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Temperature Dependence of the Stability of Zinc Borates

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The temperature dependence of the stability of various zinc borates has been investigated in the range 600 to 900°C using X-ray powder diffraction techniques. At low temperatures, 640 to 700°C, the only zinc borates detected are α-$3ZnO.B_2O_3$ and $ZnO.2B_2O_3$; super-position of these patterns accounts for the pattern of α-$ZnO.B_2O_3$ reported previously. At temperatures of 71°C and above, $ZnO.2B_2O_3$ decomposes to $4ZnO.3B_2O_3$ and boric oxide. However, this decomposition is very sluggish and $ZnO.2B_2O_3$ may be detected at temperatures as high as 900°C.

1. Introduction

During an investigation into the phase equilibria in the system CaO-ZnO-B_2O_3 at 850°C using X-ray powder diffraction techniques [1] difficulties were experienced in interpreting the patterns obtained due to the contradictory nature of some of the work on the zinc oxide-boric oxide system. Because of this it was decided to investigate the variously reported zinc borates in the range 600 to 900°C.

1.1. Previous Work

The phase diagram of the zinc oxide-boric oxide system is confused. Ingerson, Morey, and Tuttle [2] investigated the system using a quench technique and reported the existence of two intermediate compounds; $ZnO.B_2O_3$ and $5ZnO.2B_2O_3$. Toropov and Konovalov [3] investigated the system using heating curves and concluded that three phases exist: $ZnO.3B_2O_3$, which dissociated at 900°C, $ZnO.B_2O_3$ and $3ZnO.B_2O_3$. In neither of these investigations were any X-ray powder patterns reported.

Swanson and Tatge [4] reported an X-ray pattern for a cubic form of $ZnO.B_2O_3$, while some time later Harrison and Hummel [5] redetermined the entire system using X-ray, quench and differential thermal analysis techniques. They reported the existence of two phases $ZnO.B_2O_3$ and $5ZnO.2B_2O_3$ and also that both were polymorphic. According to them the low temperature (α) $ZnO.B_2O_3$ inverted sluggishly to the cubic high temperature (β) form at 600°C and very rapidly at 900°C. In the range 650 to 850°C both forms could be obtained together by devitrification of the glass although solid state reactions suggested a smaller co-existence range. In addition, low temperature (α) $5ZnO.2B_2O_3$ inverted rapidly to the high temperature (β) form at 964°C. X-ray powder data are given for these compounds.

Leonov [6, 7] examined this system using X-ray diffraction techniques and concluded that there were two zinc borates: $ZnO.B_2O_3$, for which his pattern agreed with that obtained for the cubic form previously [4, 5] and $3ZnO.B_2O_3$. However, his pattern for the latter does not agree with any reported previously or since. This may be due to the fact that his pattern also contained diffraction lines of ZnO and $ZnO.B_2O_3$ due to incompleteness of the reaction.

Subsequently, Smith, García-Blanco, and Rivoir [8-10] showed from single crystal studies that the cubic compound of empirical formula $ZnO.B_2O_3$ had the composition $4ZnO.3B_2O_3$.

As a result of an investigation using X-ray and differential thermal analysis techniques Bauer [11] reported the existence of three phases: $ZnO.2B_2O_3$ which can be made at 600°C and is stable up to 900°C, but above this temperature it dissociates into $ZnO.B_2O_3$ and B_2O_3; $ZnO.B_2O_3$ and $3ZnO.B_2O_3$. X-ray powder patterns of all three are given and examination of these shows agreement of this pattern of $ZnO.B_2O_3$ with the cubic form reported previously [4-7]. However, he claimed that the low temperature form did not exist but was a mixture of $ZnO.2B_2O_3$ and $3ZnO.B_2O_3$ and, from the results of differential thermal analysis, these reacted to form $ZnO.B_2O_3$ above 880°C. In addition, Bauer's pattern for $3ZnO.B_2O_3$ agrees with Harrison and Hummel's [5] pattern for low (α) $5ZnO.2B_2O_3$, i.e. here Bauer's work did not indicate another phase in the system but a repositioning of one already known. Later, Weir and Schroeder [12] came to the conclusion that this compound was in fact $5ZnO.2B_2O_3$ rather than $3ZnO.B_2O_3$; they also confirmed the existence of $ZnO.2B_2O_3$.

