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Phase equilibria in the system Na_2O–B_2O_3–Ga_2O_3 at 600 °C

A. WHITAKER, R. A. LEIGHTON*
Department of Physics, Brunel University, Uxbridge, Middlesex, UK

Phase equilibria in the system Na_2O–B_2O_3–Ga_2O_3 were investigated at 600 °C using quenching and X-ray powder techniques. Many, but not all the binary phases reported previously were confirmed, no new binary phases were found. The ternary phase diagram was solved and a new phase, $3Na_2O \cdot 4B_2O_3 \cdot Ga_2O_3$, discovered. The X-ray powder data are given for this and also for β-Ga_2O_3 and $Na_2O \cdot Ga_2O_3$. Solid solution effects were investigated for the primary and binary phases by comparison of patterns; no solid solution effects were detected. These results are compared with those of investigations of two pseudo-binaries reported previously, both of which reported other ternary phases which could not be confirmed. Although there is some conflict between the results, it is pointed out that the validity of one pseudo-binary is doubtful due to chemical analysis of one ternary phase, while the report on the other pseudo-binary gives an X-ray powder pattern of a ternary phase which is probably impure.

1. Introduction

Res *et al.* [1] have produced a series of porous glass-ceramics. Essentially the method of production is to replace silica in sodium borosilicate glasses by some other oxide and obtain an homogeneous glass. These glasses of various compositions are heat treated to induce phase separation, then the sodium borate-rich phase is leached out with boiling water to leave a porous matrix of glass or ceramic. It is claimed that this porous matrix often has improved heat and alkali resistance.

One of the systems that Res *et al.* examined was Na_2O–B_2O_3–Ga_2O_3 [1]. In this they concentrated on a region low in Na_2O (5%–20%), high in Ga_2O_3 (30%–75%) with the remainder B_2O_3 (5%–65%). X-ray diffraction analysis of several matrices showed that the only phase identified was β-Ga_2O_3. This seems somewhat inconsistent with previous investigators, as the region covered included the composition $Na_2O \cdot 2B_2O_3 \cdot Ga_2O_3$ which is claimed to exist [2] (the original composition of one of the X-rayed matrices was very similar in composition to this). Because of this it was decided to investigate the sub-solidus phase diagram; a temperature of 600 °C was chosen in an attempt to investigate most of the diagram rather than just the region examined by Res *et al.* [1]. A temperature much larger than this would cause many of the sodium borates to melt, while work on the sodium galliates has been limited to temperatures of 600 °C and above.

1.1. Previous work

The ternary system has not been investigated systematically, but some work has been reported on two pseudo-binary systems. In the pseudo-binary system $Na_2O \cdot B_2O_3$–Ga_2O_3, Rza-Zade *et al.* [3] have reported the existence of two phases $2Na_2O \cdot 2B_2O_3 \cdot Ga_2O_3$ and $Na_2O \cdot B_2O_3 \cdot Ga_2O_3$, which melt at 775 and 890 °C, respectively. X-ray data for both are included. In the other pseudo-binary system, $Na_2O \cdot 2B_2O_3$–Ga_2O_3, Rza-Zade *et al.* [2] report the existence of two more ternary phases, $Na_2O \cdot 2B_2O_3 \cdot Ga_2O_3$, melting at 900 °C and $2Na_2O \cdot 4B_2O_3 \cdot Ga_2O_3$ melting at 610 °C. No X-ray data were given for these.

In addition to this work on the ternary system, data exist for all three binary systems. A great deal of work has been reported on various sodium borates but the earliest comprehensive attempt to study the entire binary was that of Morey and Merwin [4] who reported the existence of five sodium borates: $2Na_2O \cdot B_2O_3$, melting point (m.p.) 625 °C; $Na_2O \cdot 2B_2O_3$, m. p. 966 °C; $Na_2O \cdot 2B_2O_3$, m. p. 742 °C; $Na_2O \cdot 3B_2O_3$, incongruent m. p. 766 °C; and $Na_2O \cdot 4B_2O_3$, m. p. 816 °C. In addition, they noted that there were three polymorphs of $Na_2O \cdot 2B_2O_3$ and two of $Na_2O \cdot 4B_2O_3$. No X-ray data were obtained.

The binary system was subsequently redetermined by Milman and Bouaziz [5] who reported the phase diagram to be much more complex. They reported the existence of 22 sodium borates (including the various polymorphs), eleven new. Their complete list is as given below.

$3Na_2O \cdot B_2O_3$, m. p. 675 °C.
$5Na_2O \cdot 2B_2O_3$, peritectoid at 420 °C.
$2Na_2O \cdot B_2O_3$, m. p. 640 °C.

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* *Present address*: British Aerospace, Six Hills Way, Stevenage, Hertfordshire, UK.

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$3Na_2O \cdot 2B_2O_3$, peritectoid at 575 °C; however, this could not be identified by X-ray diffraction methods.

$Na_2O \cdot B_2O_3$, m. p. 968 °C; according to the reference this compound is dimorphic with a transition temperature of 730 °C, the β-form exists below the temperature but is metastable.

$2Na_2O \cdot 3B_2O_3$, peritectoid at 720 °C, however, the X-ray pattern obtained at this composition was that due to a mixture of β-$Na_2O \cdot B_2O_3$ and α-$Na_2O \cdot 2B_2O_3$.

