Phase equilibria in the system CdO-B$_2$O$_3$-GeO$_2$ at 800°C

A. WHITAKER, M. G. PIKE
Department of Physics, Brunel University, Uxbridge, Middlesex, UK

Phase equilibria in the system CdO−B$_2$O$_3$−GeO$_2$ were investigated at 800° C using X-ray powder diffraction techniques. The binary phases reported previously as produced by solid-state reactions were confirmed and, in addition, a new one CdO·2GeO$_2$ was found. The ternary phase diagram was solved and a new phase CdO·B$_2$O$_3$·GeO$_2$ was discovered. X-ray powder data are given for both these new phases. Solid solution effects were investigated for the primary and binary phases by comparison of patterns; no solid solutions were detected. The relationship of the phase diagram to the composition of photoconductive oxide glasses is discusssed in the light of previous suggestions made of possible mechanisms responsible for the photoelectric effects.

1. Introduction

The existence of electronic conduction in glasses containing a variable valency ion has been demonstrated by several authors [1–4]. More recently Strickler and Roy [5] have found a new family of photoconducting oxide glassy materials containing no variable valency ions. Their study was limited to systems capable of yielding glasses with a high concentration of heavy metal oxide, this being one of the requirements for Goodenough's hypothesis [6] of conduction in certain metal oxides. Investigation showed that the highest photocurrents were obtained from compositions grouped around the general formula 65 mol % MO−20 mol % R$_2$O$_3$−15 mol % XO$_2$ and in particular from the systems CdO−B$_2$O$_3$−SiO$_2$ and CdO−B$_2$O$_3$−GeO$_2$. Electron microscope studies [5, 7] showed that the glasses examined had a diphasic nature. Čáslavská, Strickler and Roy [8] attempted to optimize the photoconductivity in the system CdO−B$_2$O$_3$−SiO$_2$ by adding small percentages (by weight) of cadmium oxide to compositions of general formula given above. Having found the most photoconducting glass in this system, they proceeded to make the equivalent glass in the CdO−B$_2$O$_3$−GeO$_2$ system. This corresponded to a composition of 77.59 wt% CdO−7.91 wt% B$_2$O$_3$−14.50 wt% GeO$_2$; comparing glass of this composition with the equivalent composition in the CdO−B$_2$O$_3$−

SiO$_2$ system they found that the former gave a better photoconductive response and also the spectral response was in the visual instead of the near ultra-violet region of the spectrum. They then postulated two possible hypotheses and at the same time determine the complete phase diagram at 800° C. The phase diagram CdO−B$_2$O$_3$−SiO$_2$ has already been studied at 800° C [9], and two more hypotheses were suggested to explain the results.

1.1. Previous work

The ternary system has not been investigated at any temperature but some data exist for two of the binary systems concerned.

The CdO−B$_2$O$_3$ system has been discussed in some detail in a previous paper [9] in which it was concluded that the only cadmium borates which exist are CdO·2B$_2$O$_3$, 2CdO·B$_2$O$_3$ and 3CdO·B$_2$O$_3$.

Although the CdO−GeO$_2$ phase equilibrium diagram has not been determined, there have been several reports of work completed in this system. The first appears to be that due to Ludekens [10] who attempted to prepare 2CdO·GeO$_2$ and CdO·GeO$_2$ by solid-state reactions. He reported an X-ray powder pattern of the former but the latter was impossible to synthesize in the solid state, the reaction at the composition CdO·GeO$_2$

producing $2CdO \cdot GeO_2$ and GeO_2 (hexagonal, α-quartz form). Tarte [11] confirmed the existence of this form of $2CdO \cdot GeO_2$ and showed that it had the olivine structure. Prewitt and Sleight [12] demonstrated the existence of a high pressure form of $CdO \cdot GeO_2$, this has the garnet structure and exists at 65 kilobars. It was prepared in the solid state.

Crystallization has been studied in the $Na_2O-CdO-GeO_2-H_2O$ system under hydrothermal conditions [13], at a working temperature of 450° and 900 to 1200 atm. In the absence of any sodium oxide, it was found that the stable phases were GeO_2 (tetragonal, rutile form), $CdO \cdot 2GeO_2$ and $2CdO \cdot GeO_2$. However, in 2 to 40 wt % aqueous sodium hydroxide solutions $CdO \cdot GeO_2$ could be formed but not at a $CdO : GeO_2$ ratio of 1:1, at which ratio $2CdO \cdot GeO_2$ was obtained. This was attributed to the different solubilities of the original oxides. X-ray powder diffraction patterns are given for all three cadmium germanates. The pattern for $2CdO \cdot GeO_2$ agrees with that reported previously [10, 11], while that for $CdO \cdot GeO_2$ must be suspect as in a subsequent paper [14] it is attributed to the composition $2CdO \cdot 3GeO_2 \cdot NaOH$.

