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Phase relations and flux research for ZnO crystal growth in the $ZnO–B_2O_3–P_2O_5$ system

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Abstract

The subsolidus phase relations of the ternary system $ZnO–B_2O_3–P_2O_5$ were investigated by means of X-ray diffraction (XRD). Seven binary compounds, 1 ternary compound and 10 three-phase regions were determined in this system. The phase diagrams of the pseudo-binary systems $Zn_3(BO_3)_2$–ZnO, $Zn_3(PO_4)_2$–ZnO and Zn_3BPO_7–ZnO were also determined through XRD and differential thermal analysis (DTA) methods. They all form eutectic systems with eutectic temperature about 1000 °C. $Zn_3(BO_3)_2$ and $Zn_3(PO_4)_2$ are not suitable fluxes, while Zn_3BPO_7 might be a suitable flux for ZnO crystal growth.

Keywords: $ZnO–B_2O_3–P_2O_5$ system; ZnO semiconductor; Phase diagrams; X-ray diffraction

1. Introduction

Wurtzitic ZnO is an II–VI wide band-gap semiconductor, which has excellent optical and electrical properties. It has important applications in many ways, such as transparent conducting films, gas sensors, piezoelectric transducers, varistors and surface acoustic wave devices [1]. The wide band gap of 3.4 eV and large exciton binding energy of 60 meV make ZnO advantageous to be used as UV and blue light emitting diodes and laser diodes [2–4]. Except for applications mentioned above, bulk ZnO single crystals are also strongly desired as ideal homoepitaxial substrates to improve the performance of ZnO based film devices. The main methods for ZnO crystal growth are hydrothermal, vapor transport and melt methods. The hydrothermal method can obtain large crystals but the period of crystal growth is long. The vapor transport method is not easy to manipulate. The melt method, which can grow ZnO crystals at atmospheric pressure with observable benefit, avoids the above shortcomings. However, ZnO has high melting point of 1975 °C and volatilizes seriously at high temperature. Therefore, a suitable flux for melt method is desired to grow ZnO crystals at a lower temperature. PbF_2 has been used as a flux to grow ZnO crystals, but it is noxious. The melting points of B_2O_3 and P_2O_5 are about 450 and 580 °C, respectively, and B_2O_3 is a frequently used flux for the growth of oxide crystals. So it is significant to study the ternary $ZnO–B_2O_3–P_2O_5$ system in searching for a flux to obtain excellent ZnO crystals.

1.1. $ZnO–B_2O_3$ system

The phase diagram of this system was investigated by Harrison and Hummel [5]. Two compounds with the $ZnO:B_2O_3$ molar ratios of 5:2 and 1:1 were obtained and the 3:2 and 2:1 compounds were mentioned. The melting point of $ZnO·B_2O_3$ is 982 °C and $5ZnO·2B_2O_3$ melts incongruently at 1045 °C [5]. However, six other compounds were reported with the $ZnO:B_2O_3$ molar ratios of 4:1 [6], 3:1 [7–9], 4:3 [10–12], 1:1 [13], 1:2 [14,15] and 1:3 [16]. The 4:1 compound was obtained by hydrothermal method. It belongs to the rhombohedral system with space group $R\bar{3}c$ and lattice parameters $a=b=c=9.9115(4)$ Å, $\alpha=\beta=\gamma=48.602(1)^\circ$ [6]. Chen et al. [7] obtained two polymorphic phases, i.e. the α phase and the β phase of the 3:1 compound using PbO as flux. The α-phase belongs to the triclinic system with space group $P\bar{1}$ and lattice parameters $a=6.302(2)$, $b=8.248(1)$, $c=10.020(1)$ Å,

