

# Phase relations in the system $\text{CaO-B}_2\text{O}_3\text{-SiO}_2$

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Phase relations in the lime-rich portion of the system  $\text{CaO-B}_2\text{O}_3\text{-SiO}_2$  have been studied by microscopy, infrared spectroscopy and X-ray powder diffraction of heated mixtures and quenched charges. Extensive solid solution of  $\text{B}_2\text{O}_3$  in  $\text{Ca}_2\text{SiO}_4$  occurs along the  $\text{Ca}_2\text{SiO}_4\text{-Ca}_3\text{B}_2\text{O}_6$  boundary, which has been studied in detail. It contains a ternary compound,  $\text{Ca}_{11}\text{B}_2\text{Si}_4\text{O}_{22}$ , which is stable to liquidus temperatures, melting incongruently to  $\text{Ca}_2\text{SiO}_4$  and liquid at  $1420^\circ\text{C}$ .  $\text{Ca}_{11}\text{B}_2\text{Si}_4\text{O}_{22}$  forms a eutectic with  $\text{Ca}_3\text{B}_2\text{O}_6$  at  $1400^\circ\text{C}$  and, in the ternary system, with  $\text{CaO}$  and  $\text{Ca}_3\text{B}_2\text{O}_6$  at  $1390^\circ\text{C}$ .

## 1. Introduction

The system  $\text{CaO-SiO}_2$  is one of the first binary systems of refractory oxides to be thoroughly investigated. The pioneering studies of Rankin and Wright [1], although correct in general, have had important modifications by Muan and Osborn [2], Nurse [3] and Welch and Gutt [4]. Fig. 1 shows the currently accepted phase relationships. Its interest to ceramics, cements and refractories centres on the effect of  $\text{CaO}$  on the melting point of  $\text{SiO}_2$ , the stability of  $\text{Ca}_3\text{SiO}_5$  and the refractory nature and polymorphism of  $\text{Ca}_2\text{SiO}_4$ .

The  $\text{CaO-B}_2\text{O}_3$  binary system has been studied previously; Fig. 2, after Carlson [5] shows the currently accepted version.  $\text{B}_2\text{O}_3$  itself has a low melting point and the melting point of the binary phases decreases as their boric oxide contents increase; from  $1479^\circ\text{C}$  ( $\text{Ca}_3\text{B}_2\text{O}_6$ ), to  $1298^\circ\text{C}$  ( $\text{Ca}_2\text{B}_2\text{O}_5$ ),  $1154^\circ\text{C}$  ( $\text{CaB}_2\text{O}_4$ ) and  $986^\circ\text{C}$  ( $\text{CaB}_4\text{O}_7$ ).

Studies of the ternary  $\text{CaO-B}_2\text{O}_3\text{-SiO}_2$  system have elucidated the subsolidus compatibility and liquidus phase relations [6]. This study disclosed the existence of a ternary phase, believed at that time to be  $5\text{CaO}\cdot\text{B}_2\text{O}_3\cdot\text{SiO}_2$ . Fig. 3 shows the subsolidus compatibility in the lime-rich portion of the system at lower temperatures,  $<1250^\circ\text{C}$ , such that  $\text{Ca}_3\text{SiO}_5$  is not a stable phase. Extensive solid solution of boric oxide in  $\text{Ca}_2\text{SiO}_4$  was reported but not defined in detail. However the constitution of the ternary phase was reinvestigated by Suzuki *et al.* [7], who preferred the composition  $11\text{CaO}\cdot\text{B}_2\text{O}_3\cdot 4\text{SiO}_2$ . Two polymorphs were encountered, designated  $\alpha$  (high temperature) and  $\beta$  (low temperature).

## 2. Experimental procedure

### 2.1. Preparative methods

Sources of calcium, silicon and boron were, respectively, "AnalaR"  $\text{CaCO}_3$ , optical grade quartz (0.08% non-volatile with HF which was ground to pass BS 180 mesh and acid washed), and "AnalaR" boric acid. The appropriate quantities of reagents were hand-mixed in agate mortars and fired in platinum crucibles

to successively higher temperatures in order to eliminate water and  $\text{CO}_2$  gradually and finally, to combine the components. Sintering was generally stopped below the temperature at which melting commenced. The composition of representative charges was checked by total chemical analysis for calcium, silicon and boron and found to conform to within  $\pm 1\%$  of the nominal composition.

Subsequent heatings were of two types. Preparations intended for determination of subsolidus compatibilities, generally as 1–2 g batches in platinum or gold crucibles, were sintered in electrically heated muffle furnaces in air; the temperature control was  $\pm 10^\circ\text{C}$ . However, charges intended for liquidus determinations were smaller, typically 0.1 g and these were heated in platinum foil envelopes in vertical-tube platinum resistance furnaces which afforded temperature control to  $\pm 1\text{--}2^\circ\text{C}$ . The actual temperatures were read against Pt–13% Rh thermoelements and calibrated against secondary standards: gold m.p.  $1062^\circ\text{C}$  and diopside ( $\text{CaMg}(\text{SiO}_3)_2$ ) m.p.  $1391.5^\circ\text{C}$ .

### 2.2. Examination of quenched charges

Primary tools for the determination of phase relations were optical microscopy, using a petrographic microscope, and powder X-ray diffraction, using both a focusing Hagg–Guinier camera and a Philips powder X-ray diffractometer. DTA and TG were performed simultaneously on a Stanton-Redcroft thermal analyser. Other special techniques are described at the appropriate point.

## 3. Results

### 3.1. The ternary phase

Quenching experiments and subsolidus heatings revealed the presence of one ternary phase, which had a constant composition within limits of experimental error. The formula proposed by Suzuki and Hira,  $11\text{CaO}\cdot 4\text{SiO}_2\cdot\text{B}_2\text{O}_3$ , was found to be correct. However, its powder X-ray data differ somewhat from those reported previously, and the powder patterns for

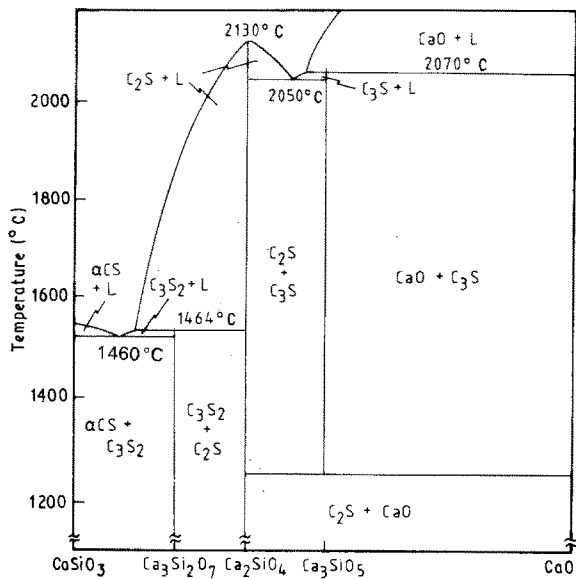


Figure 1 Condensed phase relations in the system CaO-SiO<sub>2</sub> at CaO ≥ 50 mol %. After Muan and Osborn [2]. C=CaO, S=SiO<sub>2</sub>.