Finally a study of the hydrothermal crystallisation of cadmium germanates [14] has been made. The systems studied were $CdO-GeO_2-H_2O$, $CdO-GeO_2-NaOH-H_2O$ and $CdO-GeO_2-NaCl-H_2O$. The variable parameters were the temeprature, T, the ratio $CdO : GeO_2$, N, and concentration of the solvent, c. The ranges of variation of the parameters were $T = 300$ to $500^\circ C$, N 1:6 to 6:1 and c (NaOH) 0 to 60 wt %. The pressure was kept constant but the value is not given. In the presence of pure water two cadmium germanates were reported; $2CdO \cdot GeO_2$, which is identical to that reported previously [10, 11, 13] and $CdO \cdot GeO_2$ which is not that reported previously [13]. In the presence of sodium ions, but neutral pH, two other cadmium germanates were found; $CdO \cdot 2GeO_2$ which was reported previously [13] and $2CdO \cdot 3GeO_2$. Of these two phases only the former was found to exist in alkali solutions. As already mentioned, the pattern previously reported [13] for $CdO \cdot GeO_2$ was now attributed to $2CdO \cdot 3GeO_2 \cdot NaOH$.

Thus, summarizing the information on cadmium germanates, we have that $2CdO \cdot GeO_2$ may be made in the solid state [10, 11] and that it occurs at the composition of $CdO \cdot GeO_2$ [10]. Under conditions of hydrothermal recrystallization the following germanates may also exist $CdO \cdot GeO_2$ [14], $CdO \cdot 2GeO_2$ [14] and $2CdO \cdot 3GeO_2$ [14] but the last two only exist in the presence of sodium ions and the last one not even then if the solution is alkali [14]. There would appear to be no evidence that these may be formed as a result of solid-state reactions.

There would appear to be no information available for the system $B_2O_3-GeO_2$.

Because of the manner in which the investigation was carried out, it is worth noting that a powder pattern has been reported for $Li_2O \cdot 7GeO_2$ [15].

X-ray powder diffraction data exist in the X-ray Powder Data File for the primary oxides in this system. However, since the melting point of boric oxide is $450^\circ C$ [16] it is a liquid at the investigating temperature.

2. Experimental

The investigation was started by preparing the binary compounds and by examining compacts in the boric oxide–germanium dioxide system. During the course of the work on the cadmium oxide–germanium dioxide system it was found that even after firing times of the order of 300 hours, phase equilibrium was not obtained, because of this 3 % by weight of lithium fluoride was added to all compacts to act as a mineralizer. The result of this was to reduce firing times to 90 to 120 hours.

The starting materials were: cadmium oxide, a Griffin certified reagent (not less than 99 % pure), ANALAR boric acid (not less than 99.5 % pure), germanium dioxide (Koch–Light Labs Ltd 99.999 % pure) and ANALAR lithium fluoride (not less than 98 % pure). Quantities of cadmium oxide were kept in the furnace at $800^\circ C$ to drive off any water; it was only removed and allowed to cool ready for weighing when compacts were being prepared. The amounts weighed were such as to give one gram compacts after firing.

The compacts with high boric acid content were prefired. For these the appropriate quantities were mixed, ground to a fine powder under acetone and pressed for five minutes in a $\frac{1}{2}$ in diameter steel die at $25\,000$ lbs in^{-2}. No binder was used. The compacts were then fired at $400^\circ C$ for two or three hours, removed, reground and repressed for the final firing. Compacts with low boric acid content did not require prefiring.

Both prefiring and firing were carried out in air with the compacts in platinum boats. The

temperature of firing was controlled at $800 \pm 5°C$ and the specimens air quenched. The firing times were a minimum of 90 hours and all compacts for which results are reported in Table II were fired for at least this length of time.

