V<sub>2</sub>O<sub>5</sub> mixture, and crystalline AgVO<sub>3</sub> were studied in relation to AgVO<sub>3</sub> polymorphs. A ball-milled sample of the mixture was assigned as a highly deformed  $\beta$ -AgVO<sub>3</sub> rather than the low density phase  $\alpha$ -AgVO<sub>3</sub>. Crystalline  $\alpha$ -AgVO<sub>3</sub> and  $\beta$ -AgVO<sub>3</sub> were converted into deformed  $\beta$ -AgVO<sub>3</sub> by ball milling, which produced a clear change.  $\delta$ -AgVO<sub>3</sub> is resistant to mechanical treatment and its structure was not markedly affected. The dissolved chemical species from the ball-milled sample precipitates to form  $\alpha$ -AgVO<sub>3</sub> without a seeding crystal, but other polymorphs deposit if they are present; i.e.,  $\beta$ -AgVO<sub>3</sub> and  $\delta$ -AgVO<sub>3</sub> grow on the seeding crystal.  $\odot$  2002 Elsevier Science (USA)

*Key Words:* ball milling; mechanochemistry; silver vanadate; dissolution–precipitation.

# **INTRODUCTION**

Silver vanadate is one of the most complicated binary metal oxides, with a number of phases even in the case of a single atomic composition. Materials have often been formed by heating the component metal oxides, Ag<sub>2</sub>O and  $V_2O_5$ , mainly due to the convenience of controlling the composition (1, 2). Silver vanadate, AgVO<sub>3</sub>, is also prepared by such a method, while  $\alpha$ -AgVO<sub>3</sub> can be conventionally formed from aqueous systems with NH<sub>4</sub>VO<sub>3</sub> and AgNO<sub>3</sub>. In a previous work, the authors reported that three types of monoclinic AgVO<sub>3</sub> ( $\alpha$ -AgVO<sub>3</sub>,  $\beta$ -AgVO<sub>3</sub>, and  $\delta$ -AgVO<sub>3</sub>) can be formed by reacting vanadium pentoxide hydrate  $V_2O_5 \cdot nH_2O$  with AgNO<sub>3</sub> (3). Crystal parameters for each sample are  $\alpha$ -AgNO<sub>3</sub>, a = 10.437 Å, b = 9.897 Å, c = 5.532 Å,  $\beta = 99.69^{\circ}; \beta$ -AgVO<sub>3</sub>, a = 18.106 Å, b = 3.5787 Å, c =8.043 Å,  $\beta = 104.44^{\circ}$ ;  $\delta$ -AgVO<sub>3</sub>, a = 18.775 Å, b = 3.580 Å,  $c = 17.779 \text{ Å}, \beta = 113.16^{\circ}$  (3). Textures of the sediments were all needles. Furthermore,  $\alpha$ -AgVO<sub>3</sub> was formed by

quenching the melt of  $AgVO_3$  (4). It was found that each of these has a reversibly deformed modification at high temperature (5).

Mechanochemical treatment of the solid material has been developed to produce new compounds in solid state chemistry. This technique is convenient to use and does not consume much energy. It can affect the solid properties in two ways: destruction of the skeleton of the raw material to give an amorphous phase and generation of various chemical processes (e.g., chemical reactions, transformation, crystallization) (6–8).  $V_2O_5$  is a rather soft material that melts at a relatively low temperature (674°C) and thus might be deformed by this treatment into an amorphous phase that should be chemically reactive. Coexistence of Ag<sub>2</sub>O might lead directly to the formation of silver vanadate.

The present paper examines the possibility of forming a new amorphous phase by ball milling from a mixture of  $V_2O_5$  and  $Ag_2O$  and crystalline  $AgVO_3$  phases. The physicochemical properties of treated samples are discussed in relation to the phase properties of  $AgVO_3$ .

