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Phase equilibria in the system $CdO–ZnO–B_2O_3$ at 850°C

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Phase equilibria in the system $CdO–ZnO–B_2O_3$ were investigated at 850 °C using quenching and X-ray powder diffraction techniques. The binary phases reported previously were confirmed. The ternary phase diagram was solved and a new phase postulated: $3CdO \cdot 3ZnO \cdot 2B_2O_3$. X-ray powder data are given for this. Solid solution effects were investigated for the primary and binary phases by comparison of patterns; none were detected. These results are compared with those of a previous determination and the differences discussed.

1. Introduction

Ohno [1] claimed a region of cadmium–zinc borates which fluoresced when manganese activated. As a result of this, Harrison and Hummel [2] determined the sub-solidus phase relationships in the temperature range 700–900 °C. However, their phase diagram was based on the binary phase diagram for $CdO–B_2O_3$ reported by Subbarao and Hummel [3] and that for $ZnO–B_2O_3$ reported by Harrison and Hummel [4]. Since these binary systems were reported, further work has been done on both, and some of the binary phases have been shown to be either at different compositions or not to exist. In these circumstances the reported ternary [2] cannot be entirely correct and so was re-investigated.

1.1. Previous work

As already mentioned, the ternary system has been investigated in the subsolidus region [2], as a result of which, two ternary phases were reported, $2CdO \cdot ZnO \cdot 2B_2O_3$, which melts at 797 °C and $CdO \cdot 2ZnO \cdot B_2O_3$, which melts at 860 °C; the X-ray diffraction patterns were reported for both.

Subbarao and Hummel [3] investigated the entire $CdO–B_2O_3$ phase diagram using differential thermal analyses and X-ray powder diffraction techniques. They reported the existence of four intermediate phases $2CdO \cdot 3B_2O_3$, $3CdO \cdot 2B_2O_3$, $2CdO \cdot B_2O_3$ and $3CdO \cdot B_2O_3$. The last two were claimed to be dimorphic with transition temperatures of 900 and 870 °C, respectively. X-ray diffraction data were reported for all phases but the patterns for $3CdO \cdot 2B_2O_3$ and $2CdO \cdot B_2O_3$ were very similar.

Subsequently, Hart and Steward [5] investigated these compounds in the temperature range 725–850 °C using X-ray examination, differential thermal analysis and high-temperature microscopy. They concluded that the compound $3CdO \cdot 2B_2O_3$ could not be prepared; the X-ray data they report for the other three phases are similar, but not identical, to those given by Subbarao and Hummel [3].

Finally, Hand and Krogh-Moe [6] reported the existence of $CdO \cdot 2B_2O_3$ and showed that there were no phases between this and $2CdO \cdot B_2O_3$. X-ray data are given for both $CdO \cdot 2B_2O_3$ and $2CdO \cdot B_2O_3$; those for the latter are in very good agreement with those of Hart and Steward [5]. As single crystals of $CdO \cdot 2B_2O_3$ and $2CdO \cdot B_2O_3$ were grown from melts of composition $2CdO \cdot 3B_2O_3$ and $3CdO \cdot 2B_2O_3$ respectively, this would appear conclusive.

Subsequently the crystal structure of $CdO \cdot 2B_2O_3$ was determined [7], removing any doubt that the chemical composition could be incorrect. Thus it appears that the only cadmium borates that exist are $CdO \cdot 2B_2O_3$, $2CdO \cdot B_2O_3$ and $3CdO \cdot B_2O_3$.

A considerable amount of work has been completed on the $ZnO–B_2O_3$ phase diagram [4, 8–18], much of it confusing and contradictory. This was summarized [19] in an article in which further results were reported. This report concluded that in the range 640–900 °C, three zinc borates may be found; α-$3ZnO \cdot B_2O_3$, $4ZnO \cdot 3B_2O_3$ and $ZnO \cdot 2B_2O_3$. Up to 700 °C, only α-$3ZnO \cdot B_2O_3$ and $ZnO \cdot 2B_2O_3$ are detected, while at 710 °C $4ZnO \cdot 3B_2O_3$ is obtained, accompanied by the decomposition of $ZnO \cdot 2B_2O_3$. However, the decomposition is very sluggish and all three compounds may co-exist up to 900 °C. According to Hamson and Hummel [4], $3ZnO \cdot B_2O_3$ is dimorphic with a transition temperature of 964 °C, the high-temperature form being called β (these authors actually place this phase at a composition of $5ZnO \cdot 2B_2O_3$ as do some of the others). Since the summarizing article, the structure of $ZnO \cdot 2B_2O_3$ has been determined [20]; those of $3ZnO \cdot B_2O_3$ [18] and $4ZnO \cdot 3B_2O_3$ [12–14] had already been reported, and so the doubt concerning the compositions of the phases must be considered settled.

