Phase relations in the ZnO-V_2O_5-K_2O system*

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The subsolidus phase relations of a ZnO-V_2O_5-K_2O system are investigated by X-ray powder diffraction. There is 1 ternary compound, 11 binary compounds and 14 three-phase regions in this system. The phase diagrams of V_2O_5-K_2O with the K_2O content ranging from 0 to 71 mol% and pseudo-binary system of ZnO-$K_2ZnV_2O_7$ are also studied by X-ray powder diffraction and differential thermal analysis methods.

Keywords: ZnO-V_2O_5-K_2O system, ZnO-$K_2ZnV_2O_7$ system, V_2O_5-K_2O system, X-ray diffraction

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1. Introduction

Wurtzite ZnO with a wide band gap of 3.37 eV and a large exciton binding energy of 60 meV has important applications in many functional devices, owing to its excellent optical and electrical properties.[1−3] Moreover, bulk ZnO single crystals are strongly desired as homoepitaxial substrates to improve the performance of ZnO-based film devices. ZnO has a high melting point of 1975 °C and volatilizes seriously at high temperature. The ZnO crystal is grown mainly by hydrothermal, vapour transport and fused salt methods. With the hydrothermal method, the growth of ZnO crystal is very slow and observation of the growth process is impossible. As for the vapour transport method, the manipulation of this technique is difficult. However, the above shortcomings can be overcome by the fused salt method, which is used to grow ZnO single crystals at atmospheric pressure and low temperature with observable benefits. Therefore, it is fundamentally important to search for a suitable flux for the ZnO crystal growth through the fused salt method. ZnO is possibly melted in the flux of alkali-metal oxides, and V_2O_5 with a lower melting point of 670 °C and a higher boiling temperature of 2052 °C is generally used as the flux. In this paper, we investigate subsolidus phase relations and the phase diagram of a pseudo-binary system relevant to ZnO in a ZnO-V_2O_5-K_2O system.

1.1. K_2O-ZnO system

In K_2O-ZnO system, 4 compounds with the K_2O:ZnO molar ratios of 2:1 (K_4ZnO_3), 1:1 (K_2ZnO_2), 1:3 ($K_2Zn_3O_4$) and 1:6 ($K_2Zn_6O_7$) were reported in Refs. [4]–[7]. All the compounds were prepared from the binary oxide ZnO and K_2O with the respective components in sealed Ag or Pt capsules and sintered at a low temperature for a long time. As an example, $K_2Zn_3O_4$ was obtained by heating oxide mixtures with K:Zn=2.2:3 at 800 °C for 35 days (for the K_2O-rich compounds, their sinter temperatures were lower and the sinter times were longer). Using this method, small single crystals of these four compounds with different compositions were obtained for the determination of their crystal structures. Their space groups and lattice parameters are shown in Table 1.[4−27]

1.2. ZnO-V_2O_5 system

ZnO-V_2O_5 system was studied extensively.[8−14,28−33] The essential investigations were those that involved

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phase equilibrium. However, the determined phase diagrams are different from each other. Four compounds were reported in this system with the $ZnO:V_2O_5$ molar ratios of 1:1 (ZnV_2O_6), 2:1 ($Zn_2V_2O_7$), 3:1 ($Zn_3V_2O_8$), and 4:1 ($Zn_4V_2O_9$). Their space group and lattice parameters are shown in Table 1.

Table 1. Crystallographic data of compounds for the ZnO-V_2O_5-K_2O system.

