Journal of Alloys and Compounds 509 (2011) 380–383

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Subsolidus phase relations in the $ZnO–WO_3–Bi_2O_3$ system

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ARTICLE INFO

Article history:
Received 23 August 2010
Received in revised form 3 September 2010
Accepted 3 September 2010
Available online 16 September 2010

Keywords:
$ZnO–WO_3–Bi_2O_3$ system
ZnO crystal growth
Phase diagrams
X-ray diffraction

ABSTRACT

The subsolidus phase relations of the ternary system $ZnO–WO_3–Bi_2O_3$ were investigated by means of X-ray diffraction (XRD). Six binary compounds and seven 3-phase regions were determined, and no ternary compounds were found in this ternary system. The phase diagram of pseudobinary system $ZnO–Bi_2WO_6$ was also constructed through XRD and differential thermal analysis (DTA) methods, which forms eutectic system with eutectic temperature about 945 °C, the corresponding eutectic component is 35 mol% ZnO and 65 mol% Bi_2WO_6.

1. Introduction

Due to its wide band (3.437 eV at 2 K) and large exciton binding energy (60 meV), zinc oxide material can be potentially applied in many areas, such as ultra violet (UV) detectors, UV light emitters, spin functional devices, acoustic wave devices and piezoelectric transducers [1,2]. To achieve these applications, the most critical problem is to obtain high quality ZnO films homoepitaxially grown on the ZnO single-crystal substrates. There are several methods to grow large scale ZnO single crystals: hydrothermal solution method [3–7], vapor transport method [8,9], melt growth [10,11] and molten salt method [12–15]. It has been found that the growth speed of hydrothermal solution method is too slow, vapor transport method is very difficult to manipulate, and melt growth is unsuitable for the high melting point of ZnO (1975 °C) and high volatility at high temperature. Therefore, molten salt method is still a practicable method for the large-scale growth of ZnO, which uses flux to lower the temperature in the process of crystal growth. PbF_2 was reported as flux to grow ZnO crystals, but it is noxious [9]. Using fluxes such as KOH [16], LiOH + NaOH/KOH [17] and KOH + NaOH [18], the obtained ZnO are small needles or micaceous crystals. Previously our research team has studied the subsolidus phase relations in the system $ZnO–A_2O_5–WO_3$ (A = V, P) [19,20], and it revealed that suitable flux might exist in these systems. Bi_2O_3 and WO_3 melt congruently at 820 °C and 1472 °C, respectively, which are suitable to be flux. On the other hand, tungstate is the prevalent flux for molten salt method. In this work, we investigated the $ZnO–Bi_2O_3–WO_3$ ternary system to search for potential flux for ZnO crystal growth.

1.1. $ZnO–WO_3$ system

The $ZnO–WO_3$ system was reported by Yanushkevich et al. [21] and Shchenev et al. [22]. In their reports, only one intermediate compound $ZnWO_4$ with monoclinic structure was found, and its congruently melting point is 1210.5 °C [22].

1.2. $WO_3–Bi_2O_3$ system

The phase relation of $WO_3–Bi_2O_3$ system has been studied extensively. Although several investigations of the system have been conducted, the results were different from each other [23–28]. A latest whole phase diagram of $Bi_2O_3–WO_3$ system was reported by Hoda and Chang [28] in 1974, in which four intermediate phases including $Bi_2W_2O_9$, Bi_2WO_6, $Bi_{14}W_2O_{27}$, and $Bi_{14}WO_{24}$ were described. From their research, compound $Bi_2W_2O_9$ was found decomposing to Bi_2WO_6 above 680 °C and melting incongruently at 925 °C, while compound Bi_2WO_6 melts incongruently at 1080 °C and no phase transition will happen up to 850 °C. A recent study by Watanabe and Ono [29] further shows that compound $Bi_{14}W_2O_{27}$ stabilize above 670 °C. Below 670 °C, $Bi_{14}W_2O_{27}$ sluggishly decomposed and yielded the bismuth-rich limit of solid solution and a small quantity of $Bi_{14}WO_{24}$. As for $Bi_{14}WO_{24}$, three stable polymorphs were identified [30]: the low-temperature monoclinic form, the intermediate orthorhombic form, and the

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0925-8388/$ – see front matter
doi:10.1016/j.jallcom.2010.09.031

high-temperature face-centered cubic form. Meanwhile, their relationships were shown: the reversible monoclinic-to-orthorhombic transition at about 40 °C was displacive, while a reconstructive order–disorder transition occurred reversibly at 780 °C from the orthorhombic form to the face-centered cubic form.