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$\alpha = 89.85(1)^\circ$, $\beta = 89.79(1)^\circ$, $\gamma = 73.25(1)^\circ$. The β-phase crystallizes in the monoclinic system with space group $C2/c$ and lattice parameters $a = 23.840(1)$, $b = 5.049(1)$, $c = 8.388(1)$ Å, $\beta = 102.905(9)^\circ$. However, Garcia-Blanco and Fayos [8] and Baur and Tillmanns [9] reported that the 3:1 compound had the space groups of $I2/c$ and Ic respectively, with the same lattice parameters $a = 23.406$, $b = 5.048$, $c = 8.381$ Å and $\beta = 97^\circ 32'$. The 4:3 compound belongs to the cubic system with space group $I\bar{4}3m$ and $a \approx 7.48$ Å [10–12]. Martinez-Ripoll et al. [14] reported that the 1:2 compound crystallized in the orthorhombic symmetry with the space group $Pbca$ and lattice parameters $a = 13.714(5)$, $b = 8.091(5)$, $c = 8.631(5)$ Å. Huppertz and Heymann [15] obtained an orthorhombic 1:2 compound under high pressure with space group $Cmcm$ and lattice parameters $a = 10.850(1)$, $b = 6.489(1)$, $c = 5.173(1)$ Å. Toropov and Konovalov [16] reported that the 1:3 compound decomposed at 900 °C, but no structural data were reported.

1.2. $ZnO–P_2O_5$ system

For this system, four compounds were reported with the $ZnO:P_2O_5$ molar ratios of 3:1 (orthophosphate), 2:1 (pyrophosphate), 1:1 (metaphosphate) and 1:2. The orthophosphate melts at 1060 °C, the pyrophosphate melts at 1017 °C and the metaphosphate melts at 872 °C [17]. The 3:1 compound has three polymorphic forms of α, β and γ. Crystal of α-phase was obtained by slowly cooling the melt of $ZnCl_2$ and $Zn_3(PO_4)_2$ from 650 °C to room temperature, of which the space group is $C2/c$ with lattice parameters $a = 8.14(2)$, $b = 5.63(1)$, $c = 15.04(4)$ Å and $\beta = 105^\circ 08'$ [18]. The α-phase is stable below 942 °C and transforms above this temperature to β-phase. Crystal of β-phase was grown by slowly cooling the melt of $Zn_3(PO_4)_2$ through the melting point (1062 °C), followed by a quench to room temperature [19]. The space group of the β-phase is $P2_1/c$ with lattice parameters $a = 9.393(3)$, $b = 9.170(6)$, $c = 8.686(3)$ Å and $\beta = 125.73(1)^\circ$ [19]. Crystal of γ-phase was obtained by slowly cooling the melt of $ZnCl_2$ and $Zn_3(PO_4)_2$ from 900 °C to room temperature [20], and the space group is $P2_1/c$ with lattice parameters $a = 5.074(8)$, $b = 8.469(1)$, $c = 8.766(15)$ Å and $\beta = 120^\circ 51'(10)$ [20]. The 2:1 compound was also reported to have three polymorphic forms of α, β and γ. Crystal of α-phase was grown by slowly cooling a melt obtained from the decomposition of $ZnNH_4PO_4$ from 1070 °C to about 900 °C [21]. The space group of the α-phase is $I2/c$ with lattice parameters $a = 20.068(15)$, $b = 8.259(6)$, $c = 9.099(8)$ Å, $\beta = 106.35(5)^\circ$ and $V = 1447.1$ Å^3 [21]. Crystal of β-phase was also grown from a melt obtained from the decomposition of $ZnNH_4PO_4$. The space group of the β-phase is $C2/m$ with lattice parameters $a = 6.61(1)$, $b = 8.29(1)$, $c = 4.51(1)$ Å, $\beta = 105.4(2)^\circ$ and $V = 238.26$ Å^3 [22]. The relationship of the lattice parameters of the α-phase and the β-phase is as follows: $a(\alpha) \approx 3a(\beta)$, $b(\alpha) \approx b(\beta)$, $c(\alpha) \approx 2c(\beta)$, $V(\alpha) \approx 6V(\beta)$. It shows that the β-phase may be the disordered phase of the α-phase. Katnack and Hummel [17] reported that the α-phase inverted rapidly and reversibly to the β-phase at 132 °C. The γ-phase of the 2:1 compound was obtained by the crystallization of an amorphous $Zn_2P_2O_7$ at 480 °C, of which the space group is $Pbcm$ with lattice parameters $a = 4.9504(5)$, $b = 13.335(2)$, $c = 16.482(3)$ Å [23]. The 1:1 compound was reported to have two polymorphic forms of α_1 and α_2. The α_1-phase belongs to the monoclinic system with lattice parameters $a = 11.78(1)$, $b = 8.302(6)$, $c = 9.927(8)$ Å and $\beta = 118.81(2)^\circ$ [24]. The space group of the α_2-phase is $C2/c$ with lattice parameters $a = 9.734(2)$, $b = 8.889(2)$, $c = 4.963(1)$ Å and $\beta = 108.49(5)^\circ$ [25]. The 1:2 compound was synthesized from acidic melt of P_2O_5, H_3PO_4 and ZnO at about 360 °C. It belongs to the monoclinic system with space group $P2_1/c$ and lattice parameters $a = 5.302(1)$, $b = 22.244(3)$, $c = 7.407(1)$ Å and $\beta = 110.11(1)^\circ$ [26].