$Na_2O \cdot 2B_2O_3$, m. p. 743 °C, which is claimed to exist in three forms, α (which is stable), β and γ (which are metastable).

$2Na_2O \cdot 5B_2O_3$, peritectoid at 686 °C.

$Na_2O \cdot 3B_2O_3$, which exists in three forms, γ, the low-temperature form, transforms to β at 580 °C and β to α at 686 °C, α melts incongruently at 765 °C.

$Na_2O \cdot 4B_2O_3$, m. p. 815 °C, for the α form: a second form β also exists but it is metastable. The transformation temperature is 785 °C.

$Na_2O \cdot 5B_2O_3$ incongruent m. p. 785 °C; this also occurs in three polymorphs α, β and γ with transition temperatures 770 and 720 °C. However, the evidence for this compound is from thermal studies. It was not possible to obtain unique X-ray powder data. The powder patterns always gave the patterns of α-$Na_2O \cdot 4B_2O_3$.

$Na_2O \cdot 9B_2O_3$; this occurs in three forms α, β and γ with a transition temperature of 325 °C between γ and β and 643 °C between β and α, the latter melting peritectically at 682 °C. But this compound was difficult to crystallize due to the high B_2O_3 content and very fast quenching techniques were required to avoid the formation of $Na_2O \cdot 4B_2O_3$. The formation of $Na_2O \cdot 9B_2O_3$ required heating for 1 month at 550 °C followed by fast quenching, while heating at 600 °C produced a viscous paste at this composition.

Milman and Bouaziz [5] give X-ray powder patterns for all compounds except $3Na_2O \cdot 2B_2O_3$, $2Na_2O \cdot B_2O_3$ and $Na_2O \cdot 5B_2O_3$ (α, β and γ) because these patterns could not be obtained and also α-$Na_2O \cdot B_2O_3$, α-$Na_2O \cdot 2B_2O_3$ and α and β-$Na_2O \cdot 4B_2O_3$ as these had been reported previously.

Although there has been no other determination of the entire binary system, work has been reported on individual compounds within it; these are now considered in order of increasing boric oxide content.

$5Na_2O \cdot B_2O_3$, m. p. 780 °C. An X-ray pattern corresponding to this composition has been reported [6].

$3Na_2O \cdot B_2O_3$. X-ray powder and single-crystal data have been reported [7]. The powder pattern does not agree with that reported previously by Milman and Bouaziz [5], but in view of the fact that this powder pattern is supported by the single-crystal data (and a successful crystal structure determination is reported), this pattern is to be preferred unless there is more than one polymorph.

$2Na_2O \cdot B_2O_3$. Again both X-ray powder and single-crystal data have been reported [8]. The powder pattern is very similar but not identical to that reported previously [5].

$Na_2O \cdot B_2O_3$. An indexed powder pattern is given for a compound of this composition [9]. The pattern does not agree with that reported by Milman and Bouaziz [5], but as they only reported the pattern of the metastable β-form, this is presumably their α-form.

$Na_2O \cdot 2B_2O_3$. Again an indexed powder pattern is available [10]. Again this does not agree with those reported by Milman and Bouaziz [5] but they only reported the patterns of the metastable β and γ forms; presumably this is their α-form.

$Na_2O \cdot 3B_2O_3$. The crystal structure of the α-form of this compound has been determined [11], from which a calculated powder pattern has been reported [12]. This pattern and that due to Milman and Bouaziz [5] are similar but not identical, both patterns contain lines not in the other. The extra lines in the pattern of Milman and Bouaziz [5] could be due to the β-form and because of this, the calculated pattern is preferred for the α-form. Krogh-Moe has also determined the crystal structure of β-$Na_2O \cdot 3B_2O_3$ [13]. Another pattern for $Na_2O \cdot 3B_2O_3$ has been reported [14], this does not agree with any of the patterns of Milman and Bouaziz [5].

$Na_2O \cdot 4B_2O_3$. As already noted, Milman and Bouaziz [5] reported that there were two forms of this, α (the high-temperature form) and β (metastable) with a transition temperature of 785 °C, but gave no patterns for either of these. However, the crystal structure of the high-temperature form has been determined [15] and a powder pattern calculated from this has been reported [16]. The powder pattern of the another form has also been reported [17]; as the latter was originally due to Bouaziz, presumably this is the β-form of Milman and Bouaziz [5].

Thus, assuming that all previous observations are correct the following sodium borates may be expected at 600 °C.

$5Na_2O \cdot B_2O_3$ [6].

$3Na_2O \cdot B_2O_3$ [5, 7].

$2Na_2O \cdot B_2O_3$ [4, 5, 8].

$Na_2O \cdot B_2O_3$ [4, 5, 9].

$2Na_2O \cdot 3B_2O_3$ [5], but a unique X-ray powder pattern could not be obtained.

$Na_2O \cdot 2B_2O_3$ [4, 5, 10].

$2Na_2O \cdot 5B_2O_3$ [5], again unique X-ray powder patterns have not been reported.

$Na_2O \cdot 3B_2O_3$ [4, 5, 11–14]

$Na_2O \cdot 4B_2O_3$ [4, 5, 15–17].

$Na_2O \cdot 5B_2O_3$ [5], but again unique X-ray powder patterns are not available.