Phase	Space group	Lattice parameters						Ref.
		a/Å	b/Å	c/Å	α/(°)	β/(°)	γ/(°)	
K_4ZnO_3	$P\bar{1}$	11.033(3)	8.813(3)	6.982(2)	109.65(2)	89.56(2)	102.41(3)	[4]
K_2ZnO_2	$Ibam$	5.967	10.480	5.402				[5]
$K_2Zn_3O_4$	$C2/c$	14.827(2)	13.373(1)	5.719(1)		102.79(1)		[6]
$K_2Zn_6O_7$	$P4_2nm$	10.91(2)		3.32(5)				[7]
ZnV_2O_6	$C2$	9.242(8)	3.526(3)	6.574(6)		111.55(25)		[8]
	$C2/m$	9.2651(9)	3.5242(5)	6.5889(8)		111.37(1)		[9]
	$C2$	9.2479(0)	3.5294(3)	6.5755(2)		111.346(4)		this work
	$C2/m$	9.2483(0)	3.5295(30	6.5760(2)		111.345(5)		this work
$Zn_2V_2O_7$	$C2/c$	7.429(5)	8.340(3)	10.098(3)		111.37(5)		[10]
	$C2/m$	6.9324(2)	8.4394(2)	5.0326(1)		108.272(2)		[11]
	$C2/c$	7.4301(4)	8.3238(1)	10.0928(3)		111.328(2)		this work
$Zn_3V_2O_8$	$Cmca$	6.088(3)	11.489(3)	8.280(3)				[12]
	$Abam$	8.29	11.52	6.09				[13]
	$Cmca$	6.1134	11.5295	8.3004				this work
$Zn_4V_2O_9$	$P2_1$	10.488(5)	8.198(6)	9.682(5)		118.66(4)		[14]
	$P2_1$	10.4877(4)	8.1869(1)	9.6779(7)		118.645(5)		this work
$K_2V_8O_{21}$	$C2/m$	14.9402(2)	3.61823(4)	14.7827(2)		91.072(1)		[15]
	$C2/m$	14.951(1)	3.6220(4)	14.797(1)		91.032(8)		this work
KV_3O_8	$P2_1/m$	7.640(2)	8.380(3)	4.979(2)		96.95(3)		[16]
	$P2_1/m$	7.63	8.43	4.97		96.75		[17]
	$P2_1/m$	4.976(2)	8.383(2)	7.641(2)		96.94(3)		[18]
	$P2_1/m$	7.6418(2)	8.3886(4)	4.9772(2)		97.006(4)		this work
$K_3V_5O_{14}$	$P31m$	8.6796(20)		4.9914(8)				[19]
	$P31m$	8.6901(5)		5.0063(4)				[20]
	$P31m$	8.6833(9)		4.9923(3)				this work
KVO_3	$Pbcm$	5.176(2)	10.794(3)	5.680(2)				[21]
	$Pmab$	5.70(1)	10.82(2)	5.22(1)				[22]
	$Pmab$	5.70(1)	10.83(3)	5.19(1)				[23]
	$Pmab$	5.6929(5)	10.7997(7)	5.1843(4)				this work
$K_5V_3O_{10}$	$P4_12_12$	8.1757(6)		18.7313(7)				[24]
	$P4_12_12$	8.0158(10)		18.693(6)				this work
$K_4V_2O_7$	$C2/m$	10.222(1)	6.2309(8)	7.282(1)		101.31(1)		[25]
	$C2/m$	10.195(1)	6.234(1)	7.269(1)		101.327(1)		this work
$K_3VO_4(\beta)$	$I\bar{4}2m$	5.93(1)		8.11(2)				[26]
$K_3VO_4(\gamma)$	$P2_13$	8.304(2)						[26]
$K_2ZnV_2O_7$	$P4_2/m$	8.363		11.354				[27]
	$P4_2/m$	8.3580(2)		11.3404(6)				this work

The ZnV_2O_6 compound melts incongruently at 645 °C, depositing a high-temperature β-$Zn_2V_2O_7$ modification.[28]

The compound $Zn_2V_2O_7$ has two polymorphic phases, α and β.[10,11] The reported temperature of the reversible process, α-$Zn_2V_2O_7 \leftrightarrow \beta$-$Zn_2V_2O_7$, is 620 °C[29] or 615 °C.[30] The compound melts congruently at 890 °C[29] or 872 °C.[30]

