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Mechanochemical synthesis of rutile-type $CrMO_4$ (M = V, Sb) and their solid solutions

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Abstract

Grinding a mixture of hydrous amorphous chromium oxide ($Cr_2O_3 \cdot nH_2O$), vanadium oxide (V_2O_5) and antimony oxide (Sb_2O_5) was conducted by using a planetary ball mill, to investigate their mechanochemical reactions to form chromium vanadium oxide ($CrVO_4$) and chromium antimony oxide ($CrSbO_4$). The synthesis reactions proceed with an increase in grinding periods of time. The ground samples consist of agglomerates with particle size of about ten nanometers. The synthesized $CrVO_4$ sample exhibits a rutile-type tetragonal crystal structure, which is a high pressure phase. Additionally, solid solutions, $CrV_{1-x}Sb_xO_4$ ($x = 0 \sim 1$, $\Delta x = 0.25$), have been synthesized mechanochemically from the mixtures of $Cr_2O_3 \cdot nH_2O$, V_2O_5 and Sb_2O_5.

Keywords: Grinding; Mechanochemical reaction; $CrVo_4$; $CrSbO_4$; Rutile-type structure; Solid solutions

1. Introduction

Chromium vanadium oxide ($CrVO_4$) has three different crystal structures, namely orthorhombic, monoclinic and tetragonal. Orthorhombic and monoclinic $CrVO_4$ have been synthesized successfully by several methods, e.g. solid state reactions at high temperature, coprecipitation technique and chimie douce process [1–3]. $CrVO_4$ with these structures has magnetic and catalytic properties, and there have been investigations on these topics [4–6]. On the other hand, as to rutile-type tetragonal $CrVO_4$, which is a high pressure phase, little attention has been paid on its physical or chemical properties and possible utilization. One reason for this may be due to the difficulty in synthesis of rutile-type $CrVO_4$, actually until now it is synthesized by only one method, which is heating a mixture of Cr_2O_3 and V_2O_5 at 750 °C under high pressure such as 6 GPa [7,8]. It is well known that the properties of materials depend on their synthesis processes. Therefore, it is very important to find new routes for synthesis of materials, from the view point of well comprehension of characteristics of materials and finding new properties.

One of the new routes may be mechanochemical method, by which various kinds of compounds have been synthesized successfully. Moreover, many reports on high pressure polymorphism have been presented [9–19]. In this method, it is known that many factors may exhibit influence on the occurrence of mechanochemical reactions. For example, Kosova et al. investigated the effect of water in/around starting materials [20,21]. In the present work, the focus is put on the crystal structures of starting materials. We have found that the rutile-type $CrVO_4$ can be synthesized by a mechanochemical method, namely grinding a mixture of hydrous amorphous chromium oxide ($Cr_2O_3 \cdot nH_2O$) and vanadium oxide (V_2O_5), where it has been found that the crystal state of chromium oxide is of much importance for mechanochemical synthesis and the use of amorphous hydrous chromium oxide rather than the crystalline oxide allowed the successful synthesis of $CrVO_4$.

In addition to the synthesis of the rutile-type $CrVO_4$, we have attempted to synthesize $CrSbO_4$ and the solid solutions between $CrVO_4$ and $CrSbO_4$. The reason for the choice of $CrSbO_4$ is as follow. $CrSbO_4$ belongs to same

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space group as that of rutile-type $CrVO_4$, so that solid solutions between $CrVO_4$ and $CrSbO_4$ are expected to be easily synthesized by the mechanochemical method.

The main purpose of this paper is to provide fundamental information on the synthesis of rutile-type $CrVO_4$ and $CrSbO_4$ by the mechanochemical treatment of ($Cr_2O_3 \cdot nH_2O$–V_2O_5) and ($Cr_2O_3 \cdot nH_2O$–Sb_2O_5) systems. In addition, the possibility for synthesizing solid solutions of $CrV_{1-x}Sb_xO_4$ ($x = 0 \sim 1$) from the mixtures of $Cr_2O_3 \cdot nH_2O$, V_2O_5 and Sb_2O_5, has been discussed.

