

# Subsolidus phase relations in the systems $K_2O-ZnO-AO_3$ ( $A = Mo, W$ )

Liping Xue<sup>a</sup>, Zhang Lin<sup>a</sup>, Dagui Chen<sup>a</sup>, Feng Huang<sup>a,\*</sup>, Jingkui Liang<sup>a,b,c,\*</sup>

<sup>a</sup> State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, People's Republic of China

<sup>b</sup> Institute of Physics and Center for Condensed Matter Physics, Chinese Academy of Sciences, Beijing 100080, People's Republic of China

<sup>c</sup> International Center for Materials Physics, Academia Sinica, Shenyang 110016, People's Republic of China

Received 13 August 2006; received in revised form 7 November 2006; accepted 10 November 2006

Available online 14 December 2006

## Abstract

The subsolidus phase relations of the systems  $K_2O-ZnO-AO_3$  ( $A = Mo, W$ ) have been investigated by X-ray diffraction (XRD) analyses. The phase diagrams have been constructed. There are six binary compounds and two ternary compounds in the  $K_2O-ZnO-MoO_3$  system, it can be divided into 11 three-phase regions. The  $K_2O-ZnO-WO_3$  system consists of six binary compounds and one ternary compound. This system can be divided into 9 three-phase regions. DTA results indicated the compounds  $K_2MoO_4$  and  $K_2WO_4$  are not suitable to be fluxes for ZnO crystal growth.

© 2006 Elsevier B.V. All rights reserved.

**Keywords:** ZnO; X-ray diffraction; Phase diagram; DTA; Crystal growth

## 1. Introduction

Single crystal zinc oxide is a wide band gap semiconductor with great potential for a variety of commercial applications including substrates, UV detectors, acoustic wave devices, light emitting diodes, laser diodes and high frequency electronic devices because of its wide band gap of 3.37 eV and large exciton binding energy of 60 meV [1]. With the increasing need for high quality and large size ZnO crystals, several methods have so far applied to the bulk ZnO crystal growth, such as the flux method [2,3], the melt method [4,5], the hydrothermal method [6–8] and the vapor growth technique [9,10]. High-quality ZnO crystals have been grown by the vapor phase and hydrothermal methods. Rather recently, high-quality crystals have been also grown by the melt-growth technique [4,5]. This method can also produce large size diameter single-crystals, which makes them also useful for substrate applications. The ZnO melts congruently at 1975 °C and is rather volatile at higher temperatures, so the Czochralski method is not suitable for growing ZnO single crystal. In order to suppress the ZnO evaporation during

crystal growth, the crystal must be grown from a solvent with a growth temperature as low as possible. The high temperature equilibrium between  $K_2O-MoO_3$  [11,12] and  $K_2O-WO_3$  [13–15] have been investigated. According to the reported phase diagram for the system  $K_2MoO_4-ZnMoO_4$  [16], there are two ternary compounds,  $K_4Zn(MoO_4)_3$  and  $K_2Zn_2(MoO_4)_3$ , melting incongruently at 615 °C and 610 °C, respectively. The eutectic relationship was found between  $K_4Zn(MoO_4)_3$  and  $K_2Zn_2(MoO_4)_3$  at 530 °C. There is one ternary compound  $K_4Zn(WO_4)_3$  in the  $K_2WO_4-ZnWO_4$  phase diagram [16], which melts incongruently at 635 °C. If eutectic exists between ZnO and these compounds, the ZnO single crystal could be grown at very low temperature. So we have studied the phase relations of  $K_2O-ZnO-AO_3$  ( $A = Mo, W$ ) systems in order to find suitable fluxes and growth regions for growing large and high quality ZnO single crystal at relative low temperature.

## 2. Experimental

A series of samples with different compositions were all prepared by solid-state chemistry reaction in air. The purity of the starting materials (ZnO,  $K_2CO_3$ ,  $MoO_3$ ,  $WO_3$ ) is higher than 99.9%. The  $K_2CO_3$  was dried at 300 °C for 2 h to remove moisture. The raw powders with certain chemical compositions were mixed thoroughly, ground in an agate mortar, and pressed into pellets with diameter of 10 mm and thickness of 1–2 mm at a pressure around  $10^8$  Pa. Then the pellets were sintered at the proper temperature in air for about 72–96 h

\* Corresponding authors.

E-mail addresses: fhuang@fjirsm.ac.cn (F. Huang),  
jkliang@aphy.iphy.ac.cn (J. Liang).