### **EXPERIMENTAL**

#### Samples

Raw materials for ball milling were prepared as follows.  $V_2O_5$  was formed by decomposing  $NH_4VO_3$  at 400°C in air.  $Ag_2O$  was precipitated by the reaction between 0.1 mol dm<sup>-3</sup> AgNO<sub>3</sub> and 0.1 mol dm<sup>-3</sup> NaOH and subsequent washing with distilled water. Particle sizes observed by transmission electron microscopy (TEM) were about 0.01 µm for Ag\_2O and 0.3 µm for  $V_2O_5$ , the latter of which was sintered during decomposition. Well-crystallized  $\alpha$ -AgVO<sub>3</sub>,  $\beta$ -AgVO<sub>3</sub>, and  $\delta$ -AgVO<sub>3</sub> were prepared to test their durability against ball milling.  $\alpha$ -AgVO<sub>3</sub> was precipitated conventionally by mixing 0.1 mol dm<sup>-3</sup> aqueous solutions of AgNO<sub>3</sub> and NH<sub>4</sub>VO<sub>3</sub>.  $\beta$ -AgVO<sub>3</sub> for more than 1 year.  $\delta$ -AgVO<sub>3</sub> was prepared by the reaction between 0.01 mol dm<sup>-3</sup> V<sub>2</sub>O<sub>5</sub>·nH<sub>2</sub>O sol and 0.2 mol dm<sup>-3</sup> AgNO<sub>3</sub>,



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the details of which have been reported in a previous paper (3). The precipitates were washed with distilled water.

# Ball Milling

A  $V_2O_5$  plus Ag<sub>2</sub>O mixture with equal molar amounts was prepared and placed in a ball-milling apparatus that consists of 25-cm<sup>3</sup> vessels and balls of agate (diameter = 12 mm); 0.50-g samples were milled for varying periods of 0.5-2h in air. The apparatus used was a planetary type ball mill, Frisch P7. Crystalline samples were also treated as above. For comparison with ball milling, a mixed sample (0.25 g) was ground for 1 h with an agate mortar and pestle.

### Characterization of Materials

Fine properties of the produced samples were characterized by TEM. The sample powders were dispersed over a perforated carbon film that had been prepared on a copper sheet mesh. The apparatus used was a Hitachi H8100, which was operated at an accelerating voltage of 200 kV. The crystal structure was analyzed by a conventional powder XRD apparatus, RIGAKU RAD-2R, equipped with a Cu-targeted X-ray tube.

Phase changes produced by thermal treatment were studied by differential thermal analysis (DTA) using an ULVAC DTG-7000. Measurements were conducted in air at a heating rate of  $5^{\circ}$ C min<sup>-1</sup>.

FT-IR measurements were also conducted at room temperature to characterize the bonding mode in the metal oxide, by use of a JEOL JIR-100. Sample powders were mixed with previously well-pulverized KBr and pelleted without grinding since grinding produced a mechanochemical effect, *i.e.*, deformation of the structure.

## **RESULTS AND DISCUSSION**

# Mechanochemical Reactions between $V_2O_5$ and $Ag_2O$

Figure 1 shows the XRD patterns for  $V_2O_5$  and  $Ag_2O$  ball-milled for 2h. In these sample oxides, the effect of milling was discernible for the  $V_2O_5$ . As the sample amount is decreased, the effect becomes more marked, giving an amorphous phase.  $Ag_2O$  is rather resistant to having its structure changed by ball milling.

It is interesting to find that the structures of both components are broken quite rapidly when they are mixed and milled (Fig. 2a). A few minutes of milling produces broad peaks around  $2\theta = 10^{\circ}$  and  $30^{\circ}$  that are from neither V<sub>2</sub>O<sub>5</sub> nor Ag<sub>2</sub>O. This indicates that ball milling facilitates the reaction of Ag<sub>2</sub>O and V<sub>2</sub>O<sub>5</sub> species by close contact between the raw samples. High reactivity between the two oxides was ascertained by the tribochemical treatment of hand milling in an agate mortar (trace 6 of Fig. 2a). The diffraction peaks for the component oxides significantly



FIG. 1. XRD patterns of  $V_2O_5$  and  $Ag_2O$  before and after by ball milling for 2 h.  $V_2O_5$ : a1, before; a2, after.  $Ag_2O$ : b1, before; b2, after. Miller indices are for orthorhombic  $V_2O_5$  and hexagonal  $Ag_2O$ , respectively.

decrease in intensity upon milling: the peaks for  $Ag_2O$  have almost disappeared and some peaks for  $V_2O_5$  remain in a weak broadened state.

Electron microscope observation of the 2h ball-milled mixture shows both noncrystalline parts and remaining raw particles or some other phases. Figure 3a shows an electron micrograph of the apparently noncrystalline part of a ball-milled mixture. We can see fine particles in the amorphous phase of the specimen. The diffraction pattern is composed of rather clear rings in the broad halos (Fig. 3b). The indicated indexes are for the  $V_2O_5$ , while halos were not possible to identify. The diffraction rings for  $Ag_2O$  were not observed. The situation was similar for the sample milled for 10 h. This result agrees with the XRD patterns in Fig. 2a and signifies that  $Ag_2O$  migrates easily into  $V_2O_5$  to disappear.