These are no data for the CdO–ZnO phase diagram.

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2. Experimental procedure

The investigation commenced with the preparation of the binary compounds.

The starting materials were cadmium oxide (99.5% pure, Aldrich Chemical Co. Ltd), Analar zinc oxide (not less than 99.5% pure after ignition, BDH Chemicals Ltd), and Analar boric acid (not less than 99.8% pure, BDH Chemicals Ltd). Quantities of cadmium oxide and zinc oxide were stored inside the furnace at the firing temperature, until removed for compact preparation.

For compact preparation, the appropriate quantities were mixed, ground to a fine powder under acetone, and pressed for 5 min in a 0.5 in (~ 1.25 cm) diameter steel die at $6000\,\mathrm{lb\,in^{-2}}$ ($1\,\mathrm{lb\,in^{-2}} = 7.0307 \times 10^2\,\mathrm{kg\,m^{-2}}$). No binder was used. All compacts were prefired at 400 °C for 30 min to decompose the boric acid, removed, reground and repressed for the final firing.

Both prefiring and firing were carried out in air with the compacts in open platinum boats and the specimens air-quenched. Various firing times were used and these are given in Table I.

As it is claimed [1] that a ternary phase of composition $2CdO \cdot ZnO \cdot 2B_2O_3$ exists and melts at 797 °C, a firing temperature of 750 °C was chosen. However, compositions on the $2CdO \cdot B_2O_3$–$4ZnO \cdot 3B_2O_3$ tie line close to $2CdO \cdot B_2O_3$ showed evidence of cadmium oxide after firing for about 1 week (160–170 h) and so the temperature was increased to 850 ± 5 °C.

After firing, a little of the compact was ground and used as an X-ray powder specimen which was examined in an 11.46 cm diameter Debye–Scherrer camera using filtered copper radiation.

3. Results

3.1. Cadmium oxide–boric oxide binary system

$3CdO \cdot B_2O_3$: the pattern obtained was similar but not identical to either that of Subbarao and Hummel [3] for the β-form, or Hart and Steward [5], but was a better fit to the latter pattern.

$2CdO \cdot B_2O_3$: the present data agree with that of Hand and Krogh-Moe [6].