Table 1  
List of phase identification for samples with different composition in the system  $K_2O-ZnO-MoO_3$

Samples	MoO <sub>3</sub> (mol%)	ZnO (mol%)	K <sub>2</sub> O (mol%)	Phase identification
1	33.3	0	66.7	K <sub>2</sub> MoO <sub>4</sub> + K <sub>2</sub> CO <sub>3</sub>
2	10	65	25	ZnO + K <sub>2</sub> MoO <sub>4</sub> + K <sub>2</sub> CO <sub>3</sub>
3	10	20	70	ZnO + K <sub>2</sub> MoO <sub>4</sub> + K <sub>2</sub> CO <sub>3</sub>
4	20	40	40	ZnO + K <sub>2</sub> MoO <sub>4</sub> + K <sub>2</sub> CO <sub>3</sub>
5	35	15	50	ZnO + K <sub>2</sub> MoO <sub>4</sub> + K <sub>2</sub> CO <sub>3</sub>
6	40	20	40	ZnO + K <sub>2</sub> MoO <sub>4</sub>
7	25	50	25	ZnO + K <sub>2</sub> MoO <sub>4</sub>
8	10	80	10	ZnO + K <sub>2</sub> MoO <sub>4</sub>
9	25	55	20	ZnO + K <sub>2</sub> MoO <sub>4</sub> + K <sub>4</sub> Zn(MoO <sub>4</sub> ) <sub>3</sub>
10	40	25	35	ZnO + K <sub>2</sub> MoO <sub>4</sub> + K <sub>4</sub> Zn(MoO <sub>4</sub> ) <sub>3</sub>
11	30	50	20	ZnO + K <sub>4</sub> Zn(MoO <sub>4</sub> ) <sub>3</sub>
12	40	40	20	ZnO + K <sub>4</sub> Zn(MoO <sub>4</sub> ) <sub>3</sub> + K <sub>2</sub> Zn <sub>2</sub> (MoO <sub>4</sub> ) <sub>3</sub>
13	20	70	10	ZnO + K <sub>4</sub> Zn(MoO <sub>4</sub> ) <sub>3</sub> + K <sub>2</sub> Zn <sub>2</sub> (MoO <sub>4</sub> ) <sub>3</sub>
14	30	60	10	ZnO + K <sub>2</sub> Zn <sub>2</sub> (MoO <sub>4</sub> ) <sub>3</sub>
15	30	65	5	ZnO + K <sub>2</sub> Zn <sub>2</sub> (MoO <sub>4</sub> ) <sub>3</sub> + Zn <sub>3</sub> Mo <sub>2</sub> O <sub>9</sub>
16	47.5	50	2.5	K <sub>2</sub> Zn <sub>2</sub> (MoO <sub>4</sub> ) <sub>3</sub> + Zn <sub>3</sub> Mo <sub>2</sub> O <sub>9</sub> + ZnMoO <sub>4</sub>
17	43.75	50	6.25	K <sub>2</sub> Zn <sub>2</sub> (MoO <sub>4</sub> ) <sub>3</sub> + Zn <sub>3</sub> Mo <sub>2</sub> O <sub>9</sub>
18	65	30	5	K <sub>2</sub> Mo <sub>4</sub> O <sub>13</sub> + ZnMoO <sub>4</sub> + MoO <sub>3</sub>
19	80	10	10	K <sub>2</sub> Mo <sub>4</sub> O <sub>13</sub> + ZnMoO <sub>4</sub> + MoO <sub>3</sub>
20	66.7	22.2	11.1	K <sub>2</sub> Mo <sub>4</sub> O <sub>13</sub> + ZnMoO <sub>4</sub>
21	60	30	10	K <sub>2</sub> Mo <sub>3</sub> O <sub>10</sub> + ZnMoO <sub>4</sub>
22	70	15	15	K <sub>2</sub> Mo <sub>4</sub> O <sub>13</sub> + K <sub>2</sub> Mo <sub>3</sub> O <sub>10</sub> + ZnMoO <sub>4</sub>
23	55	35	10	K <sub>2</sub> Zn <sub>2</sub> (MoO <sub>4</sub> ) <sub>3</sub> + K <sub>2</sub> Mo <sub>3</sub> O <sub>10</sub> + ZnMoO <sub>4</sub>
24	60	25	15	K <sub>2</sub> Zn <sub>2</sub> (MoO <sub>4</sub> ) <sub>3</sub> + K <sub>2</sub> Mo <sub>3</sub> O <sub>10</sub> + ZnMoO <sub>4</sub>
25	60	20	20	K <sub>2</sub> Zn <sub>2</sub> (MoO <sub>4</sub> ) <sub>3</sub> + K <sub>2</sub> Mo <sub>3</sub> O <sub>10</sub>
26	65	10	25	K <sub>2</sub> Zn <sub>2</sub> (MoO <sub>4</sub> ) <sub>3</sub> + K <sub>2</sub> Mo <sub>2</sub> O <sub>7</sub> + K <sub>2</sub> Mo <sub>3</sub> O <sub>10</sub>
27	55	20	25	K <sub>2</sub> Mo <sub>2</sub> O <sub>7</sub> + K <sub>2</sub> Zn <sub>2</sub> (MoO <sub>4</sub> ) <sub>3</sub> + K <sub>4</sub> Zn(MoO <sub>4</sub> ) <sub>3</sub>
28	55	15	30	K <sub>2</sub> Mo <sub>2</sub> O <sub>7</sub> + K <sub>2</sub> Zn <sub>2</sub> (MoO <sub>4</sub> ) <sub>3</sub> + K <sub>4</sub> Zn(MoO <sub>4</sub> ) <sub>3</sub>
29	58.3	16.7	25	K <sub>2</sub> Mo <sub>2</sub> O <sub>7</sub> + K <sub>2</sub> Zn <sub>2</sub> (MoO <sub>4</sub> ) <sub>3</sub>
30	55.6	11.1	33.3	K <sub>2</sub> Mo <sub>2</sub> O <sub>7</sub> + K <sub>4</sub> Zn(MoO <sub>4</sub> ) <sub>3</sub>
31	55	5	40	K <sub>2</sub> MoO <sub>4</sub> + K <sub>2</sub> Mo <sub>2</sub> O <sub>7</sub> + K <sub>4</sub> Zn(MoO <sub>4</sub> ) <sub>3</sub>