# Ball Milling of Crystalline AgVO<sub>3</sub> Samples: $\alpha$ -AgVO<sub>3</sub>, $\beta$ -AgVO<sub>3</sub>, and $\delta$ -AgVO<sub>3</sub>

The fine structure of ball-milled  $V_2O_5$ -Ag<sub>2</sub>O may reasonably be related to the crystalline forms of AgVO<sub>3</sub> that have been found so far. Figure 2b shows the XRD patterns for the samples before and after ball milling for one 1 h. It is to be noted that the structure of  $\alpha$ -AgVO<sub>3</sub> has been destroyed and broad peaks assignable to deformed  $\beta$ -AgVO<sub>3</sub> have appeared. The structure of  $\beta$ -AgVO<sub>3</sub> was strongly modified by ball milling to give a markedly deformed form. It is interesting to find that the diffraction peaks of ball-milled



**FIG. 2.** (a) XRD pattern changes of a Ag<sub>2</sub>O–V<sub>2</sub>O<sub>5</sub> mixture as a function of ball-milling time. 1, mixture of Ag<sub>2</sub>O (stars) and V<sub>2</sub>O<sub>5</sub> (other peaks), before milling; 2, ball-milled for 5 min; 3, 2 h; 4, 5 h; 5, 10 h; 6, hand-milled with an agate pestle in an agate mortar for 1 h. (b) XRD patterns of crystalline AgVO<sub>3</sub> samples before and after ball milling for 1 h.  $\alpha$ -AgVO<sub>3</sub>: 1a, before; 1b, after.  $\beta$ -AgVO<sub>3</sub>: 2a, before; 2b, after.  $\delta$ -AgVO<sub>3</sub>: 3a, before; 3b, after.

 $\delta$ -AgVO<sub>3</sub> remain unchanged from those of the intrinsic sample, although the diffraction intensities differ greatly. The latter fact is simply explained by the pulverizing of the fibrous  $\delta$ -AgVO<sub>3</sub> precipitate; i.e., the latter sample is oriented so that the longest axis of the needle is parallel to the sample holder plate.

# Short-Range Structures of the Ball-Milled Samples by FT-IR Measurements

Figure 4 (traces a1-c2) shows the FT-IR spectra of the raw materials and ball-milled samples in the lattice vibration range. The spectra of the crystalline samples reflect the variations of the crystal structures. However, spectral analyses have not been reported so far. Here, we would like to focus our attention on the pattern changes as a result of structural changes. The ball milling strongly affects the interatomic relations in the substances, especially for  $\alpha$ -AgVO<sub>3</sub>. The treated sample gave a pattern similar to that of ball-milled  $\beta$ -AgVO<sub>3</sub>. The pattern of  $\beta$ -AgVO<sub>3</sub> was almost unchanged by ball milling except in the lower wavenumber range. Traces d1 and d2 show the marked change of the FT-IR spectrum in V<sub>2</sub>O<sub>5</sub>-Ag<sub>2</sub>O mixtures upon ball milling, in accordance with the XRD experiments (Fig. 2a, trace 3). New bands appear around 820–1050 cm<sup>-1</sup> after 5-min milling. Two-hour milling gave the final form of the spectrum, which is very similar to that of ball-milled  $\beta$ -AgVO<sub>3</sub>, but does not approach that of well-defined  $\beta$ -AgVO<sub>3</sub>. Thus, we can conclude that the structure around each ion in the ball-milled V<sub>2</sub>O<sub>5</sub>-Ag<sub>2</sub>O mixture becomes closer to that of deformed  $\beta$ -AgVO<sub>3</sub>.

The short-range structure of  $\beta$ -AgVO<sub>3</sub> from the ballmilled V<sub>2</sub>O<sub>5</sub>-Ag<sub>2</sub>O mixture was ascertained by thermal property measurements. Trace b in Fig. 5 shows a DTA curve for the ball-milled sample. Apparently no thermal property change can be seen up to the melting point of AgVO<sub>3</sub> (474°C), which is common to  $\beta$ -AgVO<sub>3</sub>. The XRD analysis indicates that heat treatment increases the growth of the  $\beta$ -AgVO<sub>3</sub> structure up to 400°C (Fig. 6). That is, there are domains seeding the crystal growth of  $\beta$ -AgVO<sub>3</sub> in the ball-milled sample.