TABLE I Specimens prepared, chemical composition and X-ray analysis

Specimen no. or compound	Chemical composition (wt %)			Firing time (h)	Phase analysis		
	CdO	ZnO	B_2O_3		Major	Minor	Trace
$CdO \cdot 2B_2O_3$	48.0		52.0	93	$CdO \cdot 2B_2O_3$		$2CdO \cdot B_2O_3$
"$2CdO \cdot 3B_2O_3$"	55.0		45.0	97	$CdO \cdot 2B_2O_3$	$2CdO \cdot B_2O_3$	
"$3CdO \cdot 2B_2O_3$"	73.5		26.5	400	$2CdO \cdot B_2O_3$		
$2CdO \cdot B_2O_3$	78.7		21.3	93	$2CdO \cdot B_2O_3$		
$3CdO \cdot B_2O_3$	84.7		15.3	405	β-$3CdO \cdot B_2O_3$		
$ZnO \cdot 2B_2O_3$		36.9	63.1	168	$4ZnO \cdot 3B_2O_3$	$ZnO \cdot 2B_2O_3$	
$4ZnO \cdot 3B_2O_3$		60.9	39.1	503	$4ZnO \cdot 3B_2O_3$	$ZnO \cdot 2B_2O_3$	α-$3ZnO \cdot B_2O_3$
$3ZnO \cdot B_2O_3$		77.8	22.2	72	α-$3ZnO \cdot B_2O_3$		
A	61.0	39.0		264	CdO + ZnO		
1	12.0	13.0	75.0	95	$CdO \cdot 2B_2O_3$	$ZnO \cdot 2B_2O_3$	$4ZnO \cdot 3B_2O_3$
2	15.0	25.0	60.0	95	$4ZnO \cdot 3B_2O_3$	$CdO \cdot 2B_2O_3$ + $ZnO \cdot 2B_2O_3$	
3	35.0	10.0	55.0	95	$CdO \cdot 2B_2O_3$	$4ZnO \cdot 3B_2O_3$	
4	7.0	44.0	49.0	95	$4ZnO \cdot 3B_2O_3$	$ZnO \cdot 2B_2O_3$	$2CdO \cdot B_2O_3$
5	30.0	23.0	47.0	96	$4ZnO \cdot 3B_2O_3$	$2CdO \cdot B_2O_3$	
6	15.0	42.0	43.0	94	$4ZnO \cdot 3B_2O_3$	$ZnO \cdot 2B_2O_3$	$2CdO \cdot B_2O_3$
7	39.0	19.0	42.0	94	$4ZnO \cdot 3B_2O_3$	$CdO \cdot 2B_2O_3$	
8	54.0	8.0	38.0	91	$CdO \cdot 2B_2O_3$	$2CdO \cdot B_2O_3$	
9	22.0	39.0	39.0	91	$4ZnO \cdot 3B_2O_3$	$CdO \cdot 2B_2O_3$	
10	54.0	17.0	29.0	1	Amorphous colourless glass		
11	29.8	38.0	32.2	96	$4ZnO \cdot 3B_2O_3$		
12	40.0	30.0	30.0	18	$4ZnO \cdot 3B_2O_3$		
13	57.0	17.0	26.0	95	$2CdO \cdot B_2O_3$		
14	67.0	9.0	24.0	72	$2CdO \cdot B_2O_3$		
15	29.0	40.0	31.0	96	$4ZnO \cdot 3B_2O_3$		
16	50.0	25.0	25.0	95	Amorphous glass		
17	29.0	44.0	27.0	93	$4ZnO \cdot 3B_2O_3$	$3CdO \cdot 3ZnO \cdot 2B_2O_3$ + α-$3ZnO \cdot B_2O_3$	
18	35.0	40.0	25.0	17	$3CdO \cdot 3ZnO \cdot 2B_2O_3$		$4ZnO \cdot 3B_2O_3$ + α-$3ZnO \cdot B_2O_3$
19	65.0	14.0	21.0	119	$2CdO \cdot B_2O_3$ + $3CdO \cdot 3ZnO \cdot 2B_2O_3$		
20	56.0	25.0	19.0	72	$3CdO \cdot 3ZnO \cdot 2B_2O_3$		
21	50.0	30.0	20.0	118	$3CdO \cdot 3ZnO \cdot 2B_2O_3$		
22	13.0	55.0	32.0	72	$4ZnO \cdot 3B_2O_3$	α-$3ZnO \cdot B_2O_3$	
23	9.0	63.0	28.0	91	$4ZnO \cdot 3B_2O_3$	α-$3ZnO \cdot B_2O_3$	
24	24.0	50.0	26.0	119	α-$3ZnO \cdot B_2O_3$	$4ZnO \cdot 3B_2O_3$	$3CdO \cdot 3ZnO \cdot 2B_2O_3$
25	20.0	55.0	25.0	71	α-$3ZnO \cdot B_2O_3$	$4ZnO \cdot 3B_2O_3$	$3CdO \cdot 3ZnO \cdot 2B_2O_3$

TABLE I. (contd)