and slowly cooled in the furnace to room temperature. The heating temperature is 450–650 °C for the  $K_2O-ZnO-MoO_3$  system and 600–850 °C for the  $K_2O-ZnO-WO_3$  system. The temperature of the furnace was measured with a Pt–PtRh thermocouple and was precisely controlled to within  $\pm 2$  °C up to 1200 °C with an intelligent controller. The above process should repeat several times until the X-ray pattern of the specimen showed no change upon successive heat treatment, which represented the equilibrium was achieved. The compositions of the samples prepared in the system  $K_2O-ZnO-MoO_3$  are shown in Table 1 and the system  $K_2O-ZnO-WO_3$  shown in Table 2.

Phase identification of the samples was carried out on a PANalytical X'Pert Pro diffractometer with Cu K $\alpha$  radiation (45 kV  $\times$  40 mA) using continuous mode at a rate of  $2\theta = 4^\circ/\text{min}$ .

The DTA investigation was conducted by NETZSCH-STA449C (Germany) in platinum crucible. The measurements were performed in the atmosphere of nitrogen in the temperature range 30–1200 °C. The heating rate was 10 K/min and the reference substance was  $\alpha\text{-Al}_2\text{O}_3$ .

### 3. Result and discussion

#### 3.1. Pseudo-binary system

##### 3.1.1. $K_2O-MoO_3$ system

The  $K_2O-MoO_3$  pseudo-binary system was reported by Spitsyn and Kuleshov [11] in 1951 and Caillet [12] in 1967. Six compounds were observed in their results,  $K_2MoO_4$ ,  $K_2Mo_2O_7$ ,  $K_2Mo_3O_{10}$ ,  $K_2Mo_4O_{13}$ ,  $K_2Mo_6O_{19}$ ,  $K_2Mo_8O_{25}$ . The former four compounds melt incongruently in both reports [11,12]. The compounds  $K_2Mo_6O_{19}$ ,  $K_2Mo_8O_{25}$  shown in Spitsyn's

reports seem more plausible, but in Caillet's [12] reports compound  $K_2Mo_6O_{19}$  exists only between 542 °C and 562 °C. Under our experimental conditions, four compounds,  $K_2MoO_4$ ,  $K_2Mo_2O_7$ ,  $K_2Mo_3O_{10}$ ,  $K_2Mo_4O_{13}$  were found. Compound  $K_2MoO_4$  belongs to the monoclinic system with space group  $C2/m$ . Its lattice parameters are  $a = 12.340$  Å,  $b = 6.081$  Å,  $c = 7.538$  Å and  $\beta = 115.74^\circ$  [17]. The compound  $K_2Mo_2O_7$  crystallizes in triclinic system with space group  $P\bar{1}$ . Its lattice parameters are  $a = 7.510$  Å,  $b = 7.240$  Å,  $c = 6.950$  Å and  $\alpha = 92.00^\circ$ ,  $\beta = 120.00^\circ$ ,  $\gamma = 82.50^\circ$  [18]. Compound  $K_2Mo_3O_{10}$  belongs to the monoclinic system with space group  $C2/c$ . Its lattice parameters are  $a = 13.990$  Å,  $b = 7.877$  Å,  $c = 8.874$  Å and  $\beta = 99.234^\circ$  [19]. Compound  $K_2Mo_4O_{13}$  belongs to a triclinic system with space group  $P\bar{1}$ . Its lattice parameters are  $a = 7.972$  Å,  $b = 8.352$  Å,  $c = 10.990$  Å and  $\alpha = 119.40^\circ$ ,  $\beta = 62.70^\circ$ ,  $\gamma = 109.80^\circ$  [20].

##### 3.1.2. $K_2O-WO_3$ system

The phase diagram of  $K_2O-WO_3$  system has been reported in the literature for many times. Hoermann [13] reported it for the first time in 1928. In his reports, only three compounds were found,  $K_2WO_4$ ,  $K_2W_3O_{10}$ ,  $K_2W_4O_{13}$ . Except the three compounds, Guerin et al. [14] also showed three intermediate phases,  $K_2W_2O_7$ ,  $K_2W_6O_{19}$ ,  $K_2W_8O_{25}$ . They indicated that pure  $K_2W_2O_7$  was difficult to obtain from  $K_2CO_3$  and  $WO_3$  but was prepared in pure form by heating  $K_2WO_4$  and  $K_2W_3O_{10}$

Download English Version:

<https://daneshyari.com/en/article/1624695>

Download Persian Version:

<https://daneshyari.com/article/1624695>

[Daneshyari.com](https://daneshyari.com)