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

3. Results
3.1. Cadmium oxide–boric oxide binary system
3.1.1. $CdO \cdot 2B_2O_3$
It proved impossible to produce a pattern of this phase alone at the nominal composition; there was always a trace of $2CdO \cdot B_2O_3$ present, presumably this is due to loss of boric oxide on firing [17]. Allowing for this, the pattern agrees with that reported by Hand and Krogh-Moe [18]

3.1.2. $2CdO \cdot B_2O_3$
The present data agree with that of Hand and Korgh-Moe [18].

3.1.3. $3CdO \cdot B_2O_3$
The pattern obtained was not identical to either that of Subbarao and Hummel [19] for the β-form or that of Hart and Steward [20]. It fits the latter pattern better at low diffraction angles but contains a few extra weak lines between 1.86 Å and 2.38 Å, these were not obtained by Hart and Steward [20] but were by Subbarao and Hummel [19]. It was particularly noticeable with this sample that the addition of 3% lithium fluoride improved crystallization, but in none of the cadmium borates were any extra powder lines detected.

3.2. Cadmium oxide–germanium dioxide binary system
Twelve compacts (which included 3% lithium fluoride) were made in this binary system. The various patterns could be accounted for by combinations of cadmium oxide, $2CdO \cdot GeO_2$, $CdO \cdot 2GeO_2$ germanium dioxide (rutile form) and $Li_2O \cdot 7GeO_2$.

3.2.1. $2CdO \cdot GeO_2$
The data agrees with that reported previously [10, 11, 13, 14].

3.2.2. $CdO \cdot 2GeO_2$
This data does not agree with that reported previously [13, 14]. It is a new phase and its powder data is given in Table I.

There were several effects due to the addition of lithium fluoride, one was the considerably reduced firing times for equilibrium, a second was the formation of the tetragonal rutile form of germanium dioxide (without lithium fluoride the hexagonal α-quartz form was obtained) and thirdly, at high concentrations of germanium dioxide, the formation of $Li_2O \cdot 7GeO_2$ was found. The effect of lithium fluoride on this transition of germanium dioxide has been reported previously [21].

TABLE I X-ray powder diffraction data for the new phases $CdO \cdot 2GeO_2$ and $CdO \cdot B_2O_3 \cdot GeO_2$

$CdO \cdot 2GeO_2$				$CdO \cdot B_2O_3 \cdot GeO_2$			
d	I	d	I	d	I	d	I
4.96	14	1.658	35	3.49	26	1.625	48
4.63	20	1.636	14	3.09	46	1.616	46
4.28	9	1.613	33	3.01	36	1.582	10
3.62	17	1.597	8	2.960	35	1.568	33
3.42	23	1.563	58	2.909	30	1.551	35
3.33	27	1.552	100	2.852	100	1.530	21
3.26	35	1.531	36	2.811	46	1.493	20
3.17	35	1.515	27	2.704	13	1.465	24
3.09	70	1.500	48	2.629	5	1.425	31
2.821	67	1.465	24	2.547	5	1.381	26
2.749	65	1.433	19	2.511	38	1.357	17
2.721	52	1.420	15	2.483	30	1.332	59
2.649	66	1.408	38	2.438	29	1.310	12
2.594	74	1.396	52	2.380	11	1.283	20
2.535	12	1.370	9	2.343	24	1.259	16
2.504	46	1.343	25	2.232	8	1.234	24
2.476	7	1.327	22	2.166	29	1.222	19
2.424	12	1.311	21	2.102	25	1.205	17
2.397	20	1.291	15	2.088	31	1.186	26
2.324	6	1.256	32	1.840	53	1.172	22
2.274	36	1.238	32	1.830	57	1.161	37
2.249	35	1.214	30	1.790	21	1.143	14
2.216	37	1.193	27	1.751	13	1.129	12
2.162	26	1.184	23	1.724	28	1.111	29
2.080	8	1.175	19	1.689	44	1.088	21
1.975	34	1.156	15	1.664	21	1.080	21
1.949	27	1.148	20				
1.914	16	1.130	31				
1.881	17	1.118	51				
1.861	25	1.106	9				
1.816	30	1.096	8				
1.798	23	1.086	61				
1.777	25	1.077	25				
1.744	39	1.065	19				
1.712	16	1.048	37				
1.674	58	1.035	8				
		1.022	8				

At a composition of $CdO \cdot GeO_2$, without the addition of lithium fluoride, the phases detected by X-ray analysis were $2CdO \cdot GeO_2$ and germanium dioxide (α-quartz form) after over 260 h firing. This confirms Ludekens observation [10].