$Na_2O \cdot 9B_2O_3$ [5].

Many of these have more than one polymorph. In addition to which not all the patterns agree for the same compound.

There has been no comprehensive study of the $Na_2O \cdot Ga_2O_3$ binary system, but the following compounds have been reported.

$5Na_2O \cdot Ga_2O_3$. Single crystals of a compound of the composition were obtained [18] by heating the components in a sealed bomb for 1 to 2 days at 600–700 °C. Single-crystal and X-ray powder data were reported. However, another report [19] claims that Na_2O–Ga_2O_3 compositions with greater than 50 mol % Na_2O are hydroscopic.

$Na_2O{\cdot}Ga_2O_3$. X-ray powder data for this compound has been reported [19]. $Na_2O{\cdot}5Ga_2O_3$ or $Na_2O{\cdot}5.2Ga_2O_3$. Two X-ray powder patterns have been reported for this compound [19, 20], at slightly different nominal compositions. The patterns are different.

In the B_2O_3–Ga_2O_3 system, the presence of one compound has been reported, $B_2O_3{\cdot}Ga_2O_3$ [21]. This was synthesized over a range of high pressures, 10–65 kbar, but in addition it was claimed that it could be produced at atmospheric pressure by heating $Ga_2O_3/3H_3BO_3$ at 750 °C for 48–72 h. However, the manner in which this was done was not indicated.

2. Experimental procedure

The investigation commenced with the examination of starting materials and by preparing binary compounds at all compositions reported in the literature.

The starting materials were Analar anhydrous sodium carbonate (not less than 99.9% pure), Analar boric acid (not less than 99.8% pure) and Ga_2O_3 (not less than 99.99% pure). Quantities of anhydrous sodium carbonate and gallium oxide were stored inside a furnace at 400 °C until required for compact preparation. Compacts with a final weight of 1 g were prepared.

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 (~ 0.27 cm) diameter steel die at 5000 $lb\,in^{-2}$ (1 $lb\,in^{-2}$ = 6.8948 × 10^3 Pa) for 5 min. No binder was used. Compacts were then prefired for 1 h at 400 °C (to decompose the boric acid), removed, reground under acetone and repressed for the final firing at 600 °C. Some time into the investigation it was noticed that some of the compacts, after final firing, were porous. This was no doubt due to the $NaCO_3$ breaking down and emitting carbon dioxide. This resulted in a new prefiring arrangement; in this, compacts were prefired for 1 h at 400 °C and then 15 min at 600 °C, then removed, reground under acetone and repressed. This new prefiring arrangement was then applied to all compacts already made.

Both prefiring and firing were carried out in air with the compacts in open platinum boats. The temperature of the final firing was controlled at 600 °C and the specimens air quenched. Various firing times were used and these are given in Table I. 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. Primary compounds

Samples of Na_2CO_3 and Ga_2O_3 were fired at 600 °C. The pattern of Na_2CO_3 agreed with that reported previously [22], while that for Ga_2O_3 agreed with the pattern of β-Ga_2O_3 reported [23]. However, the intensities in the pattern previously reported were visual estimated on a coarse scale (1–10) and a better pattern is reported in Table II. In this case the intensities were obtained from a diffractometer using filterd copper radiation. The pattern was indexed from the single-crystal investigation of Geller [24]. The same procedure could not be applied to B_2O_3 because of its low melting point, which is variously given at 450 °C [25] or 455–475 °C [26].

3.2. Sodium oxide–boric oxide binary system

Twelve compacts were made in this system, eleven corresponding to various composition claimed previously. The following sodium borates were identified.

$3Na_2O{\cdot}B_2O_3$, the pattern for which did not agree with that reported by Milman and Bouaziz [5] but did agree with that due to König and Hoppe [7].

$Na_2O{\cdot}B_2O_3$, the pattern for which agrees with the α-form [9].

$Na_2O{\cdot}2B_2O_3$, the pattern for which agrees with the α-form [10].

$Na_2O{\cdot}3B_2O_3$, the pattern for which agrees with that for the β-form [5].

$Na_2O{\cdot}4B_2O_3$, the pattern for which agrees with that for the α-form [18].

3.3. Sodium oxide–gallium oxide binary system

Although four compacts were prepared in this system only $Na_2O{\cdot}Ga_2O_3$ was found, the pattern obtained agreed with that reported previously [19]. At the nominal composition of $Na_2O{\cdot}Ga_2O_3$ this was found together with a trace of β-Ga_2O_3. The presence of this trace of β-Ga_2O_3 is attributed to a combination of two factors; the loss of Na_2O possibly during firing and the fact that gallium is a relatively good scatterer of X-rays compared with the other atoms. In view of the fact that the reported pattern of $Na_2O{\cdot}Ga_2O_3$ is of poor quality; the minimum interplanar spacing reported is 2.27 Å and the intensities are measured on a coarse scale (1–10), a fresh pattern is given in Table III. This pattern was obtained from a compact made with a 3% excess of Na_2O (compact B) and the pattern obtained from a diffractometer using filter copper radiation. No Na_2CO_3 was detected in this compact.