Subsequently, Fayos, García-Blanco, and Rivoir [13] re-examined the system using X-ray diffraction techniques and calcined and melted samples. They reported the existence of three compounds: $ZnO.2B_2O_3$ obtained at 660°C, the X-ray powder diffraction pattern being in substantial agreement with that of Bauer [11]: $4ZnO.3B_2O_3$, the cubic form giving a very similar pattern to those reported previously [3-7, 10] and $3ZnO.B_2O_3$ giving substantially the same pattern as that for α-$5ZnO.2B_2O_3$ by Harrison and Hummel [5] and for $3ZnO.B_2O_3$ by Bauer [11].

García-Blanco and Fayos [14] have since published the crystal structure of $3ZnO.B_2O_3$.

Hence it would appear that three, or maybe four, zinc borates exist: $ZnO.2B_2O_3$ [11-13] which is formed at temperature in the region of 600°C and dissociates at 900°C [11].

$4ZnO.3B_2O_3$ [8-10, 13] (or $ZnO.B_2O_3$ [2-7, 11] According to one investigation [5] this is dimorphic. The low temperature, α-form, converts sluggishly to the cubic high temperature β-form at 600°C and rapidly at 900°C. However, according to another source [11] it is monomorphic; the low temperature form is a mixture of $ZnO.2B_2O_3$ and $3ZnO.B_2O_3$ and these react to form the high temperature form at 880°C.

$3ZnO.B_2O_3$ [3, 6, 7, 11, 13, 14] (or $5ZnO.2B_2O_3$ [2, 4, 12], dimorphous, the transition temperature being 964°C [5], and possibly

$ZnO.3B_2O_3$ [3], which dissociates at 900°C. This has only been reported once and in view of the date of the investigation it would appear unlikely that this phase exists.

2. Experimental

The zinc borates were prepared from ANALAR zinc oxide ($\nless$ 99.7% pure on the ignited basis) and ANALAR boric acid ($\nless$ 99.5% pure). The zinc oxide was pre-heated at not less than 800°C for at least 1 h in a platinum boat and stored in sealed bottles prior to firing. The other component was weighed as boric acid and the total amount weighed such as to give 1 g compacts after firing.

The mixture was prefired at the temperature investigated for 5 min, 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 heated in air on platinum foils, the firing temperature being controlled to $\pm$ 5°, and then air quenched.

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

3. Results

X-ray diffraction patterns of specimens quenched from 850°C are discussed first in detail. Those from specimens of composition $ZnO.3B_2O_3$, $ZnO.2B_2O_3$, $ZnO.B_2O_3$ and $4ZnO.3B_2O_3$ were all very similar and could be interpreted as being due to a mixture of α-$ZnO.B_2O_3$ and β-$ZnO.B_2O_3$ (using the nomenclature of Harrison and Hummel [5]). It was found that the proportion of the higher temperature (β) phase increased with increasing boric oxide content; this was also found at 750, 800 and 900°C. However, the pattern of α-$ZnO.B_2O_3$ could be interpreted as being due to a mixture of α-$3ZnO.B_2O_3$ and $ZnO.2B_2O_3$ as noted by Bauer [11] and this observation was confirmed at other temperatures where so-called α-$ZnO.B_2O_3$ was produced alone. Hence it would appear that α-$ZnO.B_2O_3$ does not exist.

There was no discernible difference between the patterns for β-$ZnO.B_2O_3$ and $4ZnO.3B_2O_3$ but the latter is indicated to be the correct composition by the single crystal studies of Smith, García-Blanco, and Rivoir [8-10] and this was assumed to be correct in the remainder of the investigation.

The powder pattern of a sample of composition $5ZnO.2B_2O_3$ could be interpreted as being due to a mixture of the low temperature (α) form of $5ZnO.2B_2O_3$ or $3ZnO.B_2O_3$ (major phase) and $4ZnO.3B_2O_3$ (minor phase). While a specimen of composition $3ZnO.B_2O_3$ could be

TABLE I X-ray analysis of zinc borate patterns at various temperatures.