3.3. Boric oxide—germanium dioxide binary system

Binary compacts were prepared with and without the addition of lithium fluoride. They indicated that there was no intermediate phase formed. The tetragonal rutile form of germanium dioxide seems to be stabilized by the addition of boric oxide although the compact with the highest germanium

dioxide content contained both the rutile and α-quartz forms. The addition of 3% lithium fluoride caused two of the compacts to be better crystalline (the third was amorphous in both cases) and in addition further stabilized the rutile form of germanium dioxide so that it was the only form detected in these specimens.

3.4 Thermal equilibrium diagram

During the course of the investigation into the thermal equilibrium diagram, eighteen binary and forty-one ternary compacts were made. For the successful interpretation of the X-ray patterns it was necessary to postulate not only the binary

TABLE II Specimens prepared, chemical composition and X-ray analysis (all compositions contain an extra 3% lithium fluoride)

Specimen no. or compound	Chemical composition (weight percent)			Phase analyses		
	CdO	B_2O_3	GeO_2	Major	Minor	Trace
$3CdO \cdot B_2O_3$	84.7	15.3		β-$3CdO \cdot B_2O_3$		
$2CdO \cdot B_2O_3$	79.0	21.0		$2CdO \cdot B_2O_3$		
$CdO \cdot 2B_2O_3$	48.0	52.0		$CdO \cdot 2B_2O_3$		$2CdO \cdot B_2O_3$
$7CdO \cdot GeO_2$	81.1		18.9	CdO	$2CdO \cdot GeO_2$	
$3CdO \cdot GeO_2$	78.6		21.4	CdO	$2CdO \cdot GeO_2$	
$5CdO \cdot 2GeO_2$	75.5		24.5	$2CdO \cdot GeO_2$	CdO	
$2CdO \cdot GeO_2$	71.1		28.9	$2CdO \cdot GeO_2$		
$3CdO \cdot 2GeO_2$	64.9		35.2	$2CdO \cdot GeO_2$		
$CdO \cdot GeO_2$	55.1		44.9	$2CdO \cdot GeO_2$	$CdO \cdot 2GeO_2$	
$2CdO \cdot 3GeO_2$	45.0		55.0	$CdO \cdot 2GeO_2$	$2CdO \cdot GeO_2$	
$CdO \cdot 2GeO_2$	38.0		62.0	$CdO \cdot 2GeO_2$		
$CdO \cdot 3GeO_2$	29.0		71.0	$CdO \cdot 2GeO_2$	GeO_2 (tetragonal) + $Li_2O \cdot 7GeO_2$	
$CdO \cdot 4GeO_2$	23.5		76.5	$CdO \cdot 2GeO_2$	GeO_2 (tetragonal) + $Li_2O \cdot 7GeO_2$	
$CdO \cdot 9GeO_2$	12.0		88.0	GeO_2 (tetragonal)	$Li_2O \cdot 7GeO_2$	$CdO \cdot 2GeO_2$
1	5.0		95.0	GeO_2 (tetragonal)	$Li_2O \cdot 7GeO_2$	
2		18.2	81.8	GeO_2 (tetragonal)		
3		40.0	60.0	GeO_2 (tetragonal)		
4		66.6	33.4	amorphous		
5	15.0	40.0	45.0	GeO_2 (tetragonal)	$CdO \cdot 2B_2O_3$	$Li_2O \cdot 7GeO_2$
6	22.0	60.0	18.0	$CdO \cdot 2B_2O_3$		GeO_2 (tetragonal)
7	12.0	13.0	75.0	GeO_2 (tetragonal)		$Li_2O \cdot 7GeO_2$
8	24.0	26.0	50.0	GeO_2 (tetragonal)	$CdO \cdot 2B_2O_3$	$Li_2O \cdot 7GeO_2$
9	34.5	37.4	28.1	$CdO \cdot 2B_2O_3$	GeO_2 (tetragonal)	
10	28.0	22.0	50.0	$CdO \cdot B_2O_3 \cdot GeO_2$	GeO_2 (tetragonal)	
11	35.0	30.0	35.0	$CdO \cdot B_2O_3 \cdot GeO_2$	$CdO \cdot 2B_2O_3$	GeO_2 (tetragonal)
12	20.0	10.0	70.0	GeO_2 (tetragonal)	$CdO \cdot B_2O_3 \cdot GeO_2$	$Li_2O \cdot 7GeO_2$
13	31.5	17.1	51.4	$CdO \cdot B_2O_3 \cdot GeO_2$	GeO_2 (tetragonal)	
14	30.0	5.0	65.0	$CdO \cdot 2GeO_2$	GeO_2 (tetragonal)	$CdO \cdot B_2O_3 \cdot GeO_2$
15	32.0	12.0	56.0	$CdO \cdot B_2O_3 \cdot GeO_2$	GeO_2 (tetragonal)	$CdO \cdot 2GeO_2$
16	40.0	12.0	48.0	$CdO \cdot B_2O_3 \cdot GeO_2$	$CdO \cdot 2GeO_2$	
17	42.4	23.0	34.6	$CdO \cdot B_2O_3 \cdot GeO_2$		
18	43.0	27.0	30.0	$CdO \cdot B_2O_2 \cdot GeO_2$		$CdO \cdot 2B_2O_3$
19	43.0	32.0	25.0	$CdO \cdot B_2O_3 \cdot GeO_2$	$CdO \cdot 2B_2O_3$	
20	45.0	38.0	17.0	$CdO \cdot 2B_2O_3$ + $CdO \cdot B_2O_3 \cdot GeO_2$		