Of the other two compositions, $5Na_2O{\cdot}Ga_2O_3$ [18] was originally obtained by heating the composition in a sealed bomb. In such conditions the vapour pressure above the reaction could be completely different to that in the present work due to volatilization of Na_2O and may account for the different results. In the case of $Na_2O{\cdot}5Ga_2O_3$ [19], the phase diagram given indicates that it exists down to 600 °C, it is not clear that it was actually obtained at this temperature. Consequently, the compact was heated to 750 °C for 72 h to promote reaction and then heated at 600 °C for a further 6 h before re-analysis. The X-ray pattern showed no change and it was concluded that $Na_2O{\cdot}5Ga_2O_3$ did not exist at 600 °C.

TABLE I Specimens prepared, chemical compositions, firing times and X-ray analysis

Compound or Specimen No.	Chemical composition (wt %)			Firing time (hrs)	Phase analysis		
	Na_2O	B_2O_3	Ga_2O_3		Major	Minor	Trace
Na_2CO_3	100			46	Na_2CO_3		
Ga_2O_3			100	24	β-Ga_2O_3		
“$5Na_2O{\cdot}B_2O_3$”	81.7	18.3		121	$3Na_2O{\cdot}B_2O_3$	Na_2CO_3	
$3Na_2O{\cdot}B_2O_3$	72.8	27.2		45	$3Na_2O{\cdot}B_2O_3$		
“$5Na_2O{\cdot}2B_2O_3$”	69.0	31.0		187	$3Na_2O{\cdot}B_2O_3$		
“$2Na_2O{\cdot}B_2O_3$”	64.0	36.0		143	$3Na_2O{\cdot}B_2O_3$	α-$Na_2O{\cdot}B_2O_3$	
$Na_2O{\cdot}B_2O_3$	47.1	52.9		44	α-$Na_2O{\cdot}B_2O_3$		
“$2Na_2O{\cdot}3B_2O_3$”	37.0	63.0		192	α-$Na_2O{\cdot}B_2O_3$ + α-$Na_2O{\cdot}2B_2O_3$		
$Na_2O{\cdot}2B_2O_3$	30.8	69.2		23	α-$Na_2O{\cdot}2B_2O$		
“$2Na_2O{\cdot}5B_2O_3$”	26.3	73.7		45	β-$Na_2O{\cdot}3B_2O_3$	α-$Na_2O{\cdot}2B_2O_3$	
$Na_2O{\cdot}3B_2O_3$	22.1	77.1		50	β-$Na_2O{\cdot}3B_2O_3$		α-$Na_2O{\cdot}2B_2O_3$
A	20.5	79.5		283	α-$Na_2O{\cdot}4B_2O_3$	β-$Na_2O{\cdot}3B_2O_3$	
$Na_2O{\cdot}4B_2O_3$	18.2	81.8		49	α-$Na_2O{\cdot}4B_2O_3$		
“$Na_2O{\cdot}9B_2O_3$”	9.0	91.0		118	α-$Na_2O{\cdot}4B_2O_3$		
“$5Na_2O{\cdot}Ga_2O_3$”	62.3		37.7	67	$Na_2O{\cdot}Ga_2O_3$ + Na_2CO_3		
B	27.7		72.3	45	$Na_2O{\cdot}Ga_2O_3$		
$Na_2O{\cdot}Ga_2O_3$	24.8		75.2	67	$Na_2O{\cdot}Ga_2O_3$		β-Ga_2O_3
“$Na_2O{\cdot}5Ga_2O_3$”	6.2		93.8	90	β-Ga_2O_3	$Na_2O{\cdot}Ga_2O_3$	
“$3B_2O_3{\cdot}2Ga_2O_3$		35.8	64.2	164	β-Ga_2O_3		
“$B_2O_3{\cdot}Ga_2O_3$”		27.1	72.9	313	β-Ga_2O_3		
1	4.0	39.0	57.0	89	β-Ga_2O_3		α-$Na_2O{\cdot}4B_2O_3$
2	7.0	72.0	21.0	68	β-Ga_2O_3	α-$Na_2O{\cdot}4B_2O_3$	
3	7.0	31.0	62.0	41	β-Ga_2O_3		α-$Na_2O{\cdot}4B_2O_3$
4	11.8	52.5	35.7	90	β-Ga_2O_3	α-$Na_2O{\cdot}4B_2O_3$	
5	15.0	67.0	18.0	20	α-$Na_2O{\cdot}4B_2O_3$	β-Ga_2O_3	
6	16.0	62.0	22.0	118	β-Ga_2O_3 + α-$Na_2O{\cdot}4B_2O_3$		β-$Na_2O{\cdot}3B_2O_3$
7	13.3	46.1	40.6	90	β-Ga_2O_3 + β-$Na_2O{\cdot}3B_2O_3$		
8	19.5	66.9	13.6	22	β-$Na_2O{\cdot}3B_2O_3$	β-Ga_2O_3	
9	18.8	52.8	28.4	71	β-Ga_2O_3 + β-$Na_2O{\cdot}3B_2O_3$	$3Na_2O{\cdot}4B_2O_3{\cdot}Ga_2O_3$	
10	16.0	35.8	48.2	120	β-Ga_2O_3	$3Na_2O{\cdot}4B_2O_3{\cdot}Ga_2O_3$	
11	21.0	47.2	31.8	22	$3Na_2O{\cdot}4B_2O_3{\cdot}Ga_2O_3$	β-Ga_2O_3	β-$Na_2O{\cdot}3B_2O_3$
12	23.2	52.3	24.5	65	$3Na_2O{\cdot}4B_2O_3{\cdot}Ga_2O_3$	β-Ga_2O_3	β-$Na_2O{\cdot}3B_2O_3$
13	25.0	56.1	18.9	69	$3Na_2O{\cdot}4B_2O_3{\cdot}Ga_2O_3$	β-$Na_2O{\cdot}3B_2O_3$	
14	14.0	21.0	65.0	70	β-Ga_2O_3	$3Na_2O{\cdot}4B_2O_3{\cdot}Ga_2O_3$	
15	22.0	33.0	45.0	72	β-Ga_2O_3	$3Na_2O{\cdot}4B_2O_3{\cdot}Ga_2O_3$	
16	19.4	21.8	58.8	94	β-Ga_2O_3	$3Na_2O{\cdot}4B_2O_3{\cdot}Ga_2O_3$ + $Na_2O{\cdot}Ga_2O_3$	
17	24.0	29.0	47.0	90	β-Ga_2O_3 + $3Na_2O{\cdot}4B_2O_3{\cdot}Ga_2O_3$	$Na_2O{\cdot}Ga_2O_3$	
18	24.0	68.5	7.5	68	$3Na_2O{\cdot}4B_2O_3{\cdot}Ga_2O_3$ + β-$Na_2O{\cdot}3B_2O_3$		