1.3. $ZnO–Bi_2O_3$ system

The $ZnO–Bi_2O_3$ system has widely been studied, but the results were different from each other [31–33]. In the recent investigation, only compound $Bi_{38}ZnO_{58}$ was reported existing in the system [34], which has a crystal structure analogous to that of the body-centered cubic based-Bi_2O_3 solid solution and melts incongruently at 753 ± 2 °C to yield γ-Bi_2O_3 and liquid.

2. Experimental

Analytical grade ZnO, WO_3, α-Bi_2O_3 (Sinopharm Chemical Reagent Co., Ltd.) were used to prepare specimens by solid-state chemistry reaction and quenching methods in air. The powders of raw materials with certain chemical composition were mixed in an agate mortar to get homogeneity, and then pressed into pellets with diameter of 10 mm and thickness of 1–2 mm at pressure around 10^8 Pa. All samples were sintered from 650 to 850 °C for 2–7 days. At the end of heat-treatment process, the samples were quenched in air to room temperature. X-ray powder diffraction (XRD) method was used to identify the samples until the powder diffraction patterns showed no change between two consecutive stages, which represented the equilibrium was achieved. The temperature of the furnace was measured with a Pt–PtRh thermocouple and precisely controlled within ±2 °C up to 1200 °C with an intelligent controller. XRD diffraction data were collected on a PANalytical X'Pert Pro diffractometer with Cu Kα radiation (40 kV × 40 mA) using continuous mode at a rate of $2\theta = 4°$/min, and diffraction data of all the samples were collected at constant room temperature 25 °C.

The DTA investigation was conducted on thermal analyzer NETZSCH-DTA404PC (Germany) in platinum crucible. The measurements were performed in the atmosphere of nitrogen in the temperature range 30–1200 °C. The heating and cooling rate were both 10 K/min and the reference substance was α-Al_2O_3.

3. Results and discussion

3.1. Binary systems

In the $ZnO–WO_3$ binary system, our result coincides with the report that only one intermediate compound $ZnWO_4$ is found

Table 1
List of phase identification for samples with different composition in the $ZnO–WO_3–Bi_2O_3$ system.