Specimen no. or compound	Chemical composition (wt %)			Firing time (h)	Phase analysis		
	CdO	ZnO	B_2O_3		Major	Minor	Trace
26	71.0	10.0	19.0	96	β-$3CdO \cdot B_2O_3$	$2CdO \cdot B_2O_3$	
27	19.0	60.0	21.0	99	α-$3ZnO \cdot B_2O_3$	$3CdO \cdot 3ZnO \cdot 2B_2O_3$	
28	30.0	50.0	20.0	118	$3CdO \cdot 3ZnO \cdot 2B_2O_3$		α-$3ZnO \cdot B_2O_3$
29	35.6	45.1	19.3	71	$3CdO \cdot 3ZnO \cdot 2B_2O_3$	ZnO	
30	40.0	41.0	19.0	96	$3CdO \cdot 3ZnO \cdot 2B_2O_3$		
31	50.1	31.8	18.1	95	$3CdO \cdot 3ZnO \cdot 2B_2O_3$		
32	55.0	27.0	18.0	96	$3CdO \cdot 3ZnO \cdot 2B_2O_3$		
33	58.1	23.8	18.1	72	$3CdO \cdot 3ZnO \cdot 2B_2O_3$		β-$3CdO \cdot B_2O_3$
34	63.0	20.0	17.0	99	β-$3CdO \cdot B_2O_3$	$3CdO \cdot 3ZnO \cdot 2B_2O_3$	
35	17.0	64.0	19.0	93	ZnO	α-$3ZnO \cdot B_2O_3$ + $3CdO \cdot 3ZnO \cdot 2B_2O_3$	
36	23.0	60.0	17.0	71	ZnO	$3CdO \cdot 3ZnO \cdot 2B_2O_3$ + α-$3ZnO \cdot B_2O_3$	
37	29.0	55.0	16.0	72	$3CdO \cdot 3ZnO \cdot 2B_2O_3$	ZnO	
38	5.0	83.0	12.0	71	ZnO	α-$3ZnO \cdot B_2O_3$	
39	14.0	78.0	8.0	74	ZnO	$3CdO \cdot 3ZnO \cdot 2B_2O_3$	α-$3ZnO \cdot B_2O_3$
40	44.0	40.0	16.0	76	$3CdO \cdot 3ZnO \cdot 2B_2O_3$	ZnO	
41	38.0	48.0	14.0	71	$3CdO \cdot 3ZnO \cdot 2B_2O_3$	ZnO	
42	30.0	60.0	10.0	67	ZnO	$3CdO \cdot 3ZnO \cdot 2B_2O_3$	
43	60.0	25.0	15.0	72	β-$3CdO \cdot B_2O_3$	$3CdO \cdot 3ZnO \cdot 2B_2O_3$	ZnO
44	50.0	35.0	15.0	72	$3CdO \cdot 3ZnO \cdot 2B_2O_3$	β-$3CdO \cdot B_2O_3$ + ZnO	
45	45.5	42.5	12.0	96	ZnO	β-$3CdO \cdot B_2O_3$	$3CdO \cdot 3ZnO \cdot 2B_2O_3$
46	72.0	15.0	13.0	97	β-$3CdO \cdot B_2O_3$	ZnO	
47	55.0	35.0	10.0	95	ZnO	β-$3CdO \cdot B_2O_3$	
48	27.0	68.0	5.0	97	ZnO		β-$3CdO \cdot B_2O_3$
49	83.0	13.0	4.0	95	CdO		β-$3CdO \cdot B_2O_3$
50	45.0	51.0	4.0	95	ZnO + CdO		

Notes:
1. Binary compacts in inverted commas are claimed to exist by other investigators.
2. The following compacts melted: 10, 12, 16, 18.
3. The following compacts fused (appeared glazed) 13, 17, 20, 24, 32, 33, 43.

$CdO \cdot 2B_2O_3$: at the nominal composition, it was not possible to obtain a pattern of this phase alone; there was always a trace of $2CdO \cdot B_2O_3$ present. Allowing for this the pattern agrees with that of Hand and Krogh-Moe [6]. The difficulty of producing a pattern of this compound at the nominal composition has already been reported [21, 22] and it has been attributed to a loss of boric oxide during firing.

3.2. Zinc oxide–boric oxide binary system

$3ZnO \cdot B_2O_3$: the pattern obtained fitted the various other patterns that have been reported for the α polymorph of this compound [15, 23, 24].

$4ZnO \cdot 3B_2O_3$: at this composition and temperature it was found that all three zinc borates co-exist. The major phase was $4ZnO \cdot 3B_2O_3$, as identified from the pattern given by Fayos *et al.* [17]. It has already been reported that all three zinc borates co-exist at this temperature and composition [19], and this has been interpreted as being due to the sluggish decomposition of $ZnO \cdot 2B_2O_3$ with the simultaneous formation of $4ZnO \cdot 3B_2O_3$ at temperatures of 710 °C and above. In the present investigation, even prolonged firing (503 h at 850 °C) could not convert all the $ZnO \cdot 2B_2O_3$.

$ZnO \cdot 2B_2O_3$: the patterns of both $4ZnO \cdot 3B_2O_3$ and $ZnO \cdot 2B_2O_3$ were found, confirming a previous report [19], the pattern of the latter agreeing with that of Martinez-Ripoll *et al.* [20].