Temperature	Composition					
	$ZnO.3B_2O_3$	$ZnO.2B_2O_3$	$ZnO.B_2O_3$	$4ZnO.3B_2O_3$	$5ZnO.2B_2O_3$	$3ZnO.B_2O_3$
900° C	—	$4ZnO.3B_2O_3$ (major) $ZnO.2B_2O_3$ (minor)	—	$4ZnO.3B_2O_3$ (major) $ZnO.2B_2O_3$ (minor) α-$3ZnO.B_2O_3$ (trace)	α-$3ZnO.B_2O_3$ (major) $4ZnO.3B_2O_3$ (minor)	α-$3ZnO.B_2O_3$ (only)
850° C	$4ZnO.3B_2O_3$ (major) $ZnO.2B_2O_3$ (minor)	$4ZnO.3B_2O_3$ (major) $ZnO.2B_2O_3$ (minor)	$4ZnO.3B_2O_3$ (major) $ZnO.2B_2O_3$ (minor) α-$3ZnO.B_2O_3$ (trace)	$4ZnO.3B_2O_3$ (major) $ZnO.2B_2O_3$ (minor) α-$3ZnO.B_2O_3$ (trace)	α-$3ZnO.B_2O_3$ (major) $4ZnO.3B_2O_3$ (minor)	α-$3ZnO.B_2O_3$ (only)
800° C	—	$4ZnO.3B_2O_3$ (major) $ZnO.2B_2O_3$ (major)	—	$4ZnO.3B_2O_3$ (major) $ZnO.2B_2O_3$ (major) α-$3ZnO.B_2O_3$ (minor)	α-$3ZnO.B_2O_3$ (major) $4ZnO.3B_2O_3$ (minor)	α-$3ZnO.B_2O_3$ (only)
750° C	—	$4ZnO.3B_2O_3$ (major) $ZnO.2B_2O_3$ (major)	—	$4ZnO.3B_2O_3$ (major) $ZnO.2B_2O_3$ (major) α-$3ZnO.B_2O_3$ (minor)	α-$3ZnO.B_2O_3$ (major) $4ZnO.3B_2O_3$ (minor)	α-$3ZnO.B_2O_3$ (major) ZnO (trace)
725° C	—	$4ZnO.3B_2O_3$ (major) $ZnO.2B_2O_3$ (major)	—	$4ZnO.3B_2O_3$ (major) $ZnO.2B_2O_3$ (major) α-$3ZnO.B_2O_3$ (minor)	α-$3ZnO.B_2O_3$ (major) $4ZnO.3B_2O_3$ (minor)	α-$3ZnO.B_2O_3$ (major) $4ZnO.3B_2O_3$ (trace)
710° C	—	$4ZnO.3B_2O_3$ (major) $ZnO.2B_2O_3$ (major)	—	$4ZnO.3B_2O_3$ (major) $ZnO.2B_2O_3$ (major) α-$3ZnO.B_2O_3$ (minor)	α-$3ZnO.B_2O_3$ (major) $4ZnO.3B_2O_3$ (minor)	α-$3ZnO.B_2O_3$ (major) ZnO (trace)
700° C	—	$ZnO.2B_2O_3$ (only)	—	$ZnO.2B_2O_3$ (major) α-$3ZnO.B_2O_3$ (minor)	α-$3ZnO.B_2O_3$ (only)	α-$3ZnO.B_2O_3$ (only)
670° C	—	$ZnO.2B_2O_3$ (only)	—	$ZnO.2B_2O_3$ (major) α-$3ZnO.B_2O_3$ (minor)	α-$3ZnO.B_2O_3$ (only)	α-$3ZnO.B_2O_3$ (only)
640° C	—	$ZnO.2B_2O_3$ (only)	—	$ZnO.2B_2O_3$ (major) α-$3ZnO.B_2O_3$ (minor)	α-$3ZnO.B_2O_3$ (only)	α-$3ZnO.B_2O_3$ (major) ZnO (trace)

interpreted as that of $5ZnO.2B_2O_3$ or $3ZnO.B_2O_3$ alone. These two specimens were chemically analysed and in both cases the actual compositions were very close to the theoretical ones, thus confirming the correct composition as $3ZnO.B_2O_3$.

Bearing these conclusions in mind the full interpretation of the powder patterns obtained is given in table I.

Specimens fired at 600°C did not reach equilibrium; the major component of all patterns from specimens fired at this temperature was zinc oxide.

4. Discussion

As already mentioned in the previous section, specimens fired at 600°C did not reach equilibrium; this agrees with Bauer [11] who used activated zinc oxide to obtain a reaction at this temperature.