Samples	ZnO (mol%)	WO_3 (mol%)	Bi_2O_3 (mol%)	Phase identification
1	75	25	0	$ZnO + ZnWO_4$
2	50	50	0	$ZnWO_4$
3	25	75	0	$ZnWO_4 + WO_3$
4	0	80	20	$WO_3 + Bi_2W_2O_9$
5	0	66.7	33.3	$Bi_2W_2O_9$
6	0	60	40	$Bi_2W_2O_9 + Bi_2WO_6$
7	0	50	50	Bi_2WO_6
8	0	35	65	$Bi_2WO_6 + Bi_{14}W_2O_{27}$
9	0	22.2	77.8	$Bi_{14}W_2O_{27}$
10	0	17.5	82.5	$Bi_{14}W_2O_{27} + Bi_{14}WO_{24}$
11	0	12.5	87.5	$Bi_{14}WO_{24}$
12	0	10	90	$Bi_{14}WO_{24} + Bi_2O_3$
13	5	0	95	$Bi_{38}ZnO_{58}$
14	15	0	85	$Bi_{38}ZnO_{58} + ZnO$
15	40	0	60	$Bi_{38}ZnO_{58} + ZnO$
16	70	0	30	$Bi_{38}ZnO_{58} + ZnO$
17	10	80	10	$ZnWO_4 + WO_3 + Bi_2W_2O_9$
18	25	65	10	$ZnWO_4 + WO_3 + Bi_2W_2O_9$
19	10	65	25	$ZnWO_4 + WO_3 + Bi_2W_2O_9$
20	35	55	10	$ZnWO_4 + Bi_2W_2O_9$
21	20	60	20	$ZnWO_4 + Bi_2W_2O_9$
22	5	65	30	$ZnWO_4 + Bi_2W_2O_9$
23	30	55	15	$ZnWO_4 + Bi_2W_2O_9 + Bi_2WO_6$
24	20	55	25	$ZnWO_4 + Bi_2W_2O_9 + Bi_2WO_6$
25	10	55	35	$ZnWO_4 + Bi_2W_2O_9 + Bi_2WO_6$
26	35	50	15	$ZnWO_4 + Bi_2WO_6$
27	25	50	25	$ZnWO_4 + Bi_2WO_6$
28	10	50	40	$ZnWO_4 + Bi_2WO_6$
29	30	40	30	$ZnO + ZnWO_4 + Bi_2WO_6$
30	50	40	10	$ZnO + ZnWO_4 + Bi_2WO_6$
31	65	25	10	$ZnO + ZnWO_4 + Bi_2WO_6$
32	80	15	5	$ZnO + ZnWO_4 + Bi_2WO_6$
33	70	15	15	$ZnO + Bi_2WO_6$
34	33.3	33.3	33.3	$ZnO + Bi_2WO_6$
35	10	45	45	$ZnO + Bi_2WO_6$
36	75	10	15	$ZnO + Bi_2WO_6 + Bi_{14}W_2O_{27}$
37	50	15	35	$ZnO + Bi_2WO_6 + Bi_{14}W_2O_{27}$
38	30	30	40	$ZnO + Bi_2WO_6 + Bi_{14}W_2O_{27}$
39	10	30	60	$ZnO + Bi_2WO_6 + Bi_{14}W_2O_{27}$
40	55	10	35	$ZnO + Bi_{14}W_2O_{27}$
41	10	20	70	$ZnO + Bi_{14}W_2O_{27}$
42	70	5	25	$ZnO + Bi_{14}W_2O_{27} + Bi_{14}WO_{24}$
43	45	10	45	$ZnO + Bi_{14}W_2O_{27} + Bi_{14}WO_{24}$
44	20	15	65	$ZnO + Bi_{14}W_2O_{27} + Bi_{14}WO_{24}$
45	5	15	80	$ZnO + Bi_{14}W_2O_{27} + Bi_{14}WO_{24}$
46	60	5	35	$ZnO + Bi_{14}WO_{24}$
47	20	10	70	$ZnO + Bi_{14}WO_{24}$
48	60	2.5	37.5	$ZnO + Bi_{14}WO_{24} + Bi_{38}ZnO_{58}$
49	40	5	55	$ZnO + Bi_{14}WO_{24} + Bi_{38}ZnO_{58}$
50	15	5	85	$ZnO + Bi_{14}WO_{24} + Bi_{38}ZnO_{58}$

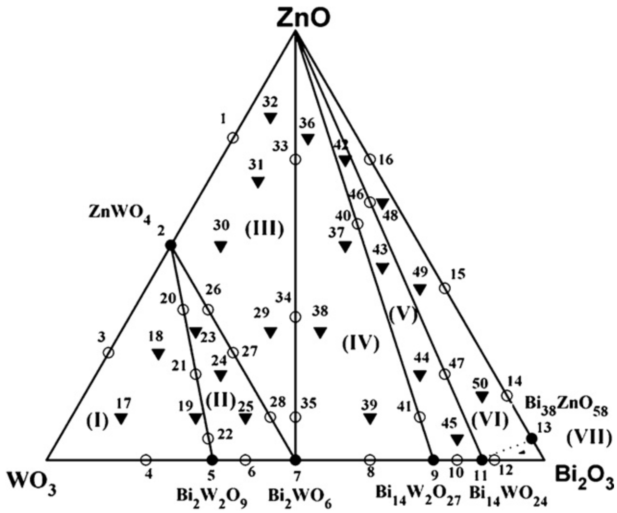

Fig. 1. Subsolidus phase relations of the system $ZnO–WO_3–Bi_2O_3$ (●: single phase, ○: two phases, and ▼: three phases).

[21,22]. This compound was easily obtained via solid-state reaction under 800 °C for 2 days, followed by cooling with the furnace. $ZnWO_4$ belongs to monoclinic structure with space group $P2/c$ and lattice parameters a = 4.69263, b = 5.72129, c = 4.92805 Å, β = 90.6320° [22].