3.3. Cadmium oxide–zinc oxide binary system

No binary was found in this system after firing for 264 h.

3.4. Ternary thermal equilibrium diagram

During the course of the investigation into the thermal equilibrium diagram, nine binary and fifty ternary compacts were made and analysed. Table I lists these compacts, firing times and the interpretation of the X-ray diffraction patterns. It proved impossible to interpret the diffraction patterns without postulating the existence of one ternary phase of composition $3CdO \cdot 3ZnO \cdot 2B_2O_3$. The X-ray pattern for this is given in Table II; this was obtained by photometering an 11.46 diameter Debye–Scherrer film taken using filtered CuK_α radiation.

The compatibility triangles consistent with these results are given in Fig. 1.

X-ray patterns containing binary phases were compared. From this comparison there appeared to be no evidence of solid-solution effects in the binary phases; however, most patterns lacked sharp lines in the back-reflection region of the X-ray patterns and because of

TABLE II X-ray powder data for $3CdO \cdot 3ZnO \cdot 2B_2O_3$

d (nm)	I	d (nm)	I
0.415	20	0.1621	3
0.2908	100	0.1578	14
0.2805	8	0.1558	29
0.2664	9	0.1474	35
0.2463	5	0.1394	19
0.2406	58	0.1378	5
0.2332	5	0.1359	5
0.2085	15	0.1295	11
0.2035	26	0.1251	6
0.1857	36	0.1221 b[a]	12
0.1833	19	0.1152	7
0.1676	8	0.1115	12

[a] b, broad diffuse line.

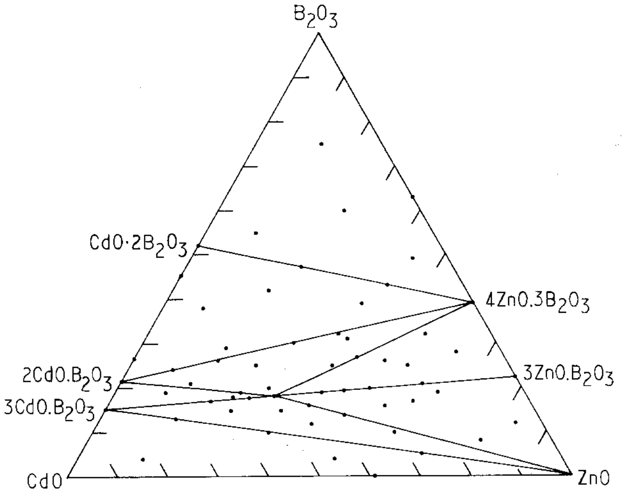

Figure 1 Phase equilibrium in the system $CdO–ZnO–B_2O_3$ at 850 °C.

this the existence of some solubility cannot be discounted.

4. Discussion

The lack of detectable solid solution mentioned in the previous section is not surprising. The published diagrams of cadmium oxide–boric oxide [3] and zinc oxide–boric oxide [4] suggest that there are no solutions in either of them. Van Vlack [25] points out that in close-packed crystal structure there can be extensive solid solution if the size of the host and substitutional ions do not differ by more than 15%, but that this limitation may be relaxed if the structures are not close-packed. In addition, solid solution is limited if the host and substitutional atoms have different valency, or for compounds having different structures.

Based on the ionic radius of O^{2-} as 0.140 nm for six-fold coordination, Shannon and Prewitt [26] give the ionic radii for six-fold coordination as $Cd^{2+} = 0.095$ nm, $Zn^{2+} = 0.075$ nm and $B^{3+} = 0.023$ nm. Thus the three ions have widely different radii and, in addition, the three primary oxides have completely different structures and so the conditions are not favourable for the formation of solid solutions. Owing to the fact that the primary oxides have different structures, the actual coordination number for the three cations in their respective oxides are six, four and three for Cd^{2+}, Zn^{2+} and B^{3+}, respectively. If this coordination is carried over into the secondary and ternary compounds, then the ionic radii become $Cd^{2+} = 0.095$ nm, $Zn^{4+} = 0.060$ nm and $B^{3+} = 0.002$ nm, and this reduces the possibility of solid-solution effects even further.