The polymorphism of $Zn_3V_2O_8$ is still under debate. Brown and Hummel,[28] Pollard,[32] and Hng and Knowles[33] pointed out that there were three polymorphic forms, and the reversible processes, α-$Zn_3V_2O_8 \leftrightarrow \beta$-$Zn_3V_2O_8$ and β-$Zn_3V_2O_8 \leftrightarrow \gamma$-$Zn_3V_2O_8$, took place at 795 °C and 815 °C, respectively. Clark and Pick[30] indicated that $Zn_3V_2O_8$ had two polymorphic phases α and β. According to

Makarov *et al.*[29] and Kurzawa *et al.*,[31] the compound had no polymorphism.

A single crystal of the 4:1 compound $Zn_4V_2O_9$, considered to be a metastable phase, was obtained from a CO_2-laser generated flux and the solid ZnO/V_2O_5 materials.[14] It melts incongruently at 910 °C and crystallizes into a monoclinic system with the space group $P2_1$.[14] The temperature range of thermal stability determined for the $Zn_4V_2O_9$ compound is between 740 °C and 900 °C.[31]

1.3. V_2O_5-K_2O system

The V_2O_5-K_2O binary system was intensively investigated,[15−26] and 7 compounds with various V_2O_5:K_2O molar ratios were reported as follows: 4:1 compound $K_2V_8O_{21}$,[15] 3:1 compound KV_3O_8,[16−18] 5:3 compound $K_3V_5O_{14}$,[19,20] 1:1 compound KVO_3,[21−23] 3:5 compound $K_5V_3O_{10}$,[24] 1:2 compound $K_4V_2O_7$,[25] and 1:3 compound K_3VO_4.[26] Their space groups and lattice parameters are listed in Table 1.

The phase diagram of this system was also determined by Canneri[34] and Holtzberg *et al.*[35] Only 3 compounds KVO_3, $K_4V_2O_7$, K_3VO_4 were found in the partial system K_2O-V_2O_5 according to Canneri's results,[34] which were all congruent compounds with melting points of 497 °C, 910 °C, and 1000 °C, respectively. Holtzberg *et al.*[35] reported 5 compounds: $K_2V_8O_{21}$ (incongruent compound melted at 520 °C), KVO_3 (congruent compound with melting point at 520 °C), $K_{32}V_{18}O_{61}$ (incongruent compound melted at 696 °), $K_4V_2O_7$(congruent compound with polymorphic phase transition at 740 °C and melting point at 910 °C), and K_3VO_4 (congruent compound with melting point at 1300 °C). For the compound $K_{32}V_{18}O_{61}$, it turns out to be $K_5V_3O_{10}$,[24] which is measured with single-crystal X-ray diffraction. In the light of the concisely demonstrated knowledge about the K_2O-V_2O_5 system, we think it is advisable to verify the phase diagram of the system and to determine the thermal properties of some of the presented compounds.

1.4. ZnO-V_2O_5-K_2O system

For this system, only two compounds $K_2ZnV_2O_7$[27] and $K_2Zn(VO_3)_4$[36] were reported. The space group of $K_2ZnV_2O_7$ was $P4_2/m$ with lattice parameters $a = 8.363$ Å and $c = 11.354$ Å. However, nothing else was reported except for the X-ray powder diffraction (XRD) data.

2. Experiment

Analytical grade ZnO, V_2O_5 and K_2CO_3 were used to prepare the specimens by solid-state reaction and quenching methods. 58 samples with different compositions of ZnO:V_2O_5:K_2O shown in Figure 1 were synthesized. The raw materials were heated with a slow heating rate at 350 °C for 24 h in order to avoid the loss of components with the volatiles of CO_2 and then weighted in the nominal compositions, ground and homogenized in an agate mortar. After being pressed into a pellet of 12 mm in diameter and 1–2 mm in thickness, the sample was sintered at 350–850 °C for 1–3 days in a stove according to different compositions. The sintered samples were ground into powder and characterized by XRD. Then the powder was pressed into pellets again and sintered at the same temperature. The above procedure was repeated until the XRD patterns showed no changes.

