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Phase Equilibria in the System CaO-ZnO-B_2O_3 at 850°C

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Phase equilibria in the system CaO-ZnO-B_2O_3 were investigated at 850° C using X-ray powder diffraction techniques. The binary phases reported previously were confirmed, but no ternary phases were found. Solid solution effects were investigated for the binary phases by comparison of the patterns, whereas for calcium oxide and zinc oxide, accurate lattice parameters were compared. No solid solutions were detected.

1. Introduction

An attempt has been made to determine the phase equilibria in the system CaO-ZnO-B_2O_3 at 850° C.

1.1 Previous Work

The ternary system has not been investigated at any temperature but two of the binary systems have been studied.

By means of heating curves Carlson [1] detected four intermediate phases in the calcium oxide–boric oxide system; $CaO.2B_2O_3$, $CaO.B_2O_3$ $2CaO.B_2O_3$ and $3CaO.B_2O_3$. The presence of these four compounds was confirmed by Fletcher, Stevenson, and Whitaker [2] who also reported X-ray diffraction patterns for the four phases. Their patterns for $CaO.B_2O_3$ and $2CaO.B_2O_3$ do not agree with those given by Hart and Brown [3] for compounds synthesised at 400° C and 500 atm pressure and it was concluded that the latter were high pressure and/or low temperature polymorphs.

The zinc oxide–boric oxide system has been investigated several times, a discussion of the results of these investigations and also of some fresh observations is given in the previous paper [4]. In this it is concluded that the stable phases at 850° C are α-$3ZnO.B_2O_3$ and $4ZnO3B_2O_3$ but $ZnO.2B_2O_3$ also exists at this temperature due to the sluggishness of its decomposition.

There has been no relevant work on the calcium oxide-zinc oxide system and the work of Segnit [5] on the calcium oxide–zinc oxide–silicon dioxide system did not include any results on or near the calcium oxide–zinc oxide system.

X-ray powder diffraction data exist for the primary oxides in this system, i.e. calcium oxide [6], zinc oxide [7] and boric oxide [8]. However, since the melting point of the latter is 450° C [9] 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 calcium oxide–zinc oxide system.

The starting materials were ANALAR calcium carbonate (not less than 99.5% pure), ANALAR zinc oxide (not less than 99.7% pure on the ignited basis) and ANALAR boric acid (not less than 99.5% pure). The zinc oxide was pre-heated at 850° C for at least 1 h in a platinum boat and stored in sealed bottles prior to weighing; the other components were weighed as calcium carbonate and boric acid. The amounts weighed were such as to give 1 g compacts after firing.

The starting materials were prefired. In this the calcium carbonate was decomposed by heating for 20 to 30 min. at 850° C; zinc oxide and/or boric acid was added and the mixture was further heated for 5 min. Boric acid, because of its volatility was not prefired with the calcium carbonate. All prefiring was carried out in platinum boats.

After prefiring, the mixture was ground to a very fine powder, mixed thoroughly and pressed for 5 min. in a $\frac{1}{2}$ in. diameter steel die at a pressure of 25000 lbs/sq in. No binder was used.

The compacts were placed on platinum foils and fired in air, and the temperature of the electrically heated furnace was controlled at

850 ± 5°C. The specimens were air quenched.

After firing for 24 h each compact was ground and a little used as an X-ray powder specimen which was then examined in an 11.46 cm diameter Debye-Scherrer camera using filtered copper radiation. The remainder of the sample was recompacted, refired for 24 h and re-examined. The process was repeated until successive X-ray films appeared identical.

Compacts containing less than 45% calcium oxide reached phase equilibrium in 24 h; those containing 45 to 62% calcium oxide required 48 h; the others required 72 h. These times were used as a guide when firing the ternary compacts.

However, the compact containing only calcium oxide and zinc oxide was fired for considerably longer period (1350 h) in an attempt to insure either reaction or solid solution.

3. Results

3.1. Calcium Oxide–Boric Oxide Binary System

It was confirmed that there were four calcium borates stable at 850°C; namely $CaO.2B_2O_3$, $CaO.B_2O_3$, $2CaO.B_2O_3$ and $3CaO.B_2O_3$. The X-ray powder patterns obtained for these phases agreed with those reported previously [2].