A concern, with firing B_2O_3-containing compacts at high temperature, is its loss due to volatilization. It has already been shown that the weight loss of a pure B_2O_3 sample is 7% after 1000 h at 730 °C [27] and also that a compact of composition 60.9 wt % ZnO–39.1 wt % B_2O_3 loses approximately 6% after firing for 80 h at 950 °C [28]. However, in the present investigation, very few compacts contained 39% B_2O_3 or were fired for longer than 80 h, and in these circumstances it is felt that B_2O_3 loss would be unlikely to invalidate the proposed phase diagram. However, the interpretation of the X-ray powder patterns show that there was undoubtedly some B_2O_3 loss in some compacts (namely nos. 17, 18 and 21).

Comparison of the present investigation with that of Harrison and Hummel [2] reveals several differences. The most obvious is the change in position of the various binary tie lines. This is inevitable; Harrison and Hummel [2] naturally assumed that the then existing binary phase diagrams were correct and as they proved to be incorrect, the positions of the various tie lines had to be adjusted.

Both studies revealed the existence of a ternary phase; however, Harrison and Hummel [2] place this phase at a composition of $CdO \cdot 2ZnO \cdot B_2O_3$ while the present investigation places it at a composition of $3CdO \cdot 3ZnO \cdot 2B_2O_3$. This is not surprising; there was no discernible difference between the X-ray powder patterns from both these compositions (excepting that one included a small amount of zinc oxide). There are slight differences between the X-ray patterns obtained for $3CdO \cdot 3ZnO \cdot 2B_2O_3$ in the present investigation and for $2CdO \cdot ZnO \cdot B_2O_3$ obtained by Harrison and Hummel [2], the most obvious being the loss of some of the weak lines in the present work. It is noticeable that some of these are close to the strongest lines of α-$3ZnO \cdot B_2O_3$ (for example 0.339, 0.323, 0.311 and 0.251 nm).

The evidence for the existence of $3CdO \cdot 3ZnO \cdot 2B_2O_3$ rather than $CdO \cdot 2ZnO \cdot B_2O_3$ comes from the interpretation of the patterns of neighbouring compacts; that there is a tie line from $4ZnO \cdot 3B_2O_3$ to $3CdO.3ZnO \cdot 2B_2O_3$ (compacts 17 and 18) and not to $CdO \cdot 2ZnO \cdot B_2O_3$, and from ZnO to $3CdO \cdot 3ZnO \cdot 2B_2O_3$ and not to $CdO \cdot 2ZnO \cdot B_2O_3$.

Harrison and Hummel [3] prepared relatively few compacts in the region of the equilibrium system surrounding $CdO \cdot 2ZnO \cdot B_2O_3$ and $3CdO \cdot 3ZnO \cdot 2B_2O_3$ and in view of the fact that the patterns from these compositions are indistinguishable, this could easily account for the difference in the interpretation of the phase equilibrium diagram.

Harrison and Hummel [3] claim that there is another ternary phase in the triangle $3CdO \cdot B_2O_3$–$CdO \cdot 2ZnO \cdot B_2O_3$–ZnO but the exact composition is not discernible because of the extensive solubility of $3CdO \cdot B_2O_3$ and ZnO in $CdO \cdot 2ZnO \cdot B_2O_3$.

Unfortunately, they do not give any evidence for the existence of this phase. They do not give a phase analysis for any of their compacts nor do they give an X-ray pattern nor melting point determination to support their view. In their phase diagram they tentatively place three tie lines which, if accurate, suggest a ternary phase of approximately composition 52% CdO–35% ZnO–13% B_2O_3. In the present work, one composition (no. 44) was near this composition, and from its X-ray powder diagram, there was no evidence of the existence of another phase at the present investigation temperature, 850 °C. This, coupled with the fact both ZnO and β-$3CdO \cdot B_2O_3$ were found in all compacts, except one, in this compatibility triangle, does not support the assertion that there is "extensive solubility of $3CdO \cdot B_2O_3$ and ZnO in $2ZnO \cdot CdO \cdot B_2O_3$" [2]. The exception (no. 42) theoretically should contain 5.52% $3CdO \cdot B_2O_3$, an amount which was probably too small to detect.

The third ternary phase reported by Harrison and Hummel [2], $2CdO \cdot 5ZnO \cdot 2B_2O_3$, melts at 797 ± 3 °C and so would be liquid during the present investigation.

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