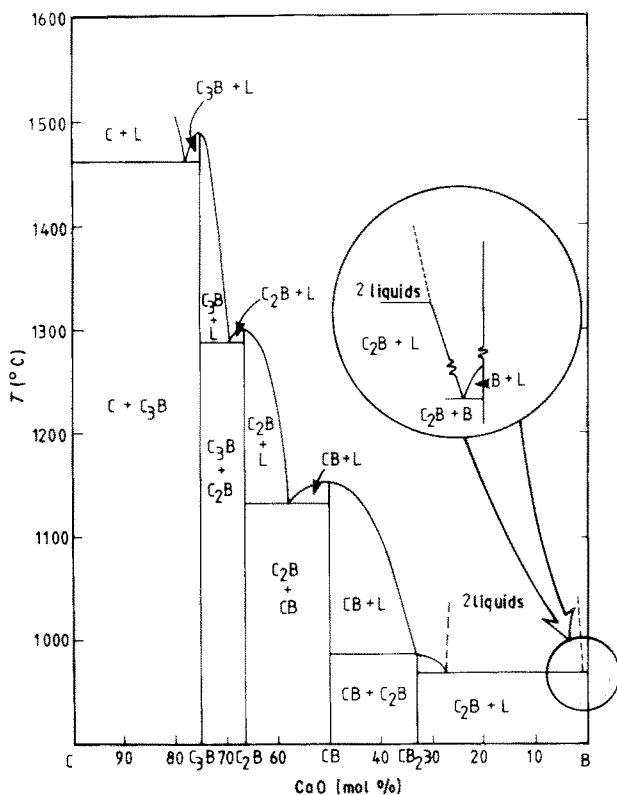


Figure 2 Condensed phase relations in the system CaO-B<sub>2</sub>O<sub>3</sub>. After Carlson [5]. C=CaO, B=B<sub>2</sub>O<sub>3</sub>. The insert shows conjectural relations at high B<sub>2</sub>O<sub>3</sub> contents.

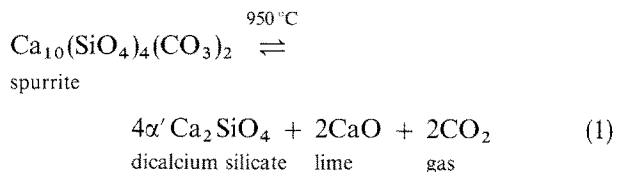
the  $\alpha$  and  $\beta$  polymorphs were reindexed with the aid of single-crystal X-ray ( $\alpha$ -phase) and electron diffraction ( $\beta$ -phase) patterns. The quality of single crystals obtained for the  $\alpha$ -polymorph did not permit a full crystal structure determination, but did allow an independent and unequivocal determination of the unit-cell dimensions which confirmed the orthogonality of this polymorph. The unit-cell dimensions for the  $\beta$ -polymorph were initially obtained to  $\pm 0.5\%$  by calibrating the electron diffraction camera with aluminium powder. Using the approximate unit-cell parameters

thus determined, the whole of the powder XRD data, obtained on a focusing camera using silicon metal or quartz as an internal standard, were subject to several cycles of least squares refinement. The final indexing is shown in Tables I and II for the  $\alpha$  and  $\beta$  polymorphs, respectively. The most probable unit cell contents for both phases are Ca<sub>11</sub>(SiO<sub>4</sub>)<sub>4</sub>(BO<sub>3</sub>)<sub>2</sub>. The assignment of boron to BO<sub>3</sub> groups is based on infrared evidence; Fig. 4 shows patterns of these two phases, as well as that of a boron-containing solid solution of dicalcium silicate. The spectra shown were obtained on a Nicolet 7199 FT-IR from KBr discs containing 1%–5% of the solid under investigation; dry nitrogen was flushed through the spectrometer. The assignment of spectral features is also shown; the pattern is quite characteristic of the presence of silicon as orthosilicate (SiO<sub>4</sub>) and boron as (BO<sub>3</sub>) groups in both polymorphs of the Ca<sub>11</sub>(SiO<sub>4</sub>)<sub>4</sub>(BO<sub>3</sub>)<sub>2</sub> phase.

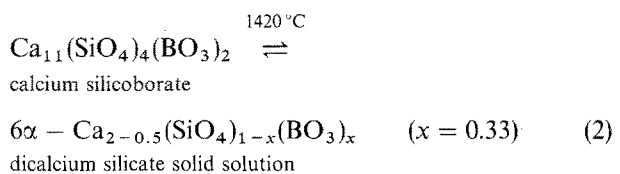
The transformation between  $\alpha$  and  $\beta$  phases of Ca<sub>11</sub>(SiO<sub>4</sub>)<sub>4</sub>(BO<sub>3</sub>)<sub>2</sub> is reversible at  $1265 \pm 7^\circ\text{C}$ . On account of the reversibility of the transformation, as well as similarities in unit-cell dimensions and powder X-ray patterns, it is suspected that the crystal structures of the two polymorphs are closely related.

The structure of both Ca<sub>11</sub>(SiO<sub>4</sub>)<sub>4</sub>(BO<sub>3</sub>)<sub>2</sub> polymorphs are at present unresolved. However, we suggest that the  $\alpha$  and  $\beta$  polymorphs have close structural relationships respectively to Ca<sub>10</sub>(SiO<sub>4</sub>)<sub>4</sub>(CO<sub>3</sub>)<sub>2</sub>. Two polymorphs of the latter are known: paraspurrite [8] and spurrite [9, 10]; these are related to the  $\alpha$  and  $\beta$  polymorphs of Ca<sub>10</sub>(SiO<sub>4</sub>)<sub>4</sub>(CO<sub>3</sub>)<sub>2</sub>, respectively.