Table I (contd.)

19	26.9	52.8	20.3	73	$3Na_2O\cdot4B_2O_3\cdot Ga_2O_3$	$\beta\text{-}Na_2O\cdot3B_2O_3$	
20	27.2	61.1	11.7	69	$3Na_2O\cdot4B_2O_3\cdot Ga_2O_3$	$\beta\text{-}Na_2O\cdot3B_2O_3+\alpha\text{-}Na_2O\cdot2B_2O_3$	
21	29.2	65.8	5.0	141	$\alpha\text{-}Na_2O\cdot2B_2O_3$	$3Na_2O\cdot4B_2O_3\cdot Ga_2O_3+\beta\text{-}Na_2O\cdot3B_2O_3$	
22	26.6	19.9	53.5	118	$Na_2O\cdot Ga_2O_3$		$3Na_2O\cdot4B_2O_3\cdot Ga_2O_3$
23	26.6	22.9	40.5	120	$Na_2O\cdot Ga_2O_3$	$3Na_2O\cdot4B_2O_3\cdot Ga_2O_3$	
24	27.5	30.9	41.6	114	$3Na_2O\cdot4B_2O_3\cdot Ga_2O_3+Na_2O\cdot Ga_2O_3$		$\beta\text{-}Ga_2O_3$
25	28.5	42.7	28.8	117	$3Na_2O\cdot4B_2O_3\cdot Ga_2O_3$		
26	29.1	48.9	22.0	70	$3Na_2O\cdot4B_2O_3\cdot Ga_2O_3$	$\alpha\text{-}Na_2O\cdot2B_2O_3$	
27	29.6	57.4	13.0	94	$3Na_2O\cdot4B_2O_3\cdot Ga_2O_3+\alpha\text{-}Na_2O\cdot2B_2O_3$		
28	36.4	55.4	8.2	71	$\alpha\text{-}Na_2O\cdot B_2O_3+3Na_2O\cdot4B_2O_3\cdot Ga_2O_3$	$\alpha\text{-}Na_2O\cdot2B_2O_3$	
29	30.2	43.7	26.1	73	$3Na_2O\cdot4B_2O_3\cdot Ga_2O_3$	$\alpha\text{-}Na_2O\cdot B_2O_3$	
30	33.9	45.6	20.5	45	$3Na_2O\cdot4B_2O_3\cdot Ga_2O_3+\alpha\text{-}Na_2O\cdot B_2O_3$	$\alpha\text{-}Na_2O\cdot2B_2O_3$	
31	40.0	49.0	11.0	92	$\alpha\text{-}Na_2O\cdot B_2O_3+3Na_2O\cdot4B_2O_3\cdot Ga_2O_3$		$\alpha\text{-}Na_2O\cdot2B_2O_3$
32	31.9	35.9	32.2	48	$3Na_2O\cdot4B_2O_3\cdot Ga_2O_3$	$Na_2O\cdot Ga_2O_3$	$\alpha\text{-}Na_2O\cdot B_2O_3$
33	37.9	42.1	20.0	164	$\alpha\text{-}Na_2O\cdot B_2O_3$	$3Na_2O\cdot4B_2O_3\cdot Ga_2O_3+Na_2O\cdot Ga_2O_3$	
34	32.5	18.3	49.2	43	$Na_2O\cdot Ga_2O_3$		$\alpha\text{-}Na_2O\cdot B_2O_3$
35	36.3	27.2	36.5	64	$Na_2O\cdot Ga_2O_3$	$\alpha\text{-}Na_2O\cdot B_2O_3$	
36	41.0	39.0	20.0	144	$\alpha\text{-}Na_2O\cdot B_2O_3$	$Na_2O\cdot Ga_2O_3$	
37	42.0	15.7	42.3	45	$Na_2O\cdot Ga_2O_3$	$3Na_2O\cdot B_2O_3$	
38	50.0	35.0	15.0	44	$\alpha\text{-}Na_2O\cdot B_2O_3+Na_2O\cdot Ga_2O_3$	$3Na_2O\cdot B_2O_3$	
39	60.0	25.0	15.0	122	$3Na_2O\cdot B_2O_3+Na_2O\cdot Ga_2O_3$		$\alpha\text{-}Na_2O\cdot B_2O_3$
40	47.0	12.0	41.0	142	$Na_2O\cdot Ga_2O_3$		$3Na_2O\cdot B_2O_3$
41	63.0	22.0	15.0	45	$3Na_2O\cdot B_2O_3+Na_2O\cdot Ga_2O_3$		
42	60.0	10.0	30.0	68	$Na_2O\cdot Ga_2O_3$	$3Na_2O\cdot B_2O_3$	
43	75.0	15.0	10.0	67	$3Na_2O\cdot B_2O_3$	$Na_2O\cdot Ga_2O_3$	
44	90.0	5.0	5.0	63	Na_2CO_3	$Na_2O\cdot Ga_2O_3$	