2. Experimental

2.1. Sample

Chromium hydroxide hydrate ($Cr(OH)_3 \cdot nH_2O$) and vanadium oxide (V_2O_5) were supplied from Wako Pure Chemical Co. (Japan), and antimony oxide from Sigma-Aldrich Co. (America). We have prepared different hydrous chromium oxide samples ($Cr_2O_3 \cdot nH_2O$) by heating $Cr(OH)_3 \cdot nH_2O$ at 5 °C/min up to different temperatures: These are 200, 300, 400, 600 and 800 °C, and the samples prepared at each temperature are denoted as CR-200, -300, -400, -600 and -800, respectively, and the as-received sample $Cr(OH)_3 \cdot nH_2O$ was denoted as CR-0. The amount of the water in these samples was measured by thermogravimetry (Model ThermoPlus2, RIGAKU Co., Japan), and the data are shown in Table 1. One of these chromium oxides was mixed with other oxide (M_2O_5, M = V or Sb).

2.2. Methods

A planetary ball mill (Model Pulverisette-7, Fritsch, Germany) was used for grinding the mixture. Two grams of the mixture were put in a zirconia pot 45 cm^3 inner volume with seven zirconia balls of 15 mm diameter. The grinding was operated in air at 700 rpm. The ground samples were characterized by X-ray diffraction (XRD) analysis (Model RINT 2200, RIGAKU Co., Japan) method using Cu$K\alpha$ radiation ($\lambda = 1.541838$ Å) to identify the phases formed in the grinding. Furthermore, four or more peak-tops of each XRD pattern were determined by peak fitting analysis with a pseudo-Voigt profile function and the lattice parameters of the samples were calculated with the CellCalc [21] based on RSLC3 algorithm [22]. Morphology of the ground products was observed by a transmission electron microscopy (Model JEM-ARM 1250, JEOL, Japan) at 300 kV. Specific surface area (SSA) of the samples was measured by nitrogen gas adsorption instrument (Model ASAP-2010, Micromeritics, Shimadzu, Japan) based on the BET method.

3. Results and discussion

3.1. Mechanochemical synthesis of $CrMO_4$ (M = V and Sb)

The sample prepared by heating $Cr(OH)_3 \cdot nH_2O$ above 400 °C (CR-400, -600 and -800) were confirmed to be the crystalline Cr_2O_3 phase by XRD analysis. On the other hand, CR-200 and -300 are entirely XRD amorphous. From the result shown in Table 1, 1.92 and 1.75 M water remains in the CR-200 and -300 samples, indicating that they are hydrous amorphous chromium oxides represented as $Cr_2O_3 \cdot nH_2O$. Fig. 1 shows XRD patterns of the mixture of CR-300 and V_2O_5 ground for different periods of time. Peaks of V_2O_5 are observed in the XRD patterns of the mixture ground for less than 30 min. This implies that the mechanochemical reaction has not been achieved within 30 min. Peak intensity of V_2O_5 decreases gradually with an increase in grinding time, while new peaks of $CrVO_4$ (Tetragonal, JCPDS No. 15-0296) appear in the patterns of the mixture ground for 60 min. Their intensity increases as the grinding progresses. This result indicates that the following mechanochemical reaction takes place during the grinding the mixture of amorphous hydrated chromium oxide and V_2O_5,