1.3. $B_2O_3–P_2O_5$ system

Only one compound BPO_4 was reported in this system, the space group is $I\bar{4}$ with lattice parameters $a = b = 4.332(6)$, $c = 6.640(8)$ Å [27].

1.4. $ZnO–B_2O_3–P_2O_5$ system

In this system only one ternary compound Zn_3BPO_7 was reported with the melting point of 927 °C [28]. The phase relations of this ternary system were not investigated yet. Zn_3BPO_7 had two polymorphic forms of α and β. Liebertz and Stähr [29] reported the space group of the α-phase was probably $Im2$ with lattice parameters $a = 8.438(5)$, $b = 4.884(5)$, $c = 12.746(5)$ Å, $V = 525.3$ Å^3 and $Z = 4$. However, Bluhm and Park [30] reported that the α-phase had the Cm symmetry with lattice parameters $a = 9.725(2)$, $b = 12.720(3)$, $c = 4.874(3)$ Å, $\beta = 119.80(4)^\circ$, $V = 523.2$ Å^3 and $Z = 4$. The space group of the β-phase was reported to be $P\bar{6}m2$ or $P\bar{6}2m$ with lattice parameters $a = b = 8.439(3)$, $c = 13.030(3)$ Å, $V = 803.6$ Å^3 and $Z = 6$ [29].

As mentioned above, the melting points of $Zn_3(BO_3)$, $Zn_3(PO_4)$ and Zn_3BPO_7 compounds are low, so the three promising binary systems $Zn_3(BO_3)_2$–ZnO, $Zn_3(PO_4)_2$–ZnO and Zn_3BPO_7–ZnO as well as the ternary system $ZnO–B_2O_3–P_2O_5$ were investigated to search for a suitable flux for ZnO crystal growth.

2. Experiment

Analytical grade ZnO, H_3BO_3 and $NH_4H_2PO_4$ were used to prepare the specimens by solid-state reaction and quenching methods. Altogether 60 specimens were prepared and their compositions were shown in Fig. 1, among which there are 29 specimens for the 3 binary subsystems and 31 specimens for the ternary system.

The powders of the raw materials in the nominal compositions were mixed in an agate mortar to get homogeneous. For the samples containing less B_2O_3 or P_2O_5, the mixture was preheated at 500 °C for 10 h at a slow heating rate in order to avoid the loss of components with the volatiles of H_2O and NH_3. After being pressed into pellets of 12 mm in diameter and 1–2 mm in thickness, samples were sintered for 1–2 days at 600–900 °C according to different compositions. The sintered samples were ground to powder and identified by XRD. Then the powder was pressed to pellets again and sintered at the same temperature. The above procedure was repeated until the XRD patterns showed no changes. The samples containing more B_2O_3 or P_2O_5, of which the melting temperatures are low, were prepared by melting the mixtures in a platinum crucible to get homogeneous. Glasses were obtained by quenching the melts. DTA was used to determine the crystallization and melting temperatures of the glasses. For each sample,