It is understood that the effect of ball milling on the structure is quite complex and cannot be described by a simple mechanism. The two main possibilities are assumed to be an adiabatic temperature increase and reconstruction under mechanical pressure. Trace a in



**FIG. 3.** (a) Transmission electron micrograph of a ball-milled  $Ag_2O-V_2O_5$  mixture and (b) its selected area electron diffraction pattern. Indexes in the latter are for  $V_2O_5$ .

Fig. 5 shows a DTA curve for the Ag<sub>2</sub>O-V<sub>2</sub>O<sub>5</sub> mixture that has just been mixed without strong mechanical power. A large exothermic peak at 381°C and an endothermic peak appeared, the latter corresponding to the melting point for  $\beta$ -AgVO<sub>3</sub>. XRD analysis substantiated that a mixture of Ag<sub>2</sub>O and V<sub>2</sub>O<sub>5</sub> reacts at a temperature higher than 381°C to form  $\beta$ -AgVO<sub>3</sub> (not shown). As the actual temperature of the milling vessel increased only slightly above room temperature, it is not necessary to take account of this temperature effect.

Another factor was considered on the basis of the solid state properties. According to the DTA measurements of the three crystalline forms of AgVO<sub>3</sub>, the crystal enthalpy decreases in the order  $\alpha$ -AgVO<sub>3</sub>,  $\delta$ -AgVO<sub>3</sub>, and  $\beta$ -AgVO<sub>3</sub> (5).



**FIG.4.** Effect of ball milling on the FT-IR spectra of crystalline AgVO<sub>3</sub> and a Ag<sub>2</sub>O-V<sub>2</sub>O<sub>5</sub> mixture.  $\alpha$ -AgVO<sub>3</sub>: a1, before; a2, after.  $\beta$ -AgVO<sub>3</sub>: b1, before; b2, after.  $\delta$ -AgVO<sub>3</sub>: c1, before; c2, after. Ag<sub>2</sub>O-V<sub>2</sub>O<sub>5</sub> mixture: d1, before; d2, after.

That is, the  $\beta$ -AgVO<sub>3</sub> is the most stable phase. The enthalpy of  $\delta$ -AgVO<sub>3</sub> is only slightly higher than that of  $\beta$ -AgVO<sub>3</sub>. In accordance with this, the densities of these materials are  $4.80 \text{ g cm}^{-3}$  for  $\alpha$ -AgVO<sub>3</sub>,  $5.04 \text{ g cm}^{-3}$  for  $\delta$ -AgVO<sub>3</sub>, and



**FIG. 5.** DTA curves of a  $Ag_2O-V_2O_5$  mixture (a) before and (b) after ball milling determined in air at the heating rate  $5^{\circ}C$  min<sup>-1</sup>.

**FIG. 6.** Growth of  $\beta$ -AgVO<sub>3</sub> phase of a ball-milled Ag<sub>2</sub>O–V<sub>2</sub>O<sub>5</sub> mixture by heat treatment, which was conducted by using a DTA apparatus at the same heating rate as for thermal analysis and cooled after reaching the programmed temperature. Treatment temperatures (°C): a, room temperature; b, 200; c, 300; d, 400.

5.39 g cm<sup>-3</sup> for  $\beta$ -AgVO<sub>3</sub> (4,5). The coordination condition of the atoms in the crystal structure is more variable in  $\beta$ -AgVO<sub>3</sub> than in  $\alpha$ -AgVO<sub>3</sub>: four kinds of Ag ions and two

**FIG. 7.** XRD patterns of ball-milled samples after contacting with water. a,  $Ag_2O-V_2O_5$  mixture; b,  $\alpha$ -AgVO<sub>3</sub>; c,  $\beta$ -AgVO<sub>3</sub>; d,  $\delta$ -AgVO<sub>3</sub>; e,  $\delta$ -AgVO<sub>3</sub> precipitate added by a ball-milled Ag<sub>2</sub>O-V<sub>2</sub>O<sub>5</sub> mixture.

30

 $2\theta$ /degree

40

50

60

kinds for V are included in the structure of the former while there are two for Ag and one for V in the latter. Thus, it is reasonable to expect that the structure of  $\alpha$ -AgVO<sub>3</sub> is broken to form a state close to the deformed but dense phase of  $\beta$ -AgVO<sub>3</sub>.

The definite crystal structure of the new compound  $\delta$ -AgVO<sub>3</sub> has not been determined so far, but thermodynamic data and its density lead us to suppose that this sample has a structure that is resistant to mechanical treatment so as not to give a deformed  $\beta$ -AgVO<sub>3</sub>.