$$Cr_2O_3 \cdot nH_2O + V_2O_5 \rightarrow 2CrVO_4 + nH_2O. \quad (1)$$

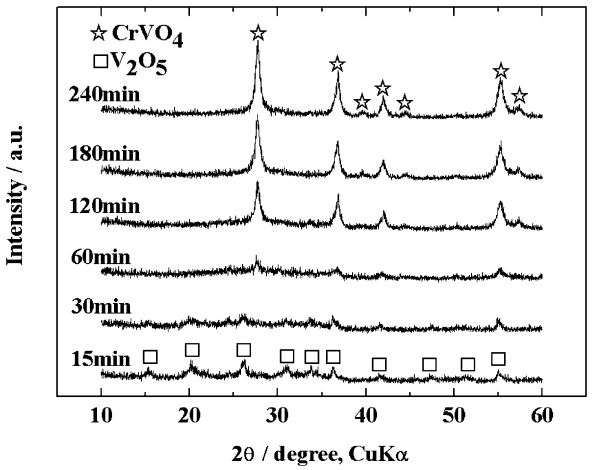

Fig. 1. Crystal growth of $CrVO_4$ from CR-300 and V_2O_5 mixture by mechanochemical treatment.

Table 1
The molar (n) amount of water in $Cr_2O_3 \cdot nH_2O$

Sample	CR-0	CR-200	CR-300	CR-400	CR-600	CR-800
n	5.75 (1.38)[a]	1.92	1.75	0.06	0.04	0.02

[a] n in $Cr(OH)_3 \cdot nH_2O$.

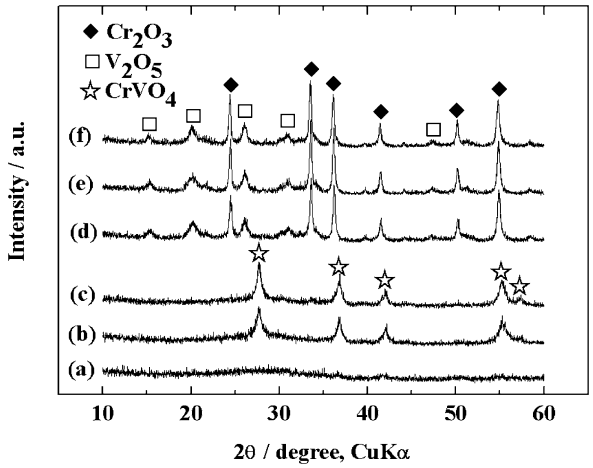

Fig. 2. Effect of crystallinities of chromium oxide on the mechanochemical reactions with V_2O_5. (after 120 min grinding). The mixture of V_2O_5 and CR-0 (a), CR-200 (b), CR-300 (c), CR-400 (d), CR-600 (e), CR-800 (f).

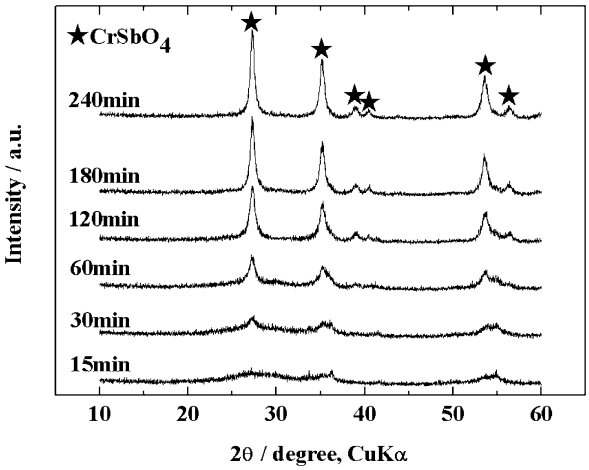

Fig. 3. Crystal growth of $CrSbO_4$ from CR-300 and Sb_2O_5 mixture by mechanochemical treatment.

In the XRD patterns of the mixtures ground for 180 min or more, the increment of the peak intensity of $CrVO_4$ approximately converges and no other peaks can be observed. This implies that $CrVO_4$ can be completely synthesized by grinding over 180 min. Tetragonal $CrVO_4$, which is in rutile-type structure, is high pressure polymorph.