Spurrite is commonly observed to develop during the early stages of cement production although the calcium silicoborate structure of spurrite has a limited lifetime in the kiln, owing to its thermodynamic instability. It decomposes according to the reaction



Compared to spurrite-paraspurrite, the calcium silicoborate structure is thermodynamically more stable and in an air atmosphere, boron is much less volatile than carbon, with the result that the borate species is retained in the system, eventually becoming incorporated into the dicalcium silicate structure by the solid solution mechanism depicted below. Ideally, as in the following calculation,  $x = 0.33$ , but the value of  $x$  can vary as will be shown subsequently.



### 3.2. Borate solid solution in dicalcium silicate

Because this topic is of considerable interest to ceramics and mineralogy it was investigated in detail. At the

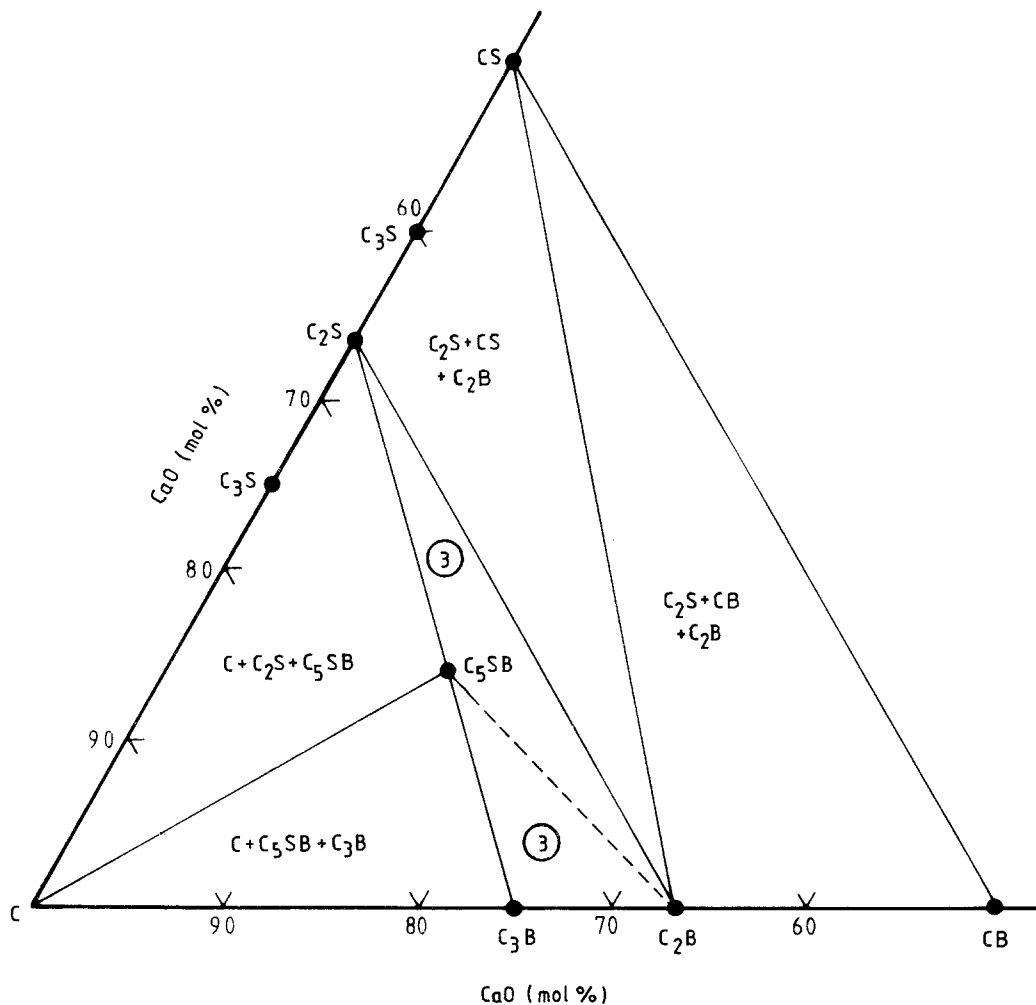
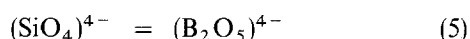
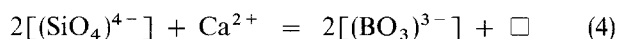
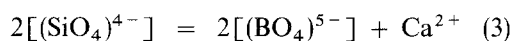


Figure 3 Lime-rich portion of the system  $\text{CaO-B}_2\text{O}_3\text{-SiO}_2$  constructed from data of Flint and Wells [6]. The temperature of the isothermal section is less than  $1250^\circ\text{C}$ , such that  $\text{Ca}_3\text{SiO}_5$  is not a stable phase. The four-phase triangle marked (3) must be subdivided into three-phase triangles: (---) the most probable arrangement. The upper part of Region 3 and contiguous regions are occupied by an ill-defined zone (not shown) of boron-containing solid solutions based on  $\text{Ca}_2\text{SiO}_4$ .

outset, three solid solution mechanisms were postulated:



where  $\square$  is a cation vacancy. Mixes proportioned according to the formulae derived from these mechanisms were prepared and subjected to prolonged sintering. Only Mechanism 4 gave pure single-phase preparations: moreover, if Mechanism 4 were correct the additional phases which would then be expected to occur in compositions derived using Mechanisms 3 and 5 were actually observed. Infrared data, Fig. 4, are also consistent with Mechanism 4, insofar as boron is shown to be entirely present as  $\text{BO}_3$  units, rather than as  $\text{BO}_4$  tetrahedra.

To account for the extent of solid solution of boron in the different polymorphs of dicalcium silicate, it was convenient to rewrite Mechanism 4 as  $\text{Ca}_{2-0.5x}[\text{SiO}_4]_{1-x}[\text{BO}_3]_x$ , so that the value of  $x$  could be related to the polymorph encountered at ambient temperature, following slow ( $1\text{--}5^\circ\text{C min}^{-1}$ ) cooling from annealing temperatures in the range  $1200\text{--}1400^\circ\text{C}$ .

The correlation between the value of  $x$  and the polymorph thus obtained is given in Table III. The phase identification was made by comparison with JCDPS cards 31–297, 33–302 and 33–303 for  $\gamma$ ,  $\beta$  and  $\alpha'$  phases, respectively. The identification of the alpha phase is, however, more tentative. The presence of the hexagonal  $\alpha$  phase could be inferred from characteristic morphological features such as the observation of cyclic twins by electron microscopy and/or the stabilization of a polymorph which from its powder pattern, appeared to be geometrically hexagonal. A partial structure determination of the alpha-like phase has been made which will be reported in greater detail elsewhere.