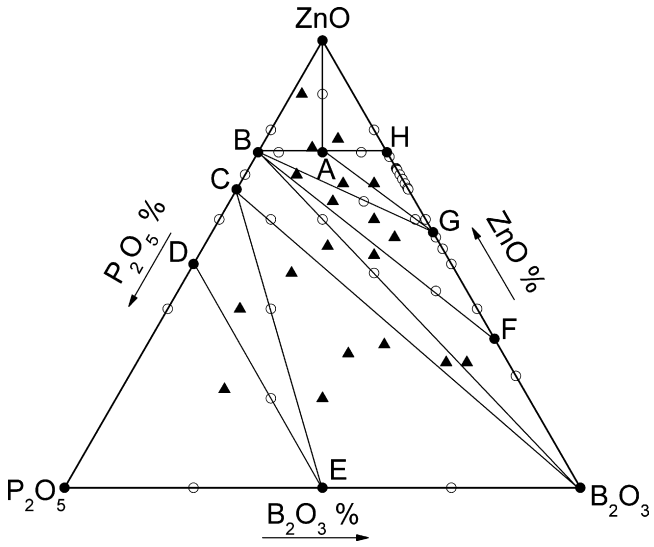

Fig. 1. Subsolidus phase relations of the ZnO–B_2O_3–P_2O_5 system. (A) Zn_3BPO_7; (B) $Zn_3(PO_4)_2$; (C) $Zn_2P_2O_7$; (D) $Zn(PO_3)_2$; (E) BPO_4; (F) ZnB_4O_7; (G) $Zn_4B_6O_{13}$; (H) $Zn_3(BO_3)_2$; (▲ three phases; ◯ two phases; ● single phase).

the glass was annealed at a proper temperature between the crystallization and melting temperatures. The samples were considered to be in equilibrium until the XRD patterns showed no changes upon the successive heat treatment.

The XRD data for phase identification were collected on an X-ray Rigaku diffractometer D/Max-2500 with Cu Kα radiation (45 kV × 250 mA) and a graphite monochromator using a continuous mode at a rate of $2\theta = 4°$/min.

The XRD patterns for indexing were collected on an automated Pan Analytical X'pert MRD (45 kV × 40 mA) high resolution diffractometer with Cu $K\alpha_1$ radiation using a X'Celerator Retroft Detector and a Ge (1 1 1) monochromator.

The thermal analyses were conducted on a RSZ type high temperature μ-DTA apparatus with Pt–PtRh thermocouples. Platinum crucibles were used as vessels and α-Al_2O_3 as a reference substance. The heating rate is 10 °C/min and the highest temperature of the DTA measurement is 1250 °C.

3. Results and discussions

3.1. Binary systems

The phase relations of the three binary systems ZnO–B_2O_3, ZnO–P_2O_5 and B_2O_3–P_2O_5 were firstly investigated. The unit cell parameters of all the compounds obtained in this work were indexed by DICVOL04 program [31].

3.1.1. ZnO–B_2O_3 system

Only three compounds with the ZnO:B_2O_3 molar ratios of 3:1 (β-phase), 4:3 and 1:2 were observed in this work. Five weight percent excessive of H_3BO_3 was used to obtain the 3:1 and 4:3 compounds. The 3:1 compound was indexed based on the monoclinic *C*2/*c* structure with lattice parameters $a = 23.835(3)$, $b = 5.042(0)$, $c = 8.381(1)$ Å, $\beta = 102.9°$, which is consistent with the β-phase of the 3:1 compound by Ref. [7] and also agrees with the reports of Refs. [8,9] when the body-center lattice is converted to the c-face-center lattice. The 4:3 compound was indexed based on a cubic unit cell with $a = 7.474(5)$ Å, which is in agreement with the results of Refs. [10–12]. The 1:2 compound has the orthorhombic *Pbca* structure as reported in Ref. [14], and the lattice parameters are $a = 13.715(8)$, $b = 8.114(9)$, $c = 8.639(5)$ Å. In our experiment, the samples with the ZnO:B_2O_3 molar ratios of 2:1 and 3:2 are all mixtures of the 3:1 and 4:3 compounds. However, occasionally, the samples with compositions of slightly more than 25 mol.% B_2O_3 are composed of the 3:1 compound and minor ZnO. This may be due to the sputtering of H_3BO_3 during sintering. The 5:2 and 1:1 compounds reported in Ref. [5] may just be the 3:1 and 4:3 compounds, respectively, due to the same reason.