Fig. 2 shows XRD patterns of the mixture of the chromium oxides prepared by heating $Cr(OH)_3 \cdot nH_2O$ at different temperature and V_2O_5 sample, ground for 120 min. An amorphous pattern can be seen in (a) which is the ground mixture of CR-0 and V_2O_5. When CR-200 or -300 was ground with V_2O_5, $CrVO_4$ phase has been formed, as shown in Fig. 2(b) and (c). When one of the corundum structural compounds, CR-400, -600 and -800 is ground with V_2O_5 sample, both starting materials remain in the ground samples and formation of $CrVO_4$ cannot be achieved. This is well consistent with our previous reports, indicating that when materials with corundum structure are used as starting materials, it is hard to cause a solid state reaction mechanochemically [23,24]. It can be understood that corundum structure of the crystalline Cr_2O_3 is too stable against grinding to react mechanochemically with V_2O_5 to form $CrVO_4$.

Fig. 3 shows XRD patterns of the mixture of CR-300 and Sb_2O_5 ground for different periods of time. The pattern of the sample ground for 15 min is almost amorphous, but new peaks of $CrSbO_4$ (Tetragonal, JCPDS No. 35-1288) appear in the pattern of the mixture ground for 30 min, and the intensity of these peaks increases with an increase in grinding time. This indicates that the following solid reaction has occurred mechanochemically by the grinding,

$$Cr_2O_3 \cdot nH_2O + Sb_2O_5 \rightarrow 2CrSbO_4 + nH_2O. \quad (2)$$

Fig. 4 shows TEM images of (A) $CrVO_4$ and (B) $CrSbO_4$ synthesized by the grinding for 180 min. Both products consist of agglomerates of fine primary particles with about 10 nm. Compared with the image of $CrVO_4$, primary particle of $CrSbO_4$ is more clearly identified. SSA of the prepared $CrVO_4$ and $CrSbO_4$ are 8.9 and 56.6 m^2/g, respectively. Both the morphology observation and SSA measurement confirm that $CrVO_4$ particles are in a more heavy state of agglomeration than that of $CrSbO_4$ particles. Generally, the samples prepared by intensive grinding exhibit agglomerates. In this case, the water in the starting sample before the grinding may play a significant role to facilitate the agglomeration. The CR-300 has 1.75 mol of water shown in Table 1. The water in the starting sample has changed into free water accompanied with progress of the mechanochemical reactions, and this free water may work like a binder of the fine particles forming agglomerates. The used amount of CR-300 sample in the starting materials for $CrVO_4$ is more than that for $CrSbO_4$ (1.00 g for $CrVO_4$, 0.72 g for $CrSbO_4$), resulting in more free water after solid state reaction. The difference in free water existence may be the reason for the difference in agglomeration between $CrVO_4$ and $CrSbO_4$ particles.

3.2. *Mechanochemical synthesis of solid solutions, $CrV_{1-x}Sb_xO_4$ ($x = 0$–1)*

The achievement of the mechanochemical synthesis of $CrVO_4$ and $CrSbO_4$ with the same crystal structure represented as rutile-type compounds, (tetragonal, $P4_2/mnm$; $Z = 1$) [25], leads us to synthesize $CrV_{1-x}Sb_xO_4$ ($x = 0-1$) solid solutions. Fig. 5 shows XRD patterns of the 180 min ground products of five sets of mixtures of CR-300, V_2O_5 and Sb_2O_5 with different composition ratio. Each XRD pattern of products shows a specific pattern of rutile-type structural compounds, except the regular shifts of XRD peaks towards somewhat lower angles with the increase of x in the composition. All the XRD patterns