### 3.3. Stability of $\text{Ca}_3\text{SiO}_5$ in the $\text{CaO-B}_2\text{O}_3\text{-SiO}_2$ system

The thermal stability of  $\text{Ca}_3\text{SiO}_5$  has been studied and reviewed by Glasser and Mohan [11]. There is general agreement that  $\text{Ca}_3\text{SiO}_5$  has a lower limit of thermal stability, below which it decomposes to  $\text{Ca}_2\text{SiO}_4$  and  $\text{CaO}$ , at  $1250 \pm 20^\circ\text{C}$ . The kinetics of its decomposition are influenced by the presence of chemical impurity (iron oxide, alkali, magnesium and aluminium

TABLE I Powder X-ray diffraction data for  $\alpha$ - $\text{Ca}_{11}(\text{SiO}_4)_4(\text{BO}_3)_2$ . Unit cell dimensions<sup>a</sup>:  $a = 0.7828(12)$  nm,  $b = 1.5950(12)$  nm,  $c = 0.6877(4)$  nm,  $\alpha = \beta = \gamma = 90.0^\circ$

Space group <sup>b</sup>			
$h\ k\ l$	$d_{\text{obs}}(\text{nm})$	$I_{\text{obs}}$	$d_{\text{calc}}(\text{nm})$
6 0 0	0.4628	7	0.4638
3 3 0			0.4613
6 1 1			0.3738
4 4 0	0.3446	9	0.3460
0 0 2			0.3439
6 3 1	0.3112	8	0.3116
6 0 2			0.2762
3 3 2	0.2760	100	0.2757
4 5 1			0.2673
9 3 0	0.2678	28	0.2672
0 6 0			0.2658
11 1 0	0.2657	56	0.2494
9 3 1			0.2491
7 5 0	0.2492	6	0.2488
9 0 2			0.22991
10 4 0	0.22844	9	0.22820
3 0 3			0.22242
12 0 1	0.21938	10	0.21974
6 6 1			0.21867
4 0 3	0.21752	8	0.21772
7 4 2			0.21783
2 2 3	0.20550	4	0.21760
6 0 3			0.20528
3 3 3	0.20415	4	0.20511
3 6 2			0.20485
5 2 3	0.20170	7	0.20158
9 6 0			0.20160
5 7 1	0.20085	4	0.20058
10 5 1			0.19938
0 8 0	0.19731	5	0.19769
7 7 0			0.19736
2 8 0	0.19209	28	0.19226
12 0 2			0.19104
1 8 1	0.19101	12	0.19014
10 4 2			0.18990
7 7 1	0.18928	11	0.18970
2 8 1			0.18950
1 7 2	0.17218	4	0.18960
14 1 1			0.17215
1 8 2	0.17173	4	0.17173
0 0 4			0.17162
11 5 2	0.17142	3	0.17138
0 9 1			0.17138
7 7 2	0.17117	3	0.17117
2 8 2			0.17064
3 6 3	0.16990	3	0.16993
16 2 0			0.16121
6 0 4	0.16141	4	0.16110
3 3 4			0.15608
15 3 2	0.15578	6	0.15601
13 7 0			0.15586
12 3 3			

TABLE I (Continued)

Space group <sup>b</sup>			
$h\ k\ l$	$d_{\text{obs}}(\text{nm})$	$I_{\text{obs}}$	$d_{\text{calc}}(\text{nm})$
3 9 2	0.15530	8	0.15531
18 0 0			0.15531
9 3 4	0.14465	5	0.14460

<sup>a</sup> Unit cell indexing is based on single-crystal data. Values in parentheses are one standard deviation of the last significant figure.

<sup>b</sup> Systematic absences observed by both single-crystal XRD and electron diffraction do not conform to any standard space group.

TABLE II Powder X-ray diffraction for  $\beta$ - $\text{Ca}_{11}(\text{SiO}_4)_4(\text{BO}_3)_2$ .  $a = 2.861(2)$  nm,  $b = 1.5974(9)$  nm,  $c = 0.6874(8)$  nm,  $\alpha = \beta = 90^\circ$ ,  $\gamma = 104.1(1)^\circ$

$h\ k\ l$	$d_{\text{obs}}(\text{nm})$	$I_{\text{obs}}$	$d_{\text{calc}}(\text{nm})$
2 0 0	0.695	30	0.694
0 2 0	0.5167	30	0.5164
4 2 0	0.4630	28	0.4637
6 0 0			0.4625
6 0 1	0.3818	24	0.3837
4 $\bar{4}$ 0			0.3800
4 3 0	0.3734	11	0.3730
8 0 0	0.3469	31	0.3469
3 4 1	0.3412	13	0.3412
$\bar{1}$ 0 2			0.3411
9 1 0	0.3173	9	0.3176
$\bar{8}$ 1 1			0.3172
*	0.31096	11	<sup>b</sup>
$\bar{3}$ 2 2	0.30692	11	0.30685
8 1 1	0.29168	7	0.29172
9 4 0	0.27612	33	0.27624
4 2 2			0.27612
6 0 2	0.27438	75	0.27587
3 5 0			0.27437
1 2 2	0.27305	100	0.27308
*	0.27126	7	<sup>b</sup>
*	0.26863	18	<sup>b</sup>
$\bar{3}$ 6 0	0.26589	94	0.26505
$\bar{2}$ 6 0			0.26577
5 5 2	0.26249	35	0.26251
0 4 0	0.25805	6	0.25818
<sup>c</sup>	0.24938	6	<sup>c</sup>
<sup>c</sup>			<sup>c</sup>
<sup>c</sup>	0.24774	6	<sup>c</sup>
<sup>c</sup>			0.24530
<sup>c</sup>	0.24357	5	<sup>c</sup>
<sup>c</sup>			0.23323
<sup>c</sup>	0.22835	9	<sup>c</sup>
<sup>c</sup>			0.22705
$\bar{9}$ 6 0	0.2712	25	0.22705
<sup>c</sup>	0.22253	7	<sup>c</sup>
<sup>c</sup>			<sup>c</sup>
<sup>c</sup>	0.22051	33	<sup>c</sup>
12 0 1	0.21915	17	0.21918
<sup>c</sup>	0.21649	22	<sup>c</sup>
<sup>c</sup>			<sup>c</sup>
<sup>c</sup>	0.21286	9	<sup>c</sup>

TABLE II (Continued)

<i>h k l</i>	$d_{\text{obs}}(\text{nm})$	$I_{\text{obs}}$	$d_{\text{calc}}(\text{nm})$
°	0.209 21	9	°
°	0.207 90	5	°
°	0.203 47	9	°
°	0.200 51	6	°
°	0.199 58	11	°
°	0.197 81	5	°
°	0.193 50	18	°
°	0.191 31	26	°
°	0.190 46	11	°
°	0.189 46	50	°
°	0.186 60	5	°
°	0.181 61	6	°

<sup>a</sup> Unit-cell dimensions based on electron diffraction study.