3.1.2. ZnO–P_2O_5 system

Three compounds with the ZnO:P_2O_5 molar ratios of 3:1, 2:1 and 1:1 were obtained in our work. XRD analysis indicates that the 3:1 compound is the α-phase as reported in Ref. [18]. According to the indexing result based on a monoclinic unit cell with the space group *C*2/*c*, the lattice parameters are $a = 8.185(2)$, $b = 5.641(4)$, $c = 14.998(4)$ Å and $\beta = 105.0(1)°$. This is in consistent with the results of Ref. [18]. The β- and γ-phases of the 3:1 compound which were reported respectively in Refs. [19,20] were not synthesized in our experimental conditions. The 2:1 compound synthesized in this work is the α-phase as nominated in Ref. [21]. It was indexed based on a monoclinic unit cell with space group *C*2/*c*. The lattice parameters $a = 19.609(7)$, $b = 8.273(9)$, $c = 9.106(7)$ Å and $\beta = 100.1(4)°$ were obtained. The result agrees with Ref. [21], in which the *I*2/*c* structure can be converted into the standard space group *C*2/*c* with lattice parameters $a = 19.563$, $b = 8.259$, $c = 9.099$ Å and $\beta = 100.2°$. The other phases [22,23] of the 2:1 compound were not obtained in this work. The 1:1 compound was obtained by annealing the vitreous sample with the ZnO:P_2O_5 molar ratio of 2:3 at 550 °C for 1 day. The shift of composition may be caused from the loss of P_2O_5 during the melting course. This sample can be indexed based on a monoclinic unit cell with space group *C*2/*c*, which is in agreement with the α_2-phase of the 1:1 compound reported in Ref. [25]. The lattice parameters $a = 9.747(5)$, $b = 8.895(8)$, $c = 4.966(7)$ Å and $\beta = 108.5(7)°$ were obtained.

3.1.3. B_2O_3–P_2O_5 system

Only one compound of BPO_4 was obtained in this system, which was indexed based on a tetragonal unit cell. The space group is $I\bar{4}$ with lattice parameters $a = b = 4.341(7)$, $c = 6.642(4)$ Å, which is the same as reported in Ref. [27].

3.2. ZnO–B_2O_3–P_2O_5 system

According to the phase identification, there are seven binary compounds and one ternary compound Zn_3BPO_7 in this ternary system. The ternary subsolidus phase relations were constructed and shown in Fig. 1. Ten ternary-phase regions were determined, and no solid-solution composition range was found between any binary or ternary compounds. In this work, the XRD pattern of Zn_3BPO_7 compound was indexed based on an orthorhombic unit cell with lattice parameters $a = 7.304(4)$, $b = 4.214(0)$, $c = 13.054(2)$ Å, $V = 401.8(2)$ Å^3 and $Z = 3$ ($M_{20} = 34.6$, $F_{20} = 27.6(0.0087, 83)$, $F_{26} = 14.3(0.0110, 166)$). In fact, all reported structures of Zn_3BPO_7 can be translated into one another depending on the different choices of the unit cell. For example, the orthorhombic unit cell indexed by us can be changed into

the hexagonal unit cell. If c is fixed, namely $c_{hex} = c_{ort}$, $a_{hex} = a_{ort}/\cos 30^\circ = 8.434$ Å $= 2b_{ort}$, $V_{hex} = 2V_{ort}$, the hexagonal unit cell just corresponds to the β-phase reported by Ref. [29]. After annealed at 500 °C for 2 weeks, the XRD patterns of Zn_3BPO_7 showed no changes, and no polymorphic transition peak was observed in DTA curves of Zn_3BPO_7. So we believe that Zn_3BPO_7 has no polymorphic phase transition above 500 °C.

The small region of ZnO–$Zn_3(BO_3)_2$–$Zn_3(PO_4)_2$ in the ternary system has rather high ZnO content. The corresponding compounds $Zn_3(BO_3)_2$, $Zn_3(PO_4)_2$ and Zn_3BPO_7 have relatively low melting points, which are 1045 °C [5], 1060 °C [17] and 927 °C [28], respectively. Besides, no solid solution forms between the three compounds and ZnO according to our investigation. If these compounds formed eutectic systems with ZnO and if the eutectic temperatures are below or close to 1000 °C, they might be the suitable fluxes for ZnO crystal growth. So the phase diagrams of the three pseudo-binary systems $Zn_3(BO_3)_2$–ZnO, $Zn_3(PO_4)_2$–ZnO and Zn_3BPO_7–ZnO were investigated.