Binary compounds in inverted commas are claimed to exist by other investigators.

TABLE II Powder diffraction data for gallium oxide β-Ga_2O_3

d (Å)	I	hkl	d (Å)	I	hkl
4.69	9	$10\bar{2}$	1.530	10	$10\bar{8}$
3.68	5	102	1.522	21	020
2.973	47	004	1.484	9	017
2.938	53	$10\bar{4}$	1.454	17	$40\bar{2}$
2.827	98	200; $20\bar{2}$	1.442	56	215; $21\bar{7}$
2.678	23	$11\bar{1}$	1.356	9	108; $12\bar{4}$
2.554	100	111	1.339	13	220; $22\bar{2}$
2.406	31	104	1.304	6	402
2.350	54	$11\bar{3}$	1.286	6	124
2.102	9	113; $21\bar{1}$	1.275	2	222
2.027	4	$10\bar{6}$	1.226	3	306
1.982	24	$21\bar{3}$	1.173	2	224
1.875	19	015	1.150	5	$41\bar{7}$
1.840	7	204	1.100	3	$50\bar{6}$
1.796	4	$30\bar{4}$	1.090	4	$32\bar{6}$
1.741	3	106	1.076	5	$12\bar{8}$; $51\bar{1}$
1.684	9	115; 302	1.051	7	$42\bar{2}$
1.630	4	$31\bar{1}$	1.035	8	415; 219; $21\overline{11}$
1.601	24	$31\bar{3}$	1.014	4	128
1.565	7	$30\bar{6}$	0.991	8	131; 0012; 422
1.545	21	311	0.954	3	326

TABLE III Powder data for $Na_2O{\cdot}Ga_2O_3$

d (Å)	I	d (Å)	I
4.40	47	1.808	13
4.29	56	1.718	5
3.390	8	1.687	5
3.027	38	1.639	17
2.969	8	1.599	3
2.823	5	1.567	5
2.753	31	1.527	23
2.656	57	1.511	8
2.632	100	1.492	14
2.553	9	1.452	9
2.447	15	1.441	5
2.376	4	1.408	5
2.353	4	1.394	14
2.317	5	1.332	5
2.275	5	1.312	5
2.192	5	1.147	8
2.039	5	1.071	6
1.994	13	1.051	3
1.912	11	1.031	3

3.4. Boric oxide–gallium oxide binary system

The only phase detected in this system was β-Ga_2O_3. The phase $B_2O_3{\cdot}Ga_2O_3$ reported as existing at 750 °C [21] could not be detected at the present working temperature of 600 °C, neither at the composition $B_2O_3{\cdot}Ga_2O_3$ nor the composition $3B_2O_3{\cdot}2Ga_2O_3$ at which it was found previously [21].

3.5. Ternary thermal equilibrium diagram

During the course of the investigation into the thermal equilibrium diagram, 18 binary and 44 ternary compacts were made, and fired and analysed. Table I lists these compacts, composition, 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 $3Na_2O{\cdot}4B_2O_3{\cdot}Ga_2O_3$. The X-ray pattern for this is given in Table IV. 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, many patterns lacked sharp lines in the back-reflection region and because of 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 binary diagrams of sodium oxide–boric oxide [5] and

TABLE IV Powder data for $3Na_2O{\cdot}4B_2O_3{\cdot}Ga_2O_3$

d (Å)	I	d (Å)	I
6.20	31	2.178	17
5.32	24	2.142	14
5.04	37	2.113	23
4.71	7	2.056	17
4.36	43	2.008	22
4.24	50	1.984	10
4.05	5	1.960	15
3.81	56	1.891	9
3.57	30	1.858	6
3.372	12	1.843	10
3.177	11	1.765	27
3.147	32	1.730	15
3.088	67	1.679	31
3.038	14	1.654	11
2.978	19	1.631	9
2.933	15	1.564	9
2.828	26	1.544	15
2.670	23	1.519	11
2.627	100	1.453	16
2.569	70	1.442	14
2.508	32	1.429	9
2.468	16	1.372	8
2.401	14	1.267	7
2.349	20	1.220	7
2.245	68	1.209	6