In the range 640 to 700°C, only patterns corresponding to α-$3ZnO.B_2O_3$ and $ZnO2B_2O_3$ were obtained at equilibrium and it was confirmed that the pattern of "α-$ZnO.B_2O_3$" reported by Harrison and Hummel [5] may be obtained by superimposing these patterns [11].

As the temperature of the reaction was raised $4ZnO.3B_2O_3$ was first detected at a temperature of 710°C and as it was not detected at 700°C, the temperature of formation would appear to be 705 ± 5°C. However, this phase transformation boundary is obtained from the disappearing phase method and so this temperature is probably too high, especially as the reaction to form this phase is sluggish. At temperatures over the range 710 to 800°C specimens of this composition consisted of three phases, α-$3ZnO.B_2O_3$, $4ZnO.3B_2O_3$ and $ZnO.2B_2O_3$, while in the range 850 to 900°C the last two of these were detected. This is due to it being more difficult to detect α-$3ZnO.B_2O_3$ in a mixture of these three phases than to detect $ZnO.2B_2O_3$. However, presumably $4ZnO.3B_2O_3$ is the stable phase of that composition.

Bearing in mind that the patterns of α-$3ZnO.B_2O_3$ and $ZnO.2B_2O_3$ together give the pattern of "α-$ZnO.B_2O_3$" of Harrison and Hummel [5] this confirms their observation that "α-$ZnO.B_2O_3$" and "β-$ZnO.B_2O_3$" co-exist over a range of temperature, although the present work suggests that this observation applies to reactions in the solid state as well as to devitrified glass. In the present work coexistence was found in the range 710 to 900°C. The former temperature agrees very well with the lowest temperature at which they observed $4ZnO.2B_2O_3$ in a solid state reaction (713°C). From an investigation of the rate of inversion from "α-$ZnO.B_2O_3$" to "β-$ZnO.B_2O_3$" they concluded that the actual inversion temperature was 600°C and the present investigation neither confirms nor contradicts this temperature although $4ZnO.3B_2O_3$ was not detected after firing the appropriate composition at 700°C for over 700 h.

Attempts were made to determine whether this temperature could be the transition temperature by taking the specimens fired at 750°C and refiring them at 700°C, but the pattern of $4ZnO.3B_2O_3$ persisted. However, this could be due to the sluggishness of the reaction or simply that the reaction is irreversible.

At the same temperature at which $4ZnO.3B_2O_3$ was first detected in specimens of the appropriate composition it was also detected in compacts of $ZnO.2B_2O_3$, thus suggesting that $ZnO.2B_2O_3$ decomposes to $4ZnO.3B_2O_3$ and B_2O_3 at temperatures of 710°C and above; this contradicts the work of Bauer [11] who states that this compound is stable up to 900°C. This discrepancy is probably due to longer firing times used in the present investigation, certainly $ZnO.2B_2O_3$ may exist up to 900°C due to the sluggishness of its decomposition.

The fact that $ZnO.2B_2O_3$ decomposes at the same temperature at which $4ZnO.3B_2O_3$ is formed suggests that the mechanism of formation of the latter is

$$4(ZnO.2B_2O_3) \rightarrow 4ZnO.3B_2O_3 + 5B_2O_3$$

and $4(\alpha\text{-}3ZnO.B_2O_3) + 5B_2O_3 \rightarrow 3(4ZnO.3B_2O_3)$ rather than

$$\alpha\text{-}3ZnO.B_2O_3 + ZnO.2B_2O_3 \rightarrow 4ZnO.3B_2O_3,$$

as the latter reaction does not explain the simultaneous formation of $4ZnO.3B_2O_3$ at the composition of $ZnO.2B_2O_3$.

5. Conclusions

In the temperature range 640 to 900°C, three zinc borates may be found; α-$3ZnO.B_2O_3$, $4ZnO.3B_2O_3$ and $ZnO.2B_2O_3$. Up to 700°C only α-$3ZnO.B_2O_3$ and $ZnO.2B_2O_3$ are detected while at 710°C $4ZnO.3B_2O_3$ is obtained accompanied by the decomposition of $ZnO.2B_2O_3$. However, the decomposition is very sluggish and all three compounds may co-exist up to 900°C.

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