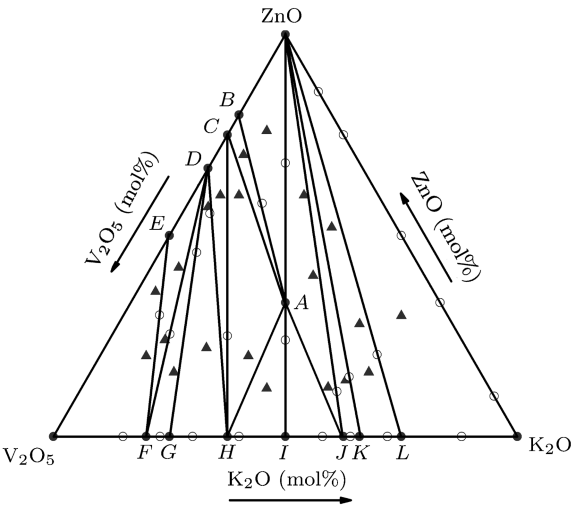


Fig. 1. Subsolidus phase relations of the ZnO-V_2O_5-K_2O system (▲ three phases; ○ two phases; ● single phases): *A*, $K_2ZnV_2O_7$; *B*, $Zn_4V_2O_9$; *C*, $Zn_3V_2O_8$; *D*, $Zn_2V_2O_7$; *E*, ZnV_2O_6; *F*, $K_2V_8O_{21}$; *G*, KV_3O_8; *H*, $K_3V_5O_{14}$; *I*, KVO_3; *J*, $K_5V_3O_{10}$; *K*, $K_4V_2O_7$; *L*, K_3VO_4.

The XRD data for the phase identification were collected at room temperature on a Rigaku D/Max-2500 X-ray diffractometer with Cu$K\alpha$ radiation (45 kV × 250 mA) and a graphite monochromator using continuous scanning mode at a rate of $2\theta = 6°$/min or an automated Pan Analytical X'pert MRD (45 kV × 40 mA) high resolution diffractometer with Cu$K\alpha$ radiation using an X'Celerator Retroft Detector and a Ge (111) monochromator.

Thermal analyses were conducted on an RSZ type high temperature differential thermal analysis (μ-DTA) apparatus with Pt-PtRh thermocouples. Platinum crucibles were used as vessels and as a reference

crucible. The heating and cooling rate was 10 °C/min and the highest temperature of the DTA measurement was 1250 °C.

3. Results and discussion

3.1. Binary systems

The phase relations of the three binary systems, ZnO-V_2O_5, ZnO-K_2O and K_2O-V_2O_5, were first investigated. The lattice parameters of the binary compounds were refined using the program Jade 5.0.[37] The obtained results are listed in Table 1.

3.1.1. ZnO-K_2O system

None of the reported compounds are observed in this work. The phase identification of the samples with various K_2O:ZnO molar ratios (1:6, 1:3, 1:1 and 2:1) reveals that the samples are a mixture of ZnO and K_2CO_3 after maintaining them at 760 °C for 4 days at the atmosphere. Almost only ZnO is left by increasing temperature to 900 °C and maintaining it at this temperature for 3 days, indicating that no compound has been synthesized in this binary system in our experimental conditions. It may be ascribed to the easy volatility of K_2O at high temperature which is obtained from the decomposition of K_2CO_3. The synthesis conditions and starting materials in our work are different from those in Refs. [4]–[7], in which the K_2O was used as starting material and the samples were sintered at a low temperature for a long time in a sealed container. According to the previous reports,[4−7] the sintering temperature decreases and sintering time increases with the content of K_2O increasing. Due to the different starting materials and synthesis conditions, no binary compound of this system is obtained by replacing K_2CO_3 with K_2O and maintaining it at high sintering temperature for short processing time.