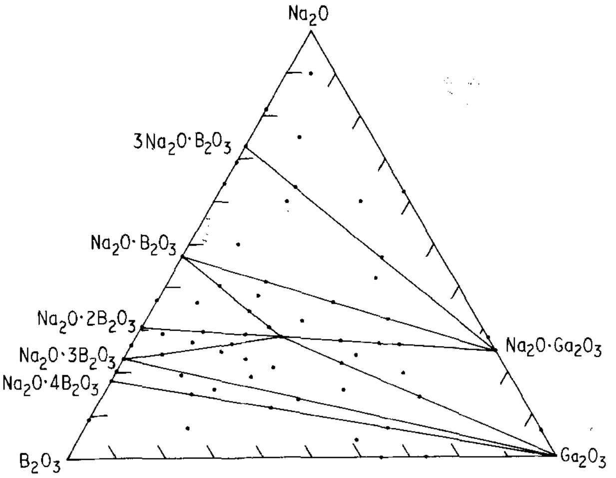

Figure 1 Phase equilibria in the system Na_2O–B_2O_3–Ga_2O_3 at 600 °C.

sodium oxide–gallium oxide [19] suggest that there are no solid solutions in either of them. Van Vlack [27] 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.

Based on the ionic radius of O^{2-} as 1.40 Å for six-fold coordination, Shannon and Prewitt [28] give the ionic radii for six-fold coordination as Na^+ 1.02 Å, B^{3+} as 0.23 Å and Ga^{3+} as 0.62 Å. Thus the three ions have widely different radii and thus the conditions are not favourable for the formation of solid solutions.

A concern with firing at high temperature is the loss of B_2O_3 due to volatilization. However, it has already been shown that the weight loss of a pure B_2O_3 sample is 7% after 1000 h at 730 °C [29], and as in the present investigation, only five compacts were fired for more than 150 h, it would appear that the loss of B_2O_3 would be negligible. Certainly any loss of B_2O_3 would be too small to invalidate the proposed phase diagram.

Previous work on the ternary system, suggested evidence for two ternary compounds on the $Na_2O\cdot 2B_2O_3$–Ga_2O_3 pseudo-binary; $Na_2O\cdot 2B_2O_3\cdot Ga_2O_3$ (compact 10 in the present work) and $2Na_2O\cdot 4B_2O_3\cdot Ga_2O_3$ (compact 11) [2], together with two ternary compounds on the $Na_2O\cdot B_2O_3$–Ga_2O_3 pseudo-binary; $Na_2O\cdot B_2O_3\cdot Ga_2O_3$ (compact 16) and $2Na_2O\cdot 2B_2O_3\cdot Ga_2O_3$ (compact 24) [3]. The X-ray patterns obtained during the present work require one ternary phase, of composition $3Na_2O\cdot 4B_2O_3\cdot Ga_2O_3$ (compact 25) and this corresponds to none of the other four. At first this seems irreconcilable.

Consider the two pseudo-binaries in turn as experimental procedures were different in parts.

In the case of $Na_2O\cdot 2B_2O_3$–Ga_2O_3 [2], charges of sodium tetraborate and gallium oxide were placed in a platinum crucible and melted in an electric furnace at 1000–1100 °C with periodic mixing. The firing time depended on the composition. There is no mention of purity of the initial chemicals or of the actual firing times used, the latter would certainly affect the volatilization of B_2O_3. The fired samples were analysed by differential thermal analysis and according to the paper were confirmed by infrared spectroscopy and density determinations. The chemical analyses of the two ternaries are also given. The phase diagram obtained from the differential thermal analyses indicates peaks at 33 and 50 mol % Ga_2O_3 (corresponding to $2Na_2O\cdot 4B_2O_3\cdot Ga_2O_3$ and $Na_2O\cdot 2B_2O_3\cdot Ga_2O_3$, respectively). The infrared spectra covers the composition range 0–33 mol % and then 100 mol % Ga_2O_3; none are given to confirm the existence of $Na_2O\cdot 2B_2O_3\cdot Ga_2O_3$. The curve of density versus mol % Ga_2O_3 is given and it is pointed out that two maxima on this curve correspond to 33 and 50 mol % Ga_2O_3, i.e. to the maxima on the phase diagrams. However, there is a third maxima on the density composition curve at about 20 mol % Ga_2O_3 and this does not correspond to any feature on the phase diagram. Thus the use of maximum densities can hardly be used as confirmation. Even more interesting are the chemical analyses of the two ternary phases; these are given, together with calculated weight per cent in Table V. It can be seen from this that the chemical composition of the so-called $2Na_2O\cdot 4B_2O_3\cdot Ga_2O_3$ is completely different to that calculated. In fact, it is considerably closer to the ternary $3Na_2O\cdot 4B_2O_3\cdot Ga_2O_3$ found in the present investigation.

In view of the large discrepancy between analysed and calculated chemical compositions, this casts doubts on the validity of the results of the pseudo-binary $Na_2O\cdot 2B_2O_3$–Ga_2O_3 and it also raises the possibility that the previous observations claimed to be on $2Na_2O\cdot 4B_2O_3\cdot Ga_2O_3$ [3] were, in fact, observations of the properties of $3Na_2O\cdot 4B_2O_3\cdot Ga_2O_3$. It is interesting that the discrepancy in composition is essentially a loss of B_2O_3, which is known to volatalize at high temperatures [29, 30]; although the chemical analysis of $Na_2O\cdot 2B_2O_3\cdot Ga_2O_3$ is in good agreement with that calculated and so seems to suggest that the error is not systematic.