Table II continued

phase $CdO \cdot 2GeO_2$ but a ternary phase $CdO \cdot B_2O_3 \cdot GeO_2$. Table I gives X-ray powder data for both of these. These data was obtained with Co K_α radiation to improve the resolution of the patterns, the resulting films were then photometered. Table II lists the compacts, compositions and interpretation of the X-ray diffraction patterns. All these compacts include 3% lithium fluoride. The subsolidus compatibility triangles at 800° C consistent with these results are shown in Fig. 1.

X-ray powder patterns containing binary phases were compared and from this there appeared to be no evidence of solid solution effects. Unfortunately most of the patterns lacked sharp lines in the back reflection region; because of this, the limit of detectability is poor and the existence of slight solubility cannot be discounted.

Boric oxide was not detected by X-ray diffraction in those compacts in which the chemical composition indicated that it should be present. This is no doubt due to its glassy nature after quenching; it melts at 450° C [16] and Berger [22] has reported that it is very difficult to crystallize.

4. Discussion

The lack of solid solution, mentioned in the previous section, is not unexpected. The published binary phase diagram of cadmium oxide–boric oxide suggests that there is no solid solution in this system. In addition Van Vlack [23] points out that, in close-packed crystal structures, 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. Van Vlack [24] gives the ionic radii for six-fold coordination as Cd^{2+} 1.03 Å, B^{3+} 0.25 Å and Ge^{4+} 0.53 Å, hence the three ions have widely different radii. In addition, the three ions have different valencies and the three oxides different structures, thus it can be seen that the conditions are not favourable for the formation of solid solution.

A noticeable aspect of the work is that $2CdO \cdot B_2O_3 - 2CdO \cdot GeO_2$ is a stable tie line and