3.1.2. ZnO-V_2O_5 system

In the ZnO-V_2O_5 system, the existence of four binary compounds ZnV_2O_6, $Zn_2V_2O_7$, $Zn_3V_2O_8$ and $Zn_4V_2O_9$ is confirmed and the XRD patterns have been refined using the Rietveld method[38,39] by the fullprof program.[40]

The structure of ZnV_2O_6 has been refined with the model in Refs. [8] and [9], separately. The Rietveld refinement results are very similar.

The sample of $Zn_2V_2O_7$ has been sintered at 450 °C for 2 days in a stove, and the low-temperature phase (α) is obtained. The DTA measurements shown in Fig. 2(a) indicate that the $Zn_2V_2O_7$ undergoes a phase transition at 601 °C and melts congruently at 865 °C, which are in good agreement with the results in Refs. [28]–[31].

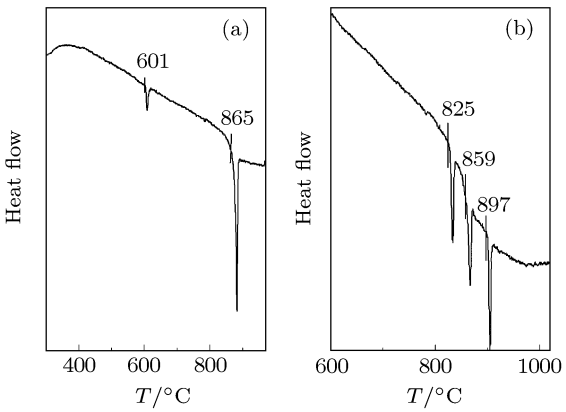


Fig. 2. Heating DTA curves of the samples (a) $Zn_2V_2O_7$ and (b) $Zn_3V_2O_8$.

The sample of $Zn_3V_2O_8$ has been synthesized by sintering at 450 °C for 2 days. As shown in Fig. 2(b), there are three endothermic peaks on the DTA heating curve and the corresponding values are 825 °C (peritectoid temperature $\alpha + \beta \rightarrow \gamma$), 859 °C (eutectic temperature $L \rightarrow \alpha + \beta$) and 897 °C (liquidus temperature), which accord well with the results in Refs. [29] and [31].

The 4:1 compound has been prepared by solid-state reaction and quenching methods. The sample has been sintered at 700 °C for 4 days and cooled slowly in the furnace to room temperature. The phase identification of the sample reveals that it is a mixture of ZnO and $Zn_3V_2O_8$. With the same cooling method, both the sintering temperature and sintering time have been increased, but the phase identification shows the same result as the above mentioned. However, pure $Zn_4V_2O_9$ is obtained when the sample is quenched into liquid nitrogen from 850 °. Its peritectoid melting point is 898 °, which is in good agreement with the results in Refs. [29]–[31].

The obtained space groups and lattice parameters are mentioned above, four compounds in the ZnO-V_2O_5 system are listed in Table 1.

3.1.3. K_2O-V_2O_5 system

The XRD identification results show that there are 7 compounds observed in this work, with the K_2O content < 71 mol%: $K_2V_8O_{21}$, KV_3O_8, $K_3V_5O_{14}$, KVO_3, $K_5V_3O_{10}$, $K_4V_2O_7$ and K_3VO_4. Their space groups and lattice parameters are shown in Table

1. In this composition range, no any other compound is observed. The dependence of average atomic volume on K_2O composition in this system is shown in Fig. 3 and shows a linear relationship.