<sup>b</sup> Unindexed line.

<sup>c</sup> Many possible Miller indices, which cannot be differentiated.

oxides, and also by water vapour) but these impurities do not significantly affect its thermodynamic stability boundaries, especially the lower temperature bound. On the other hand, when solid solution occurs, this lower limit of stability may be appreciably altered; thus Shame and Glasser [12] found that aluminium (substituting for silicon) in conjunction with fluorine (substituting for oxygen) extended the thermodynamic stability range of  $\text{Ca}_3\text{SiO}_5$  and its solid solutions and lowered its decomposition temperature to a minimum of 1050 °C. Therefore, the role of boron in affecting the stability of  $\text{Ca}_3\text{SiO}_5$  was examined in more detail.

The stability of boron-containing  $\text{Ca}_3\text{SiO}_5$  was determined with reaction batches made from pre-formed, phase-pure  $\text{Ca}_3\text{SiO}_5$  to which  $\text{Ca}_3(\text{BO}_3)_2$  was added. Initially several firings at 1500 °C were required to prepare the boron-free  $\text{Ca}_3\text{SiO}_5$  product, which was accepted when powder X-ray diffraction and chemical free lime determinations disclosed that all CaO had reacted and that  $\text{Ca}_2\text{SiO}_4$  was absent. The product consisted of triclinic (T)  $\text{Ca}_3\text{SiO}_5$  which had a typical Blaine surface area of 200  $\text{m}^2\text{g}^{-1}$ ; this corresponds to an equivalent spherical radius of ~5  $\mu\text{m}$ . Electron microscopic examination disclosed two crystallite morphologies; rounded agglomerates ~50–60  $\mu\text{m}$ , consisting of very small crystallites, and individual faceted crystals up to ~30  $\mu\text{m}$  length with columnar morphology. The product was kept dry until required, when 5–10 g were mixed with previously prepared  $\text{Ca}_3(\text{BO}_3)_2$ . Approximately 1 g was annealed isothermally at various temperatures between 1000 and 1700 °C. Fig. 5 shows three time-temperature-transformation curves for the thermally activated decomposition of  $\text{Ca}_3\text{SiO}_5$  to  $\text{Ca}_2\text{SiO}_4$  and CaO in the presence of  $\text{Ca}_3\text{B}_2\text{O}_6$  equivalent to

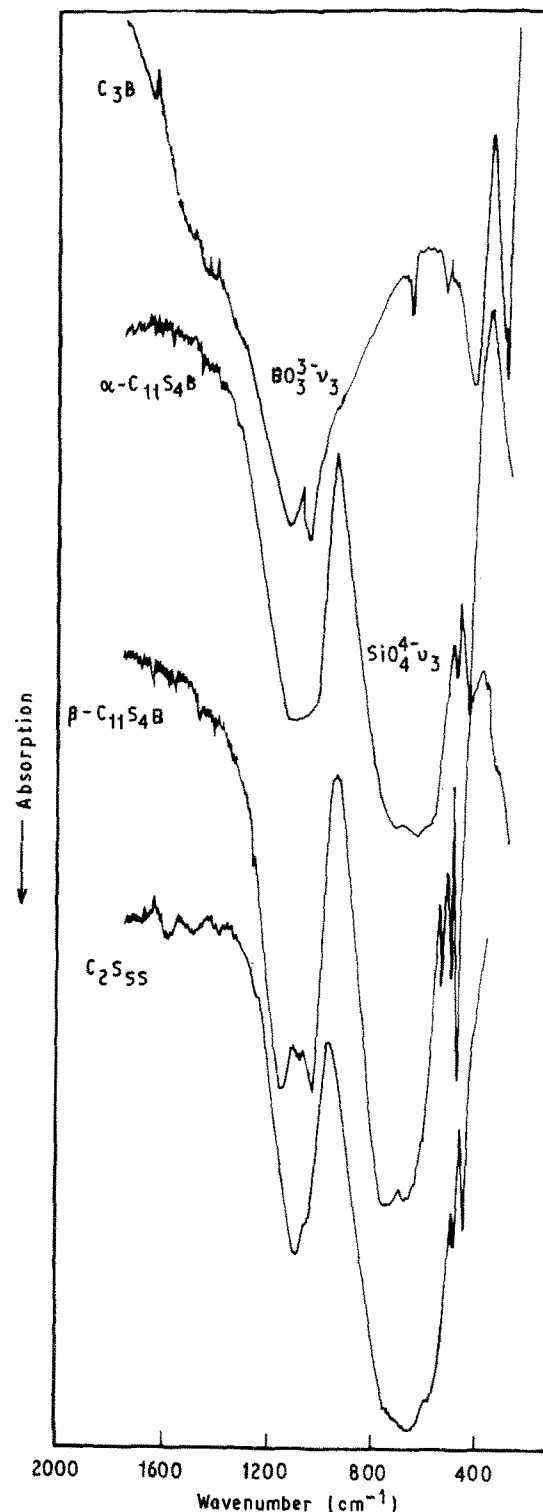


Figure 4 Fourier transform transmission infrared patterns at 25 °C of some  $\text{CaO-B}_2\text{O}_3\text{-SiO}_2$  phases.