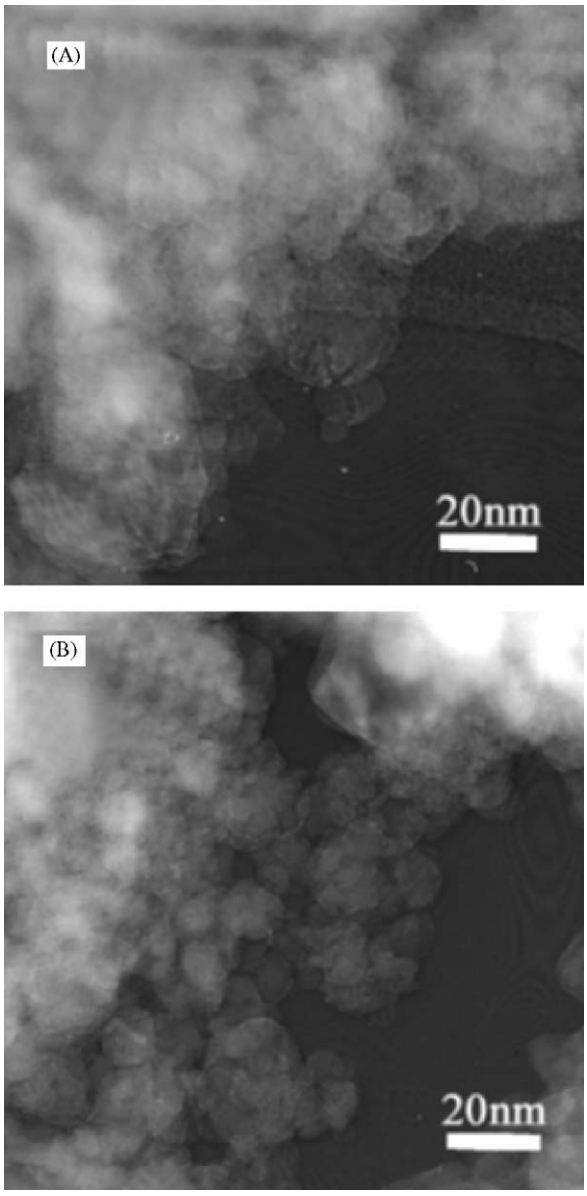

Fig. 4. TEM images of (A) $CrVO_4$ and (B) $CrSbO_4$ prepared by grinding for 180 min.

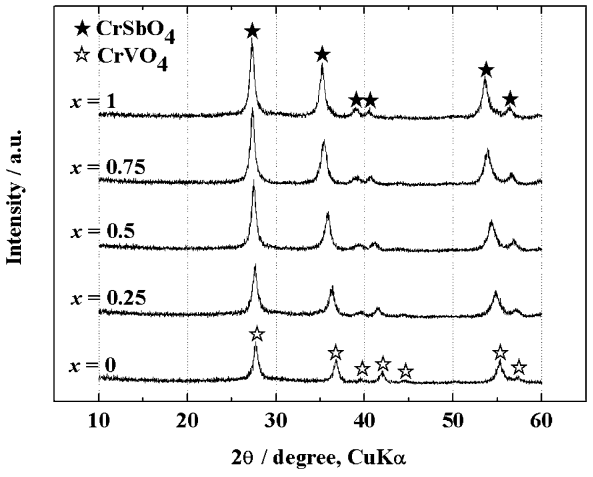

Fig. 5. XRD patterns of the solid solutions, $CrV_{1-x}Sb_xO_4$, synthesized at different x.