In the $Bi_2O_3–WO_3$ binary system, via solid-state reaction under 650 °C for 2 days, four compounds $Bi_2W_2O_9$, Bi_2WO_6, $Bi_{14}W_2O_{27}$ and $Bi_{14}WO_{24}$ with WO_3:Bi_2O_3 molar ratios of 2:1, 1:1, 2:7 and 1:7, respectively, were found. Our result is in good agreement with Ref. [28]. $Bi_2W_2O_9$ belongs to orthorhombic system with space group $Pbn2_1$. Its lattice parameters are a = 5.4137 Å, b = 5.4319 Å, c = 23.6945 Å and β = 90° [35]. Bi_2WO_6 has orthorhombic structure with space group $B2cb$. The corresponding lattice parameters are a = 5.4570 Å, b = 5.4360 Å, c = 16.4270 Å and β = 90° [36,37]. The compound $Bi_{14}W_2O_{27}$ belongs to tetragonal system with space group $I4_1/a$, its lattice parameters are a = 12.5143 Å, c = 11.2248 Å and β = 90° [38]. Another compound $Bi_{14}WO_{24}$ belongs to monoclinic system with space group $P2_1$ and its lattice parameters are a = 17.3796 Å, b = 17.3847 Å, c = 26.1636 Å and β = 90.279° [30].

Only one compound $Bi_{38}ZnO_{58}$ was observed in the $ZnO–Bi_2O_3$ binary system, which is in good agreement with Ref. [33]. The compound was obtained via solid-state reaction under 650 °C for 7 days. And compound $Bi_{38}ZnO_{58}$ belongs to cubic system with space group $I2_3$ and lattice parameters are a = 10.2060 Å, β = 90°, which agrees with Ref. [39].

3.2. *ZnO–WO3–Bi2O3 ternary system*

The subsolidus phase relations of the system $ZnO–WO_3–Bi_2O_3$ are shown in Fig. 1. And the phase identification for samples with different compositions in this ternary system is shown in Table 1. There are six binary compounds in $ZnO–WO_3–Bi_2O_3$ ternary system. The subsolidus phase relations of the ternary system consists of six tie lines: $ZnWO_4–Bi_2W_2O_9$, $ZnWO_4–Bi_2WO_6$, $ZnO–Bi_2WO_6$, $ZnO–Bi_{14}W_2O_{27}$, $ZnO–Bi_{14}WO_{24}$ and $Bi_{14}WO_{24}–Bi_{38}ZnO_{58}$; seven 3-phase regions: (I) $ZnWO_4–WO_3–Bi_2W_2O_9$, (II) $ZnWO_4–Bi_2W_2O_9–Bi_2WO_6$, (III) $ZnO–ZnWO_4–Bi_2WO_6$, (IV) $ZnO–Bi_2WO_6–Bi_{14}W_2O_{27}$, (V) $ZnO–Bi_{14}W_2O_{27}–Bi_{14}WO_{24}$, (VI) $ZnO–Bi_{14}WO_{24}–Bi_{38}ZnO_{58}$, and (VII) $Bi_{14}WO_{24}–Bi_{38}ZnO_{58}–Bi_2O_3$. No ternary compound is found in all the regions. It is difficult to obtain homogeneous specimens to prove the region VII exist. Therefore, the dashed lines were used to indicate the phase relations of region VII. The region III has rather high ZnO content, in which no ternary compound is found and binary compounds

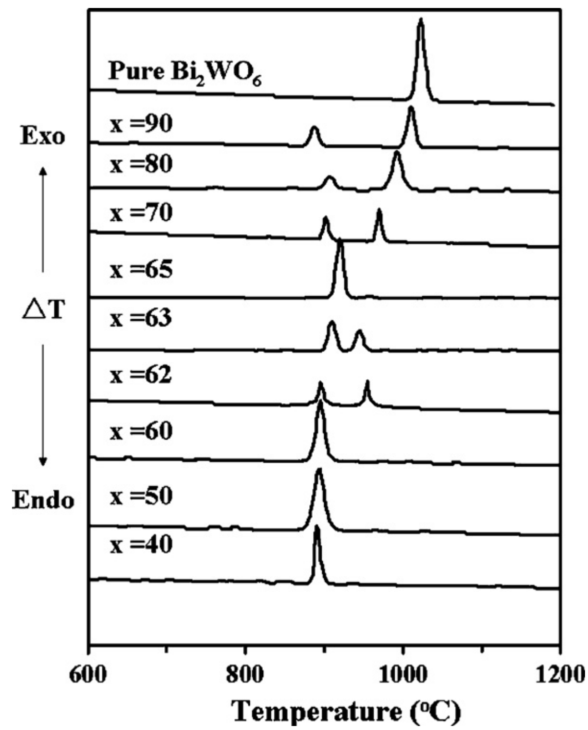

Fig. 2. DTA cooling curves of x mol% Bi_2WO_6 + (100 − x) mol% ZnO.