2.8 wt %  $\text{B}_2\text{O}_3$  in the bulk composition. The extent of decomposition was determined from the chemical free lime content using the modified Franke method. The three isotherms selected, namely 1200, 1270 and 1400 °C, were chosen because one lies below the reported lower stability temperature of pure  $\text{Ca}_3\text{SiO}_5$  while the other two lie within the reported stability range of pure  $\text{Ca}_3\text{SiO}_5$ . Yet decomposition of  $\text{Ca}_3\text{SiO}_5$  occurred rapidly on all isotherms, illustrating the destabilizing effect of  $\text{B}_2\text{O}_3$  on  $\text{Ca}_3\text{SiO}_5$ . Decomposition also occurred on other selected isotherms (which were studied in less detail) up to and including 1700 °C; indeed, the rate of decomposition to CaO and

TABLE III Polymorphism of boron-substituted dicalcium silicate solid solutions

Value of $x$ in $\text{Ca}_{2-0.5x}(\text{SiO}_4)_{1-x}(\text{BO}_3)_x$	Polymorph obtained at ambient
0.00	$\gamma$
0.02	$\beta$
0.02–0.16	$\alpha'$
0.16–0.33	$\alpha$

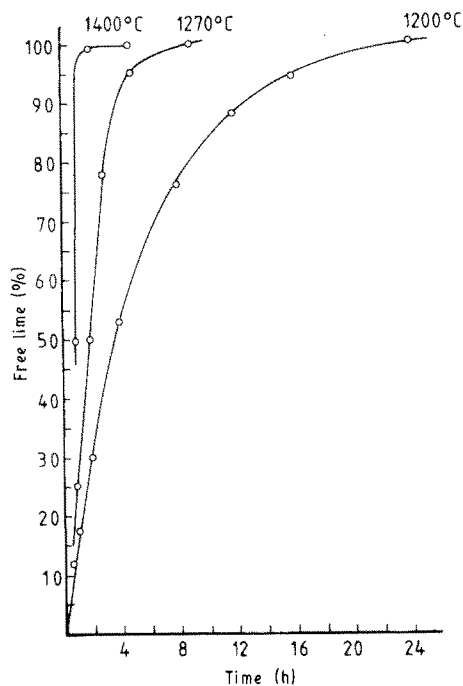


Figure 5 Time-temperature-transformation curves for initially phase-pure  $\text{Ca}_3\text{SiO}_5$ , as measured by CaO formation.

$\text{Ca}_2\text{SiO}_4$  became so rapid as to occur virtually instantaneously on the scale of Fig. 5. It is therefore certain that  $\text{Ca}_3\text{SiO}_5$  has no stable expression at ternary liquidus temperatures at any temperatures below 1700 °C.

### 3.4. Liquidus and subsolidus phase relations

Because the stability of  $\text{Ca}_2\text{SiO}_4$  and its solid solutions appear to be crucial to the general nature of the phase relations, the join  $\text{Ca}_2\text{SiO}_4\text{--Ca}_3\text{B}_2\text{O}_6$  was studied in detail. Approximately 20 compositions were prepared. These were most closely spaced in the range 60–100 mol %  $\text{Ca}_2\text{SiO}_4$ . The results are shown in Fig. 6. The melting point of  $\text{Ca}_2\text{SiO}_4$  is very high, ~2100 °C, but liquidus temperatures drop rapidly upon addition of  $\text{B}_2\text{O}_3$ , to a liquidus peritectic located at 1425 °C and 64 mol %  $\text{Ca}_2\text{SiO}_4$ . This peritectic is, of course, the incongruent melting point of  $\text{Ca}_{11}\text{B}_2\text{Si}_4\text{O}_{22}$  (abbreviated  $\text{C}_{11}\text{BS}_4$ ). Upon addition of more  $\text{Ca}_3\text{B}_2\text{O}_6$ , liquidus temperatures fall much less rapidly, eventually reaching a eutectic located at 1400 °C and 28 mol %  $\text{C}_2\text{S}$ . Table IV gives selected data.

The composition of solid solutions based on  $\text{Ca}_2\text{SiO}_4$  are coincident with this join, so the max-

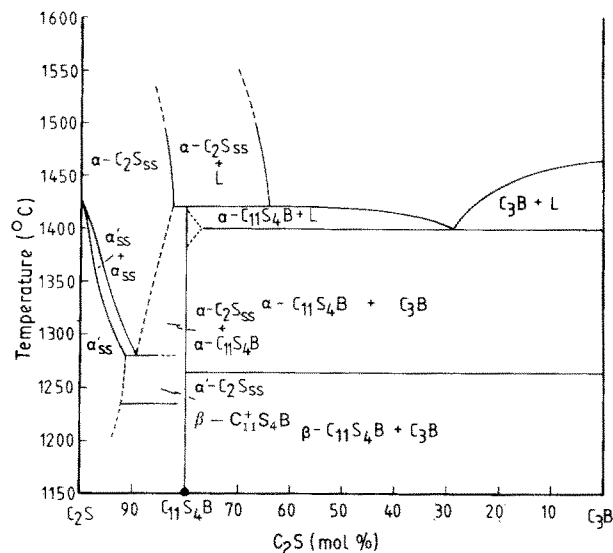


Figure 6 Phase relations along the join  $\text{Ca}_2\text{SiO}_4\text{--Ca}_3\text{B}_2\text{O}_6$  showing mainly melting relations at < 1500 °C, formation of a binary phase and solid solution of boric oxide in  $\text{Ca}_2\text{SiO}_4$  polymorphs.

imum possible extent of solid solution is encountered. This maximum occurs at 1425 °C, where the solid solution based on  $\text{Ca}_2\text{SiO}_4$  contains ~17 mol %  $\text{Ca}_3\text{B}_2\text{O}_6$ . Boron-rich solid solutions of  $\text{Ca}_2\text{SiO}_4$  are readily preserved to ambient temperatures with rapid cooling, but with slow cooling they tend to exsolve  $\text{Ca}_{11}(\text{SiO}_4)_4(\text{BO}_3)_2$  while the remaining low boron content dicalcium silicate phase undergoes phase transformations appropriate to its decreased boron content. The dotted line shows the approximate boundary of the field of  $\alpha$   $\text{Ca}_2\text{SiO}_4$ -type solid solutions and their prolongation to lower temperatures. At the same time the temperature of the  $\alpha$ - $\alpha'$  inversion, which occurs at ~1455 °C for pure  $\text{Ca}_2\text{SiO}_4$ , is also depressed by the solid solution of boron. The intersection of these latter features gives rise to a eutectoid at 1280 °C and 11 mol %  $\text{Ca}_3\text{B}_2\text{O}_6$ . The field of borate-containing  $\alpha'$   $\text{Ca}_2\text{SiO}_4$  solid solution compositions is somewhat more limited, reaching a maximum of 8 mol %  $\text{Ca}_3\text{B}_2\text{O}_6$  at 1280 °C. The two-phase field of ( $\alpha + \alpha'$ ) solid solutions is very narrow, and the inversion temperature appears to be essentially sharp by thermal analysis, although with increasing tendency towards hysteresis as increased solid solution shifted the phase transition to progressively lower temperatures.

There is some suggestion that a limited solid solution of  $\text{Ca}_3\text{B}_2\text{O}_6$  in  $\text{Ca}_{11}(\text{SiO}_4)_4(\text{BO}_3)_2$  occurs at high temperatures, within 50 °C of its melting point. Because the extent and shape of this solid solution field is not known accurately, its existence is suggested in Fig. 6 by dashed lines.

