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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,

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

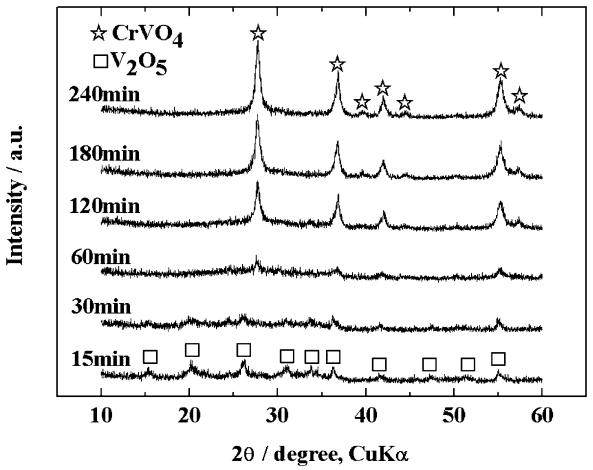

Fig. 1. Crystal growth of $CrVO_4$ from CR-300 and V_2O_5 mixture by mechanochemical treatment.

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 $Cr(OH)_3 \cdot nH_2O$.