3.3. Pseudo-binary systems

$Zn_3(BO_3)_2$, $Zn_3(PO_4)_2$ and Zn_3BPO_7 were synthesized respectively and used as starting materials. The compositions of the samples were listed in Table 1. The samples were believed to be in equilibrium when the XRD patterns showed no changes after repeated sintering. Then the DTA measurement was conducted. The DTA curve of the sample containing 10 mol.% ZnO and 90 mol.% Zn_3BPO_7 is shown in Fig. 2 as an example to illustrate the DTA analysis. The onset temperature of the sharp peak is taken as the invariant reaction temperature. The ending temperature of the relaxative peak is considered to be the liquidus temperature. The results of DTA analysis were listed in Table 1. The phase diagrams of the three pseudo-binary systems were constructed in Figs. 3–5, respectively. It is believed that they form eutectic systems, but for the $Zn_3(BO_3)_2$–ZnO and Zn_3BPO_7–ZnO systems, the eutectic compositions degenerate to the pure $Zn_3(BO_3)_2$ and Zn_3BPO_7, respectively. The dashed lines denote the predicted liquidus were not observed due to the temperature limit of 1250 °C.

Table 1
Results of DTA measurement for the three pseudo-binary systems $Zn_3(BO_3)_2$–ZnO, $Zn_3(PO_4)_2$–ZnO and Zn_3BPO_7–ZnO

No.	$Zn_3(BO_3)_2$ (mol.%)	ZnO (mol.%)	Transition temperature (°C)	Eutectic temperature (°C)	Melting temperature (°C)
1	100	0			1054
2	90	10		1057	
3	80	20		1054	
4	70	30		1054	

No.	$Zn_3(PO_4)_2$ (mol.%)	ZnO (mol.%)	(α → β) Transition temperature (°C)	Eutectic temperature (°C)	Melting temperature (°C)
1	100	0	963		1058
2	90	10	937	983	1054
3	80	20	935	974	1043
4	73	27	924	972	1008
5	70	30	922	981	1016
6	67	33	924	969	
7	62	38	923	974	
8	60	40	937	978	
9	58	42	920	975	
10	55	45	933	968	
11	53	47	922	963	
12	50	50	935	982	
13	40	60	934	980	
14	30	70	932	980	
15	20	80	934	980	
16	10	90	932	978	
17	0	100			1975

No.	Zn_3BPO_7 (mol.%)	ZnO (mol.%)	Transition temperature (°C)	Eutectic temperature (°C)	Melting temperature (°C)
1	100	0			899
2	90	10		897	1030
3	80	20		903	1104
4	70	30		900	1205
5	60	40		903	
6	50	50		903	
7	40	60		900	
8	30	70		904	
9	20	80		904	
10	10	90		893	
11	0	100			1975

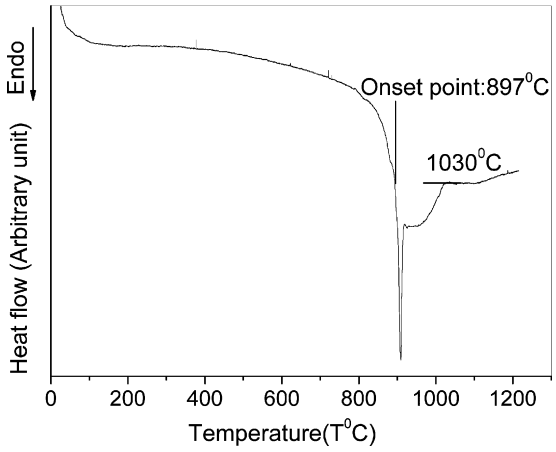

Fig. 2. DTA heating curve of the sample containing 90 mol.% Zn_3BPO_7 and 10 mol.% ZnO. Heating rate 10 °C/min.

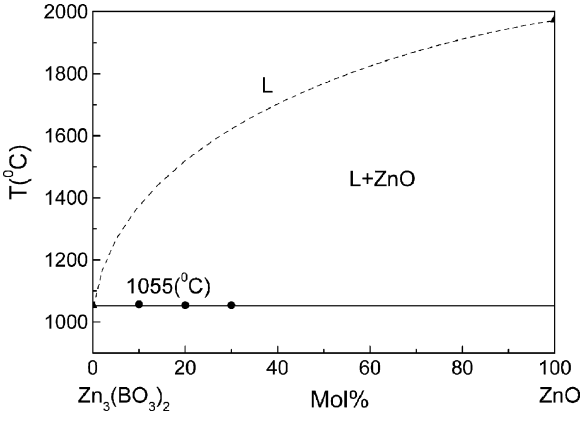

Fig. 3. Phase diagram of the $Zn_3(BO_3)_2$–ZnO pseudo-binary system.