If this version of the system is compared with those reported previously in the literature, principally that of Suzuki and Hira [13], a number of important differences emerge. Two are noteworthy. In the title study, the upper stability limit of  $\text{Ca}_{11}(\text{SiO}_4)_4(\text{BO}_3)_2$  lies at higher temperatures, with the result that it develops a primary phase field at liquidus temperatures: Suzuki and Hira show a field of stability only

TABLE IV Representative compositions studied

	CaO (mol %)	SiO <sub>2</sub> (mol %)	B <sub>2</sub> O <sub>3</sub> (mol %)	Temp. (°C)	Time (h)	Starting material	Final products	
Liquidus	68.75	25.0	6.25	1400	1	C <sub>2</sub> S, C <sub>3</sub> B	C <sub>11</sub> S <sub>4</sub> B	
	69.2	23.1	7.7	1400	1	C <sub>2</sub> S, C <sub>3</sub> B	C <sub>11</sub> S <sub>4</sub> B	
	69.2	23.1	7.7	1400	1	C <sub>11</sub> S <sub>4</sub> B, C <sub>3</sub> B	C <sub>11</sub> S <sub>4</sub> B	
	69.7	21.2	9.1	1400	1	C <sub>2</sub> S, C <sub>3</sub> B	C <sub>11</sub> S <sub>4</sub> B	
	69.7	21.2	9.1	1400	1	C <sub>11</sub> S <sub>4</sub> B, C <sub>3</sub> B	C <sub>11</sub> S <sub>4</sub> B, C <sub>3</sub> B	
	70.6	17.6	11.8	1400	1	C <sub>2</sub> S, C <sub>3</sub> B	C <sub>11</sub> S <sub>4</sub> B, C <sub>3</sub> B	
	71.4	14.3	14.3	1400	1	C <sub>2</sub> S, C <sub>3</sub> B	C <sub>11</sub> S <sub>4</sub> B, C <sub>3</sub> B	
	72.2	11.1	16.7	1400	1	C <sub>2</sub> S, C <sub>3</sub> B	C <sub>11</sub> S <sub>4</sub> B, C <sub>3</sub> B	
	73.0	8.1	18.9	1400	1	C <sub>2</sub> S, C <sub>3</sub> B	C <sub>11</sub> S <sub>4</sub> B, C <sub>3</sub> B	
	73.7	5.3	18.9	1400	1	C <sub>2</sub> S, C <sub>3</sub> B	C <sub>11</sub> S <sub>4</sub> B, C <sub>3</sub> B	
	68.75	25.0	6.25	1420	0.5	C <sub>2</sub> S, C <sub>3</sub> B	C <sub>11</sub> S <sub>4</sub> B	
	69.7	21.2	9.1	1420	0.5	C <sub>2</sub> S, C <sub>3</sub> B	C <sub>11</sub> S <sub>4</sub> B, C <sub>3</sub> B	
	70.7	17.6	11.8	1420	0.5	C <sub>2</sub> S, C <sub>3</sub> B	C <sub>11</sub> S <sub>4</sub> B, C <sub>3</sub> B	
	71.4	14.3	14.3	1420	0.5	C <sub>2</sub> S, C <sub>3</sub> B	C <sub>11</sub> S <sub>4</sub> B, C <sub>3</sub> B	
	72.2	11.1	16.7	1420	0.5	C <sub>2</sub> S, C <sub>3</sub> B	C <sub>11</sub> S <sub>4</sub> B, C <sub>3</sub> B	
	73.0	8.1	18.9	1420	0.5	C <sub>2</sub> S, C <sub>3</sub> B	C <sub>11</sub> S <sub>4</sub> B, C <sub>3</sub> B	
	68.2	27.0	4.8	1500	0.5	C <sub>2</sub> S, C <sub>3</sub> B	α	
	68.75	25.0	6.25	1500	0.5	C <sub>2</sub> S, C <sub>3</sub> B	C <sub>11</sub> S <sub>4</sub> B/α, liquid <sup>a</sup>	
	69.2	23.1	7.7	1500	0.5	C <sub>2</sub> S, C <sub>3</sub> B	C <sub>11</sub> S <sub>4</sub> B/α, liquid <sup>a</sup>	
	69.7	21.2	9.1	1500	0.5	C <sub>2</sub> S, C <sub>3</sub> B	C <sub>11</sub> S <sub>4</sub> B, C <sub>3</sub> B/α, liquid <sup>a</sup>	
	70.2	19.4	10.4	1500	0.5	C <sub>2</sub> S, C <sub>3</sub> B	C <sub>11</sub> S <sub>4</sub> B, C <sub>3</sub> B/α, liquid <sup>a</sup>	
	Subsolidus	85.0	7.5	7.5	1300	12	C <sub>11</sub> S <sub>4</sub> B, C <sub>3</sub> B, C	C <sub>11</sub> S <sub>4</sub> B, C <sub>3</sub> B, C
		84.0	12.5	3.5	1300	12	C <sub>11</sub> S <sub>4</sub> B, C	C <sub>11</sub> S <sub>4</sub> B, C
		83.5	1.5	1.5	1300	12	α', C	α', C
		78.0	11.5	10.5	1300	12	C <sub>2</sub> S, C <sub>3</sub> B, C	C <sub>2</sub> S, C <sub>3</sub> B, C
		75.0	20.0	5.0	1300	12	C <sub>3</sub> S, C <sub>3</sub> B	C <sub>11</sub> S <sub>4</sub> B, C
		75.0	24.6	0.4	1270	48	C <sub>3</sub> S, C <sub>3</sub> B	C <sub>3</sub> S, α', C <sup>b</sup>
		75.0	24.2	0.8	1270	48	C <sub>3</sub> S, C <sub>3</sub> B	C <sub>3</sub> S, α', C <sup>b</sup>
		75.0	23.8	1.2	1270	48	C <sub>3</sub> S, C <sub>3</sub> B	C <sub>3</sub> S, α', C <sup>b</sup>
		75.0	23.4	1.6	1270	48	C <sub>3</sub> S, C <sub>3</sub> B	C <sub>3</sub> S, α', C <sup>b</sup>
		75.0	22.7	2.3	1200	°	C <sub>3</sub> S, C <sub>3</sub> B	α', C <sup>b</sup>
		75.0	22.7	2.3	1270	°	C <sub>3</sub> S, C <sub>3</sub> B	α', C <sup>b</sup>
		75.0	22.7	2.3	1400	°	C <sub>3</sub> S, C <sub>3</sub> B	α', C <sup>b</sup>
75.0		22.7	2.3	1700	°	C <sub>3</sub> S, C <sub>3</sub> B	α', C <sup>b</sup>	
75.0		22.0	3.0	1270	48	C <sub>3</sub> S, C <sub>3</sub> B	α', C <sup>b</sup>	
75.0		21.3	3.7	1270	48	C <sub>3</sub> S, C <sub>3</sub> B	α', C <sup>b</sup>	
75.0		12.5	12.5	1300	12	C <sub>3</sub> S, C <sub>3</sub> B	C <sub>11</sub> S <sub>4</sub> B, C <sub>3</sub> B, C <sup>b</sup>	
72.5		22.0	5.5	1300	12	C <sub>2</sub> S, C <sub>3</sub> B, C	C <sub>11</sub> S <sub>4</sub> B, C	
70.0		28.5	1.5	1300	12	C <sub>3</sub> S, C <sub>2</sub> S, C <sub>3</sub> B	C <sub>3</sub> S, α'	
68.7		29.3	2.0	1300	12	C <sub>2</sub> S, C, C <sub>3</sub> B	α', C <sub>3</sub> S	
69.0		28.0	2.3	1300	12	C <sub>2</sub> S, C, C <sub>3</sub> B	α', C	
66.8		32.9	0.3	1300	12	C <sub>2</sub> S, α'	β, α' <sup>d</sup>	
66.9		32.4	0.7	1300	12	C <sub>2</sub> S, α'	β, α' <sup>d</sup>	
67.0		31.9	1.0	1300	12	C <sub>2</sub> S, α	β, α' <sup>d</sup>	
67.1		31.5	1.4	1300	12	C <sub>2</sub> S, α'	β, α' <sup>d</sup>	
67.2		31.0	1.7	1300	12	C <sub>2</sub> S, α'	α' <sup>d</sup>	
67.4		30.6	2.1	1300	12	C <sub>2</sub> S, α'	α' <sup>d</sup>	
67.5		29.6	2.8	1300	12	α'	α'	
67.6		29.6	2.8	1300	12	α'	α' <sup>d</sup>	
68.0		27.5	4.5	1100	24	C <sub>11</sub> S <sub>4</sub> B(β), α'	C <sub>11</sub> S <sub>4</sub> B(β) <sup>d</sup> α'	
68.0		27.5	4.5	1270	24	C <sub>11</sub> S <sub>4</sub> B(β)C <sub>2</sub> S	C <sub>11</sub> S <sub>4</sub> B, α'	
68.0		27.5	4.5	1350	24	C <sub>11</sub> S <sub>4</sub> B, α'	α, α', C <sub>11</sub> S <sub>4</sub> B	
68.8		25.0	6.2	1000	24	C <sub>11</sub> S <sub>4</sub> B(β)	C <sub>11</sub> S <sub>4</sub> B(β) <sup>d</sup>	
68.8		25.5	6.2	1260	1	C <sub>11</sub> S <sub>4</sub> B(β)	C <sub>11</sub> S <sub>4</sub> B(β)	
68.8		25.0	6.2	1270	1	C <sub>11</sub> S <sub>4</sub> B(β)	C <sub>11</sub> S <sub>4</sub> B	
68.0		25.0	6.2	1500	1	C <sub>11</sub> S <sub>4</sub> B	C <sub>11</sub> S <sub>4</sub> B/α	
70.0		20.0	10.0	1000	24	C <sub>11</sub> S <sub>4</sub> B(β)	C <sub>11</sub> S <sub>4</sub> B(β)	
70.0		20.0	10.0	1300	1	C <sub>11</sub> S <sub>4</sub> B(β), C <sub>3</sub> B	C <sub>11</sub> S <sub>4</sub> B, C <sub>3</sub> B	
68.0		14.5	17.5	1000	168	C <sub>11</sub> S <sub>4</sub> B(β), C <sub>3</sub> B	CS(β), C <sub>3</sub> B	
66.7		28.7	4.6	1300	72	CC, BH, S	α', RK	
66.7		28.0	5.3	1300	72	CC, BH, S	α', RK	
66.2		33.1	0.7	1300	72	CC, BH, S	β	
65.8	32.9	1.3	1300	72	CC, BH, S	β		
65.3	32.7	2.0	1300	72	CC, BH, S	α', RK		
64.9	32.5	2.6	1300	72	CC, BH, S	α', RK		
66.6	16.9	16.5	1000	168	C <sub>2</sub> S, C <sub>2</sub> B	CS, C <sub>3</sub> B		
62.5	25.0	12.5	1000	168	C <sub>3</sub> B, CS	C <sub>3</sub> B, CS		
60.0	35.0	5.0	1000	168	CC, BH, SH	C <sub>3</sub> B, CS <sup>e</sup>		