# Interaction of Ball-Milled Samples with Water

Amorphous  $V_2O_5$  is reactive with water to form  $V_2O_5 \cdot nH_2O$  with a layered structure, while crystalline  $V_2O_5$  is stable and does not react with water (9). However, when the material is composed of an amorphous region and/or a disordered structure inside, dissolution of such part and precipitation of  $V_2O_5 \cdot nH_2O$  continue until the crystalline  $V_2O_5$  phase completely disappears (10). In the previous work,  $\alpha$ -AgVO<sub>3</sub>,  $\beta$ -AgVO<sub>3</sub>, and  $\delta$ -AgVO<sub>3</sub> were all formed through a dissolution–precipitation reaction from the composite materials of  $V_2O_5 \cdot nH_2O$  with Ag<sup>+</sup>, i.e., intercalation compounds. Thus, reactivity of the mechanically deformed AgVO<sub>3</sub> with water might be expected.

Here, the ball-milled samples of the V<sub>2</sub>O<sub>5</sub>-Ag<sub>2</sub>O mixture,  $\alpha$ -AgVO<sub>3</sub>,  $\beta$ -AgVO<sub>3</sub>, and  $\delta$ -AgVO<sub>3</sub>, were immersed in water at room temperature. Their XRD patterns are shown in Fig. 7. It is interesting to find the  $\alpha$ -AgVO<sub>3</sub> phase formed from the ball-milled V<sub>2</sub>O<sub>5</sub>-Ag<sub>2</sub>O mixture after overnight immersion: the pattern shown was taken for the sample immersed for 11 days. Electron microscopic observation

FIG. 8. Electron micrograph of needle-like particles of  $\alpha$ -AgVO<sub>3</sub> formed by hydrating a ball-milled Ag<sub>2</sub>O-V<sub>2</sub>O<sub>5</sub> mixture.





Intensity

0

10

20

149

showed that fine needle-like crystallites had grown through this reaction, indicating that dissolution of the ball-milled powder sample and crystallization of  $\alpha$ -AgVO<sub>3</sub> had occurred (Fig. 8).

In the case of ball-milled samples of crystalline  $AgVO_3$ , the crystalline change upon contact with water was small; i.e., deformed structures of  $\beta$ -AgVO<sub>3</sub> and  $\delta$ -AgVO<sub>3</sub> were almost unchanged. This is in contrast to the system prepared from the V<sub>2</sub>O<sub>5</sub>-Ag<sub>2</sub>O mixture and suggests that the short-range structure of the latter sample is much less well defined than that from crystalline AgVO<sub>3</sub>. In other words, even though the long-range ordering was damaged by ball milling for the crystalline AgVO<sub>3</sub>, short-range structure and coordination between atoms were not changed. Thus, deformed internal species are not dissolved in water and the deformed structure is maintained.

The sample from  $\delta$ -AgVO<sub>3</sub> shows a similar behavior to the above one: the  $\delta$  phase has grown to a well-crystallized form. The reason for this stems from the originally stable structure of both  $\beta$ -AgVO<sub>3</sub> and  $\delta$ -AgVO<sub>3</sub>.

The above fact leads us to test the dissolution of ballmilled  $Ag_2O-V_2O_5$  and epitaxial precipitation on the stable crystal instead of formation of  $\alpha$ -AgVO<sub>3</sub>. A small amount of ball-milled  $Ag_2O-V_2O_5$  was added stepwise every few days until finally the amount added was equal to the  $\delta$ -AgVO<sub>3</sub> phase. The result is shown by trace e in Fig. 7 in which there are no signals due to structures other than  $\delta$ -AgVO<sub>3</sub>.

#### CONCLUSIONS

1. Ball milling of an  $Ag_2O-V_2O_5$  mixture gives an amorphous  $AgVO_3$  phase, which dissolves in water and recrystallizes as  $\alpha$ -AgVO<sub>3</sub>.

2. Ball milling of crystalline  $\alpha$ -AgVO<sub>3</sub> and  $\beta$ -AgVO<sub>3</sub> gives deformed  $\beta$ -AgVO<sub>3</sub>, which is resistant to dissolving in water and neither improves the crystallinity of  $\beta$ -AgVO<sub>3</sub> nor crystallizes in another form.

3. The  $\delta$ -AgVO<sub>3</sub> was deformed by ball milling but retained its structure. The ball-milled material is resistant to reaction with water.

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