However, due to the large discrepancy between analysed and calculated compositions for $2Na_2O\cdot 4B_2O_3\cdot Ga_2O_3$ it would be unwise to accept the reported results as those for the $Na_2O\cdot 2B_2O_3$–Ga_2O_3 pseudo-binary.

In the case of $Na_2O\cdot B_2O_3$–Ga_2O_3 pseudo-binary [3], $Na_2O\cdot B_2O_3$ was first made by fusing H_3BO_3 and Na_2CO_3 at 1050 °C and then this metaborate was fused with Ga_2O_3 at temperatures up to 1200 °C. Again there is no mention of firing times. The phase diagram was obtained using differential thermal analysis and the presence of the two compounds, $Na_2O\cdot B_2O_3\cdot Ga_2O_3$ and $2Na_2O\cdot 2B_2O_3\cdot Ga_2O_3$, confirmed by infrared spectroscopy. The X-ray powder diffraction patterns were given but no chemical analyses were obtained at either of these compositions and neither of the present patterns at these composi-

TABLE V Analytical [2] and calculated compositions of ternary phases on the $Na_2O\cdot 2B_2O_3$–Ga_2O_3 pseudo-binary

	Anal. comp. (wt %)			Calc. Comp. (wt %)		
	Na_2O	B_2O_3	Ga_2O_3	Na_2O	B_2O_3	Ga_2O_3
$2Na_2O\cdot 4B_2O_3\cdot Ga_2O_3$	25.66	42.83	31.54	21.01	47.21	31.78
$Na_2O\cdot 2B_2O_3\cdot Ga_2O_3$	16.57	37.43	45.17	15.95	35.82	48.23
$3Na_2O\cdot 4B_2O_3\cdot Ga_2O_3$				28.53	42.72	28.75

tions agree with those published previously [3]. This cannot be reconciled. However, one point is worth mentioning; in the present work the X-ray pattern corresponding to the composition $Na_2O{\cdot}B_2O_3{\cdot}Ga_2O_3$ (compact 16) was interpreted as being due to a combination of β-Ga_2O_3 (major) and $3Na_2O{\cdot}4B_2O_3{\cdot}Ga_2O_3$ and $Na_2O{\cdot}B_2O_3{\cdot}Ga_2O_3$ (minor). Examining the previously reported pattern for this [3], indicates that β-Ga_2O_3 is probably present; the strongest line is not due to β-Ga_2O_3 but the second, third, fourth and both joint fifth strongest lines may all be attributed to the strongest lines of β-Ga_2O_3 and thus the reported pattern [3] is probably not due to a pure compound. However, this does not alter the fact that the remainder of their pattern cannot be interpreted on the basis of the present work.

It has already been mentioned that Res *et al.* [1] investigated compositions in the low Na_2O, high Ga_2O_3 region of the phase diagram and X-ray analysed several compositions after leaching. Only β-Ga_2O_3 was found in every case. Of the compositions examined in this way, two were in the triangle B_2O_3–$Na_2O{\cdot}4B_2O_3$–Ga_2O_3 and one on the $Na_2O{\cdot}4B_2O_3$–Ga_2O_3 tie line, thus finding only β-Ga_2O_3 after leaching is easily explained in these cases. But two of the compositions are in the triangle $Na_2O{\cdot}3B_2O_3$–$3Na_2O{\cdot}4B_2O_3{\cdot}Ga_2O_3$–$Ga_2O_3$, one (15% Na_2O–35% B_2O_3–50% Ga_2O_3) very near to the composition $Na_2O{\cdot}B_2O_3{\cdot}Ga_2O_3$. Now, if $Na_2O{\cdot}2B_2O_3{\cdot}Ga_2O_3$ is a ternary phase, as claimed by Rza-Zade *et al.* [2], then the only way of reconciling these results would be for this compound, $Na_2O{\cdot}2B_2O_3{\cdot}Ga_2O_3$, to dissociate in boiling distilled water to form β-Ga_2O_3 together with one or more sodium borates, and this would seem to be unlikely for a compound that is claimed to be stable up to its melting point, 775 °C [2].

However, if the present phase diagram is accepted the results can be reconciled if $3Na_2O{\cdot}4B_2O_3{\cdot}Ga_2O_3$ is soluble in boiling water, in which case leaching the compact whose composition is $Na_2O{\cdot}2B_2O_3{\cdot}Ga_2O_3$ would leave only β-Ga_2O_3. To determine this, a small part (0.30 g) of compact 10, nominally $Na_2O{\cdot}2B_2O_3{\cdot}Ga_2O_3$ was boiled in 200 ml distilled water for 30 min, filtered while hot and the filtrated X-ray analysed. Only β-Ga_2O_3 was detected, thus indicating that $3Na_2O{\cdot}4B_2O_3{\cdot}Ga_2O_3$ is soluble in boiling water and confirming the observations of Res *et al.* [1]. In addition Res *et al.* [1] were unable to establish conclusively the existence of $Na_2O{\cdot}2B_2O_3{\cdot}Ga_2O_3$ by infrared spectroscopy and in these circumstances its existence must be doubtful.

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