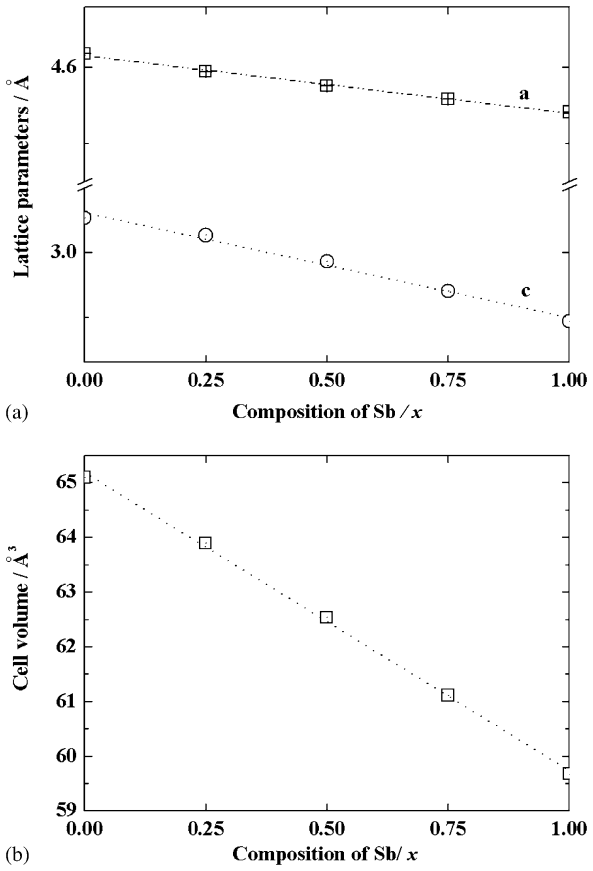

Fig. 6. Unit cell parameters in the $CrV_{1-x}Sb_xO_4$ as a function of x: (a) Lattice parameters vs. x, (b) cell volume vs. x.

could be indexed by a tetragonal structure for the solid solution. Therefore, the each product can be taken as a single-phase solid solution with a rutile-type structure (space group $P4_2/mnm$), expressed as $CrV_{1-x}Sb_xO_4$ ($x = 0-1$).

Fig. 6 shows (A) lattice parameters, a, c and (B) cell volume as a function of the mole fraction x of Sb in the product. With an increase in the number of x, the lattice parameters and volume decrease linearly. These phenomena are approximately consistent with Vegard's law, and well agree with a decrease in the ionic radius, r, from 0.6 Å (Sb^{5+} with sixfold oxide coordination) to 0.54 Å (V^{5+} with sixfold oxide coordination). This can prove that the solid solutions of $CrV_{1-x}Sb_xO_4$ are mechanochemically synthesized through the grinding the mixture of $Cr_2O_3 \cdot nH_2O$, V_2O_5 and Sb_2O_5. The reaction equation in the formation of $CrV_{1-x}Sb_xO_4$ can be given as follows:

$$Cr_2O_3 \cdot nH_2O + (1-x)V_2O_5 + xSb_2O_5 \rightarrow 2CrV_{1-x}Sb_xO_4 + nH_2O \ (x = 0-1,\ \Delta x = 0.25). \quad (3)$$

Based on the mechanochemical synthesis of the rutile-type $CrVO_4$, the synthesis of solid solutions of $CrV_{1-x}Sb_xO_4$ with the same rutile-type structure has been demonstrated. Further application and development of the mechanochemical synthesis of rutile-type $CrVO_4$ for preparing solid solutions with or doping other substances such as TiO_2/CrO_2 to modify the catalytic/magnetic properties are also under consideration.

4. Conclusion

The following conclusions can be made based on the present experimental results:

(1) $CrVO_4$ and $CrSbO_4$ with rutile-type tetragonal structure can be synthesized mechanochemically by the grinding the mixture of amorphous hydrous chromium oxide ($Cr_2O_3 \cdot nH_2O$) and vanadium oxide (V_2O_5)/antimony oxide (Sb_2O_5) in air, respectively.
(2) The particles of the $CrVO_4$ and $CrSbO_4$ products synthesized by this mechanochemical method are in the state of agglomerates, consisting of primary particle sizes of about 10 nm.
(3) The solid solutions, $CrV_{1-x}Sb_xO_4$ ($x = 0-1$, $\Delta x = 0.25$), can be synthesized by grinding the corresponding mixture of amorphous chromium oxide $Cr_2O_3 \cdot nH_2O$, V_2O_5 and Sb_2O_5.

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