3.2. Zinc Oxide–Boric Oxide Binary System

This system has been discussed in great detail in the previous paper [4], in which it was concluded that the stable zinc borates at 850°C were α-$3ZnO.B_2O_3$ and $4ZnO.3B_2O_3$, but $ZnO.2B_2O_3$ also exists at this temperature due to the sluggishness of the decomposition, The powder patterns obtained in the present investigation were substantially the same as those obtained previously for α-$3ZnO.B_2O_3$ (or α-$5ZnO.2B_2O_3$) [10-12], $4ZnO.2B_2O_3$ (or $ZnO.B_2O_3$) [10-15] and $ZnO.2B_2O_3$ [11, 12].

3.3. Calcium Oxide–Zinc Oxide Binary System

No intermediate phase was detected in this system. Accurate unit cell sizes were obtained by extrapolation against the Nelson-Riley function [16], the extrapolation being carried using a modified version of Wait's programme [17] for the ICT Atlas computer. Comparison of these results with those for the primary phases indicated that there was no detectable solid solution of calcium oxide in zinc oxide or vice versa.

3.4. Ternary Compacts

3.4.1. *Solid solution effects*

X-ray powder patterns containing binary phases were compared, from this comparison there appeared to be no evidence of the existence of solid solution effects. Unfortunately most of the patterns lacked lines in the back reflection region, because of this the limit of detection is poor and the existence of slight solubility cannot be discounted. In the case of calcium oxide and zinc oxide, again extrapolated cell sizes were obtained and again there was no evidence of any solid solution effects.

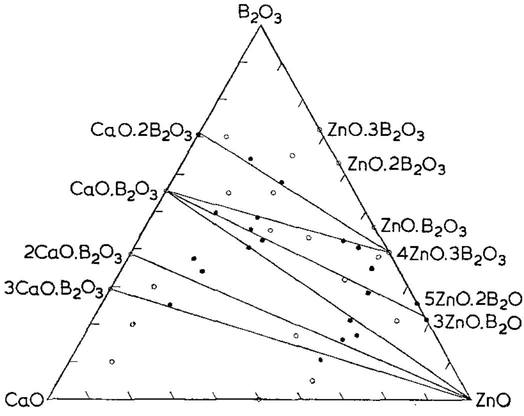

Figure 1 Phase equilibria in the system CaO-ZnO-B_2O_3 at 850°C. Closed circles indicate compacts which were analysed chemically; open circles indicate compacts at nominal chemical composition.

3.4.2. *Phase equilibria diagram*

During the course of the investigation into the phase equilibrium diagram, ten binary and thirty-three ternary compacts were made, of these, three binary and eighteen ternary were chemically analysed. Table I lists the composition of these compacts and the interpretation of the X-ray diffraction patterns. The subsolidus compatibility triangles at 850°C consistent with these results are shown in fig. 1, these are drawn assuming that $ZnO.2B_2O_3$ is not a stable phase at this temperature. As already mentioned some solid solution in the binary phases cannot be discounted, however, the published binary phase diagrams [1, 10] suggest that the extent is very small.