In the $Zn_3(BO_3)_2$–ZnO system, the eutectic temperature and the melting point of $Zn_3(BO_3)_2$ are both about 1054 °C. The liquidus temperatures were not observed for all specimens as temperature increased up to 1250 °C. The liquidus temperature is so high that $Zn_3(BO_3)_2$ is not a suitable flux to grow ZnO crystals below 1250 °C.

For the $Zn_3(PO_4)_2$–ZnO system, the melting point of $Zn_3(PO_4)_2$ is 1060 °C and the eutectic temperature is 976 °C.

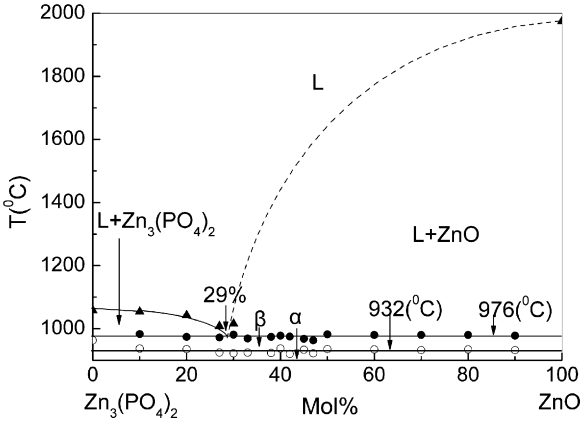

Fig. 4. Phase diagram of the $Zn_3(PO_4)_2$–ZnO pseudo-binary system.

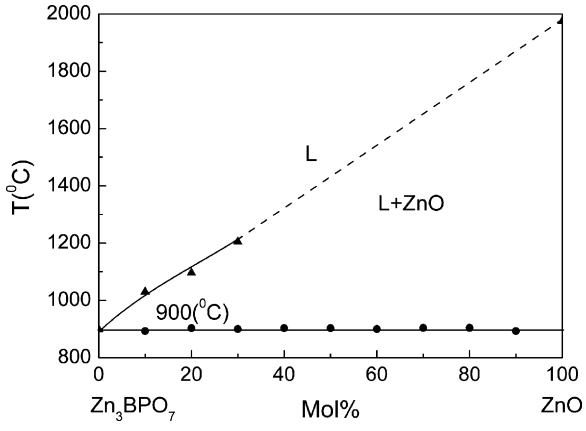

Fig. 5. Phase diagram of the Zn_3BPO_7–ZnO pseudo-binary system.

The composition of eutectic point is about 29 mol.% ZnO, however, the liquidus temperature was not observed below 1250 °C for the samples more than 33 mol.% ZnO. Theoretically, there exists a small composition range (with ZnO content from 29 mol.% to 33 mol.%) to grow ZnO crystals as the melt cools from 1250 °C. However, the range is so narrow that $Zn_3(PO_4)_2$ is also not a suitable flux to grow ZnO crystals.

For the Zn_3BPO_7–ZnO system, the melting point of Zn_3BPO_7 compound and the eutectic temperature are close to 900 °C. The liquidus temperature of 30 mol.% ZnO is 1205 °C. There is a larger composition range from 0 to 30 mol.% ZnO which is suitable to grow ZnO crystals. Theoretically, Zn_3BPO_7 is a suitable flux for ZnO crystal growth.

4. Conclusions

The following results were obtained in the present investigation on the ternary system ZnO–B_2O_3–P_2O_5. The subsolidus phase relations of the ternary system were determined by XRD. There are 7 binary compounds and 1 ternary compound in the system, which constitute 10 three-phase regions. No solid solution region was found between any binary or ternary compounds. The phase diagrams of the three pseudo-binary systems $Zn_3(BO_3)_2$–ZnO, $Zn_3(PO_4)_2$–ZnO and Zn_3BPO_7–ZnO were determined. Zn_3BPO_7 might be a suitable flux to grow ZnO crystals.

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