TABLE II continued

| Specimen no. or compound	Chemical composition (weight percent)			Phase analyses		
	CdO	B_2O_3	GeO_2	Major	Minor	Trace
21	50.0	9.0	41.0	$CdO \cdot 2GeO_2$	$CdO \cdot B_2O_3 \cdot GeO_2$ + $2CdO \cdot GeO_2$	
22	53.5	9.6	36.9	$2CdO \cdot GeO_2$	$CdO \cdot B_2O_3 \cdot GeO_2$ + $CdO \cdot 2GeO_2$	
23	52.9	14.2	32.9	$CdO \cdot B_2O_3 \cdot GeO_2$	$2CdO \cdot GeO_2$	
24	60.0	10.0	30.0	$2CdO \cdot B_2O_3$	$CdO \cdot B_2O_3 \cdot GeO_2$	
25	51.5	25.0	23.5	$CdO \cdot B_2O_3 \cdot GeO_2$	$CdO \cdot 2GeO_2$	
26	50.0	26.5	13.5	$CdO \cdot 2B_2O_3$		
27	68.1	6.9	25.0	$2CdO \cdot GeO_2$		
28	66.7	10.3	23.0	$2CdO \cdot GeO_2$		
29	65.9	11.8	22.3	$2CdO \cdot GeO_2$		
30	63.5	17.0	19.5	$2CdO \cdot GeO_2$		
31	60.0	25.0	15.0	$2CdO \cdot GeO_2$		
32	55.0	36.0	9.0	$CdO \cdot 2B_2O_3$		$2CdO \cdot GeO_2$
33	70.0	15.0	15.0	$2CdO \cdot GeO_2$	$2CdO \cdot B_2O_3$	
34	70.0	25.0	5.0	$2CdO \cdot B_2O_3$	$2CdO \cdot GeO_2$	
35	60.0	35.0	5.0	$CdO \cdot 2B_2O_3$		
36	73.0	5.0	22.0	$2CdO \cdot GeO_2$		
37	74.7	10.0	15.3	$2CdO \cdot GeO_2$		$2CdO \cdot B_2O_3$
38	76.0	14.0	10.0	$2CdO \cdot GeO_2$	$2CdO \cdot B_2O_3$	
39	76.0	9.0	15.0	$2CdO \cdot GeO_2$		$2CdO \cdot B_2O_3$
40	80.0	15.0	5.0	$2CdO \cdot GeO_2$	$3CdO \cdot B_2O_3$	
41	75.2	4.8	20.0	$2CdO \cdot GeO_2$		
42	79.0	9.0	12.0	$2CdO \cdot GeO_2$	$3CdO \cdot B_2O_3$	CdO
43	81.2	11.8	7.0	$3CdO \cdot B_2O_3$	$2CdO \cdot GeO_2$	CdO
44	80.0	5.0	15.0	CdO	$2CdO \cdot GeO_2$	
45	85.0	10.0	5.0	CdO	$3CdO \cdot B_2O_3$	$2CdO \cdot GeO_2$
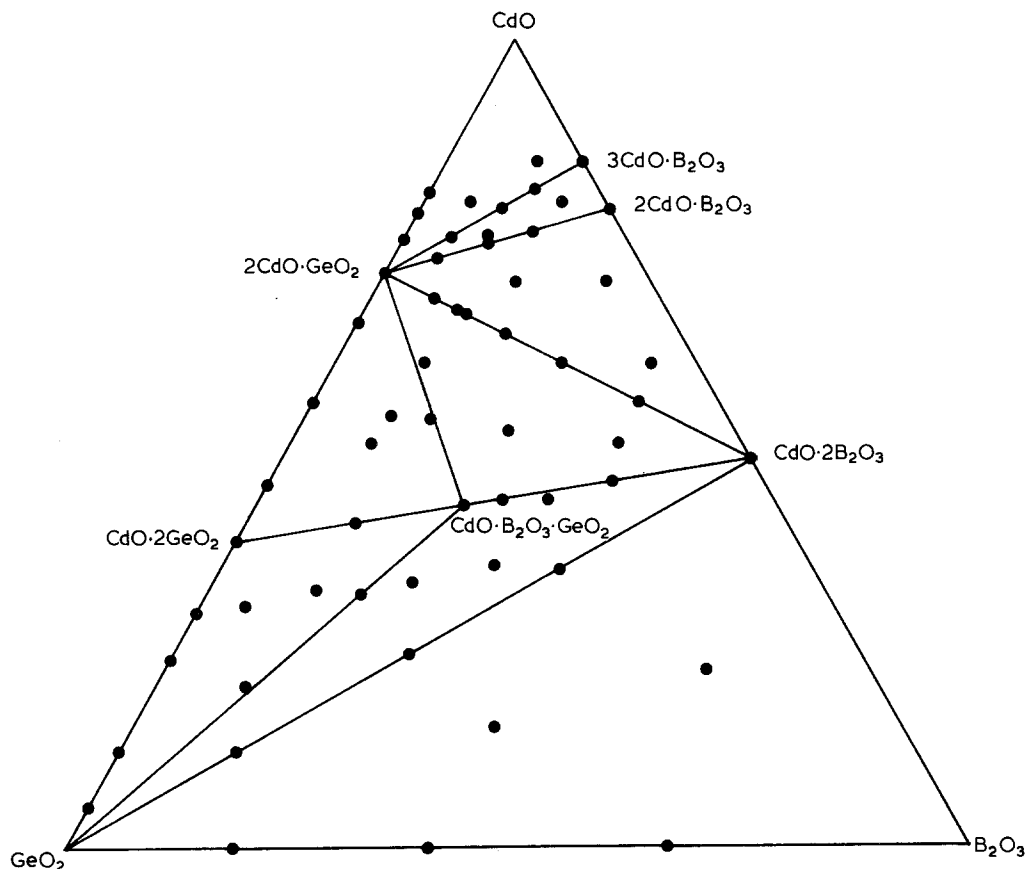
Figure 1 Phase equilibria in the system $CdO-B_2O_3-GeO_2$ at 800° C.

the photoelectric composition lies close to this. Hence, the diphasic glass that has been reported in this region [7] is probably composed of $2CdO \cdot B_2O_3$ and $2CdO \cdot GeO_2$. If homogeneous, then both these glasses are equally rich in CdO and the suggestion [5] that the good photoconductive properties are related to a CdO-rich phase cannot be correct.