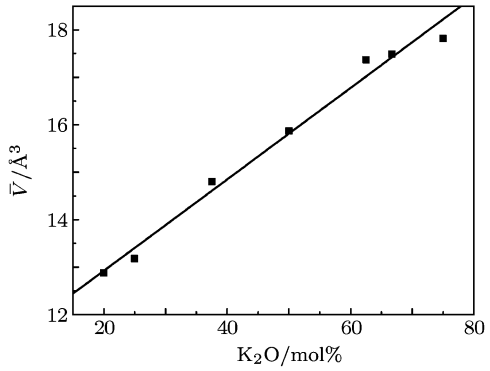


Fig. 3. Average atomic volume $\bar{V}$ dependence on K_2O composition of the binary compound in the system V_2O_5-K_2O.

The phase diagram with K_2O content ranging from 0 to 71 mol% has been determined based on XRD results and DTA analysis. The extrapolated onset temperatures of the DTA curves are given in Table 2. Figure 4 shows a phase diagram of the V_2O_5-K_2O, in which dottd lines in the range of K_2CO_3 content $\geq$ 75 mol% are obtained from the results of Ref. [35].

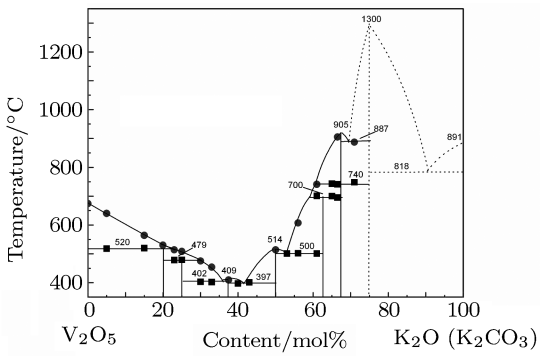


Fig. 4. Phase diagram of the V_2O_5-K_2O system.

Table 2. DTA data for some compounds of a V_2O_5-K_2O system with K_2O content ranging from 0 to 71 mol%.

K_2O(mol%)	Phase	Eutectic temperature/°C	Peritectic temperature/°C	Phase transition temperature/°C	Melting temperature/°C
5	V_2O_5+ $K_2V_8O_{21}$		518		640
15	V_2O_5+ $K_2V_8O_{21}$		520		564
20	$K_2V_8O_{21}$				530
23	KV_3O_8+$K_2V_8O_{21}$		478		514
25	KV_3O_8		479		508
30	KV_3O_8+$K_3V_5O_{14}$	403			475
33	KV_3O_8+$K_3V_5O_{14}$	402			454
37.5	$K_3V_5O_{14}$				409
40	$K_3V_5O_{14}$+ KVO_3	397			
43	$K_3V_5O_{14}$+ KVO_3	401			
50	KVO_3				514
53	KVO_3+$K_5V_3O_{10}$	501			
56	$K_5V_3O_{10}$+ KVO_3	502			607
61	$K_5V_3O_{10}$+ KVO_3	501	701	741	
65	$K_5V_3O_{10}$+ $K_4V_2O_7$		700	743	
66.5	$K_4V_2O_7$+ $K_5V_3O_{10}$		700	739	905
71	K_3VO_4+ $K_4V_2O_7$	887		752	

There are four compounds KVO_3, $K_5V_3O_{10}$, $K_4V_2O_7$ and K_3VO_4 in our partial phase diagram with the K_2O content $\geq$ 50 mol%, which is slightly different from those in Refs. [34] and [35]. The compound $K_5V_3O_{10}$ was not reported in Ref. [35], and it was described as $K_{32}V_{18}O_{61}$ in Ref. [35]. However, in the region of K_2O content $<$ 50 mol%, the difference is obvious. In this part, there are three compounds obtained from our work, in which $K_3V_5O_{14}$ melts congruently at 409 °C and the other two compounds $K_2V_8O_{21}$ and KV_3O_8 melt incongruently at 520 °C and 478 °C with the peritectic reaction, respectively. However, according to Refs. [34] and [35], there is no compound or only one compound $K_2V_8O_{21}$

in this part, respectively.