$ZnWO_4$ and Bi_2WO_6 exist, so the mixtures containing ZnO and Bi_2WO_6 in this region may be suitable flux for ZnO crystal growth.

3.3. *ZnO–Bi2WO6 pseudobinary system*

The $ZnO–Bi_2WO_6$ pseudobinary system was investigated by means of XRD and DTA methods. In our work, the XRD results indicate that there is no intermediate compound in $ZnO–Bi_2WO_6$ binary system. In heating process of DTA method, the melting endothermal peaks of compositions containing rich ZnO are difficult to determine, so the DTA cooling curves is chosen to construct the phase diagram. As shown in Fig. 2, the DTA cooling curves of $ZnO–Bi_2WO_6$ with different molar ratios were presented. The temperature of eutectic reaction and liquidus line of each composition were determined, and the phase diagram of the pseudobinary system is shown in Fig. 3. The congruent melting point of Bi_2WO_6 is

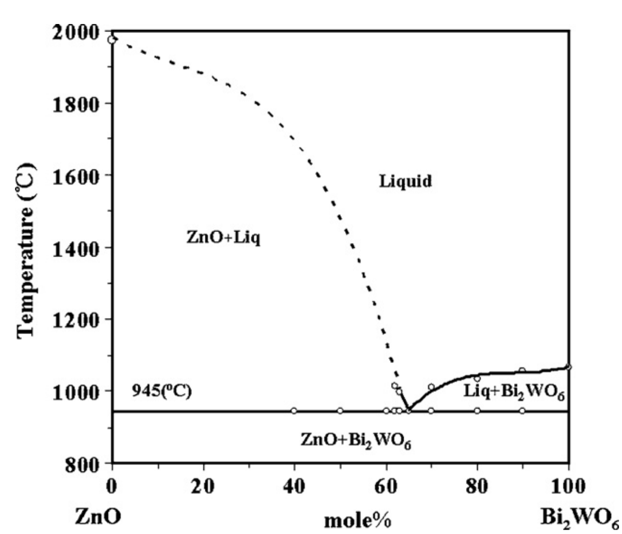

Fig. 3. Phase diagram of the $ZnO–Bi_2WO_6$ pseudobinary system.

1067 °C, but it is 1020 °C on our DTA cooling curves. This situation was caused by over-cooling of the samples. The degree of the over-cooling is about 50 °C by compared the heating and cooling curves. The curves (x = 62, 63, 70, 80, 90) have two exothermal peaks. The temperature of all the first exothermal peaks is ~945 °C (considering the degree of the over-cooling), which represents the eutectic temperature. And all the second peaks are the melting exothermal peaks. The curve of x = 65 has only one exothermal peak at 945 °C (considering the degree of the over-cooling), which indicates this composition is close to eutectic point component. Due to the high melting point of ZnO, we cannot obtain the melting exothermal peaks below 1200 °C on the curves of 40, 50, 60, so we use the dashed lines to indicate this region. As mentioned above, pseudobinary system ZnO–Bi_2WO_6 forms eutectic system.

4. Conclusion

The subsolidus phase relations of the system ZnO–WO_3–Bi_2O_3 were investigated. The ZnO–WO_3–Bi_2O_3 system comprises seven three-phase regions and six binary compounds in the system. There is no ternary compound found in this system. The phase diagram of the ZnO–Bi_2WO_6 pseudobinary system has been constructed. The eutectic point temperature is 945 °C, and eutectic point component is 35 mol% ZnO and 65 mol% Bi_2WO_6. Since there is only very narrow range suitable to grow ZnO crystals, the compound Bi_2WO_6 is not suitable flux for ZnO single crystal growth below 1250 °C.

Acknowledgements

This research is supported by National Basic Research Program of China (973 Program, 2007CB936703), National Natural Science Foundation of China (No. 60736032) and the Outstanding Youth Fund (50625205), the Major Program of Science and Technology Foundation of Fujian Province (Grant Nos. 2007HZ0005-3 and 2009HZ0009-1) and the Knowledge Innovation Program of the Chinese Academy of Sciences (KJCX2.YW.317).

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