Obviously the structure of the glass is important but comparison of the subsolidus phases may give useful information on this.

The crystal structure of $2CdO \cdot B_2O_3$ has not been determined but it has been shown that it is isomorphous with triclinic $2MgO \cdot B_2O_3$ [18], the structure of the latter has been shown to consist of MgO_6 octohedra sharing edges [25] to form infinitely long ribbons of breadth and thickness four and one octohedra, respectively. Using the atomic parameters of $2MgO \cdot B_2O_3$ [25] with the cell parameters of $2CdO \cdot B_2O_3$ [18] indicates that the closest distance of approach of the cadmium ions are the range 3.37 Å to 3.48 Å, with

an average of 3.44 Å. (As crystalline order is destroyed in the glass, the average is probably a more meaningful criterion.) In the case of $2CdO \cdot GeO_2$, again the structure has not been determined but it has been shown that it is a member of the olivine group [11] and this structure has been shown to consist of CdO_6 octohedra sharing edges [25] to form a three-dimensional network. Using the atomic parameters of $2(Fe_{0.1} Mg_{0.9})O \cdot SiO_2$ [26] with the cell paramters of $2CdO \cdot GeO_2$ [11], the closest distances of the cadmium ions are in the range 3.29 to 3.50 Å, with an average 3.43 Å. Thus the average distances are very similar for the two compounds.

According to Goodenough [6] conduction occurs by overlap of the metal d-orbitals or by interaction between a strongly polarizing cation and the oxygen p-orbitals. Furthermore he derived (p. 266) the empirical formulae to define whether overlap occurred; these are

$$R_c(3d) = \{3.05 - 0.03(Z - Z_{Ti}) - 0.04 \, \Delta \, [J(J+1)]\}.$$

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To apply to the 4d series, this should be replaced by

$$R_c(3d) = \{3.05 - 0.03(Z - Z_{Zr}) - 0.04\Delta\,[J(J+1)]\}$$

and $R_c(4d) = R_c(3d) + 0.88\,\text{Å}$.

These formulae give a critical distance of 3.69 Å [5] for the overlap of the d-orbitals and for both $2CdO \cdot B_2O_3$ and $2CdO \cdot GeO_2$ the cadmium–cadmium distances are within this critical distance.

However Goodenough [27] makes two important points; first that his formulae were meant to be applicable to partially filled d-shells, especially at the lighter end of the transition metal series and not to filled 4d shells in cadmium. Secondly, that there is a second explanation, which he feels is more logical, and this is that there is overlap of the cadmium $4d^{10}$ band and oxygen $2p^6$ bands to produce a broad 4d–2p mixed band that supports mobile carriers. If this is the case, then the Cd–O distances are more important than the Cd–Cd distances. In the case of $2CdO \cdot B_2O_3$ there are twelve independent Cd–O distances in the range 2.11 to 2.49 Å, average 2.27 Å, while for $2CdO \cdot GeO_2$ the range of Cd–O distances is 2.25 to 2.41 Å, average 2.31 Å and it is possible that the larger Cd–O distance in $2CdO \cdot GeO_2$ may restrict the movement of carriers through a glassy phase of this composition. In the case of the system $CdO–B_2O_3–SiO_2$ [9] a similar effect was found, i.e. the Cd–O distance in $2CdO \cdot SiO_2$ was larger than in $2CdO \cdot B_2O_3$.

The second suggestion made by Lonsdale and Whitaker [9] is also applicable in the present system. They pointed out that cadmium oxide is composed of CdO_6 octohedra with shared faces and that it is non-stoichiometric. This defect causes it to be a good conductor [28]. They suggest that the same effect may occur in the CdO_6 octohedra in glasses, in which case the high photoconductivity may be due to electrons moving between defect sites.

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