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

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

Specimen No. or compound	Chemical composition wt. %			Phase analyses		
	CaO	ZnO	B_2O_3	Major	Minor	Trace
$CaO.2B_2O_3$*	29.6		70.4	$CaO.2B_2O_3$		
$CaO.B_2O_3$	44.6		55.4	$CaO.B_2O_3$		
$2CaO.B_2O_3$	61.7		38.3	$2CaO.B_2O_3$		
$3CaO.B_2O_3$	70.7		29.3	$3CaO.B_2O_3$		
$ZnO.3B_2O_3$		28.0	72.0	$4ZnO.3B_2O_3$	$ZnO.2B_2O_3$	
$ZnO.2B_2O_3$		36.9	61.1	$4ZnO.3B_2O_3$	$ZnO.2B_2O_3$	
$ZnO.B_2O_3$		53.9	46.1	$4ZnO.3B_2O_3$	$ZnO.2B_2O_3$	α-$3ZnO.B_2O_3$
$4ZnO.3B_2O_3$		60.9	39.1	$4ZnO.3B_2O_3$	$ZnO.2B_2O_3$	α-$3ZnO.B_2O_3$
$5ZnO.2B_2O_3$*		75.4	24.6	α-$3ZnO.B_2O_3$	$4ZnO.3B_2O_3$	
$3ZnO.B_2O_3$		78.6	21.2	α-$3ZnO.B_2O_3$		
1	50	50		ZnO + CaO		
2	80	10	10	CaO	ZnO	$3CaO.B_2O_3$
3	35	60	5	ZnO + CaO		$3CaO.B_2O_3$
4	70	10	20	$3CaO.B_2O_3$	CaO	ZnO
5*	58.9	15.8	25.3	$3CaO.B_2O_3$	ZnO	
6*	30.4	59.3	10.4	ZnO	$3CaO.B_2O_3$	
7	60	10	30	$3CaO.B_2O_3$ + $2CaO.B_2O_3$		ZnO
8	33	50	17	ZnO	$2CaO.B_2O_3$	$3CaO.B_2O_3$
9*	22.6	61.4	15.9	ZnO	$2CaO.B_2O_3$	
10*	47.2	15.7	37.5	$2CaO.B_2O_3$	ZnO + $CaO.B_2O_3$	
11*	46.3	19.2	34.5	$2CaO.B_2O_3$	ZnO + $CaO.B_2O_3$	
12*	18.3	64.6	17.2	ZnO	$2CaO.B_2O_3$ + $CaO.B_2O_3$	
13*	32.9	26.9	40.3	$CaO.B_2O_3$	ZnO	
14*	18.0	60.5	21.1	ZnO	$CaO.B_2O_3$	
15	7	72	21	ZnO + α-$3ZnO.B_2O_3$		
16*	35.7	14.8	49.6	$CaO.B_2O_3$	α-$3ZnO.B_2O_3$	
17*	14.5	26.8	58.1	$CaO.B_2O_3$	α-$3ZnO.B_2O_3$	
18*	28.7	29.1	43.3	$CaO.B_2O_3$	α-$3ZnO.B_2O_3$	ZnO
19	14	54	32	α-$3ZnO.B_2O_3$	$CaO.B_2O_3$	ZnO
20*	10.5	61.6	27.9	α-$3ZnO.B_2O_3$		$CaO.B_2O_3$ + ZnO
21	25	30	45	$4ZnO.3B_2O_3$	$CaO.B_2O_3$ + α-$3ZnO.B_2O_3$	
22	17	40	43	$4ZnO.3B_2O_3$	$CaO.B_2O_3$	$ZnO.2B_2O_3$
23*	6.0	60.3	33.7	$4ZnO.3B_2O_3$	α-$3ZnO.B_2O_3$ + $ZnO.2B_2O_3$	
24	3	59	38	$4ZnO.3B_2O_3$	α-$3ZnO.B_2O_3$ + $ZnO.2B_2O_3$	
25*	26.6	25.1	48.3	$CaO.B_2O_3$ + $4ZnO.3B_2O_3$	$ZnO.2B_2O_3$	
26*	9.7	48.4	42.0	$4ZnO.3B_2O_3$	$ZnO.2B_2O_3$ + $CaO.B_2O_3$	
27*	6.3	53.1	40.3	$4ZnO.3B_2O_3$	$ZnO.2B_2O_3$ + $CaO.B_2O_3$	
28	30	15	55	$4ZnO.3B_2O_3$ + $CaO.B_2O_3$	$CaO.2B_2O_3$	
29	19.5	25.5	55	$4ZnO.3B_2O_3$	$CaO.2B_2O_3$	
30*	20.3	15.3	64.2	$CaO.2B_2O_3$	$4ZnO.3B_2O_3$ + $ZnO.2B_2O_3$	
31*	13.5	28.3	57.9	$4ZnO.3B_2O_3$	$CaO.2B_2O_3$ + $ZnO.2B_2O_3$	
32	23	7	70	$4ZnO.3B_2O_3$	$ZnO.2B_2O_3$ + $CaO.2B_2O_3$	
33	10	25	65	$4ZnO.3B_2O_3$	$ZnO.2B_2O_3$ + $CaO.2B_2O_3$	

*Actual chemical compositions, the remainder are nominal.

after quenching; Berger [8] has reported that it is very difficult to crystallise.

4. Discussion

The lack of solid solution, mentioned in the previous section is not entirely unexpected. Van Vlack [18] 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 substistutional atoms have different valency, or for compounds having different structures.

Van Vlack [19] gives the ionic radii for six-fold co-ordination as Ca^{2+} 1.06Å, Zn^{2+} 0.83Å and B^{3+} 0.25Å, hence the three ions have widely different radii. In addition, the three oxides have different structures, calcium oxide has the sodium chloride structure, zinc oxide the wurzite structure while boric oxide is hexagonal structure built up of two sets of BO_4 tetrahedra forming interconnected spiral chains of two types [8]. Also the boron ion has a different valency to the other two. Thus it can be seen that the conditions are not favourable for the formation of solid solutions.

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