3.1.4. Ternary compound

Only one ternary compound $K_2ZnV_2O_7$ is obtained in this work, which melts at 667 °C. It belongs to a tetragonal system with the space group $P4_2/m$ and its lattice parameters are $a = 8.3580(2)$ Å and $c = 11.3404(6)$ Å, which accord with those in Ref. [27]. The compound $K_2Zn(VO_3)_4$ is not observed under our synthetic conditions, instead it is the mixture of two phases $Zn_3V_2O_8$ and $K_3V_5O_{14}$.

3.1.5. Subsolidus phase relations

According to the result of the phase identifications of the 58 samples obtained at different synthetic temperatures, the subsolidus phase relations of the ternary system are shown in Fig. 1. There are 11 binary compounds, 1 ternary compound and 14 ternary-phase regions in this system. There is no solid solution region for any binary or ternary compounds.

3.2. Pseudo-binary system $K_2ZnV_2O_7$-ZnO

The pseudo-binary system $K_2ZnV_2O_7$-ZnO was investigated by means of XRD and DTA methods. $K_2ZnV_2O_7$ was first prepared and used as starting material. Five samples were prepared in this system with ZnO content ranging from 0 to 50 mol%. The samples have been measured by DTA and the analysis results are listed in Table 3. The phase diagram is constructed and shown in Fig. 5.

Table 3. Results of DTA measurements for the pseudo-binary system $K_2ZnV_2O_7$-ZnO.

$K_2ZnV_2O_7$/mol%	Phase	Eutectic temperature/°C	Melting temperature/°C
100	$K_2ZnV_2O_7$	–	668.0
90	$K_2ZnV_2O_7$+ZnO	663	> 1250
80	$K_2ZnV_2O_7$+ZnO	662	> 1250
70	$K_2ZnV_2O_7$+ZnO	660	> 1250
60	$K_2ZnV_2O_7$+ZnO	658	> 1250
50	$K_2ZnV_2O_7$+ZnO	655	> 1250

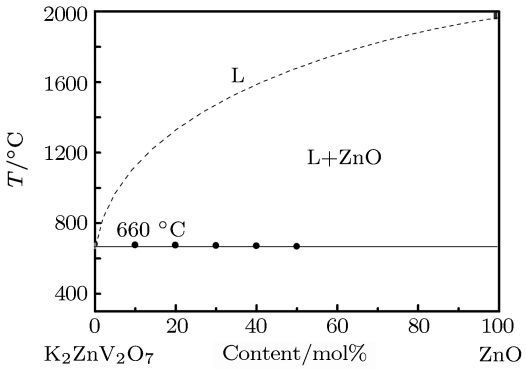


Fig. 5. Phase diagram of the pseudo-binary system $K_2ZnV_2O_7$-ZnO.

The $K_2ZnV_2O_7$-ZnO forms a eutectic system and the eutectic temperature is about 667 °C. The eutectic point degenerates to the melting point of $K_2ZnV_2O_7$. There is only one endothermal peak in the heating course lower than 1200 °C, and the temperatures are almost the same for all samples, corresponding to their eutectic temperatures. The liquidus temperatures of all the samples cannot be found, indicating that $K_2ZnV_2O_7$ is not a suitable flux to grow ZnO crystals.

4. Conclusions

The phase relations are determined for the ZnO-V_2O_5-K_2O ternary system. There are 11 binary compounds, 1 ternary compound and 14 ternary-phase regions in this system. No solid solution region is formed for any binary or ternary compound. The phase diagrams of V_2O_5-K_2O with K_2O content ranging from 0 to 71 mol% and pseudo-binary system $K_2ZnV_2O_7$-ZnO are studied. $K_2ZnV_2O_7$-ZnO is a eutectic system with a eutectic temperature of 667 °C, but the liquidus temperature is higher than 1250 °C. Therefore, $K_2ZnV_2O_7$ is not a suitable flux to grow ZnO crystals.

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