TABLE IV (Continued)

CaO (mol %)	SiO <sub>2</sub> (mol %)	B <sub>2</sub> O <sub>3</sub> (mol %)	Temp. (°C)	Time (h)	Starting material	Final products
65.0	25.0	10.0	1000	168	CC, BH, SH	C <sub>3</sub> B, CS, C <sub>11</sub> S <sub>4</sub> B <sup>e</sup>
75.0	15.0	10.0	1300	24	CC, BH, SH	C <sub>7</sub> , C <sub>3</sub> B, C <sub>11</sub> S <sub>4</sub> B
75.0	3.0	22.0	1300	24	CC, BH, SH	C, α', C <sub>11</sub> S <sub>4</sub> B
70.0	29.0	1.0	1400	24	CC, BH, SH	C <sub>3</sub> S, α'
75.0	24.0	1.0	1400	24	CC, BH, SH	C <sub>3</sub> S, α', C

## Notes

α, α'-Ca<sub>2</sub>SiO<sub>4</sub>.β, β'-Ca<sub>2</sub>SiO<sub>4</sub>.α', α'-Ca<sub>2</sub>SiO<sub>4</sub>.C<sub>2</sub>S, γ-Ca<sub>2</sub>SiO<sub>4</sub>.

RK, Rankinite.

CS, Wollastonite, βCaSiO<sub>3</sub>.(β), Low-temperature polymorph of C<sub>11</sub>S<sub>4</sub>B.<sup>a</sup> Products before the/were obtained on slow cooling, those following the/were obtained on quenching.<sup>b</sup> Free lime determinations undertaken.<sup>c</sup> Various trials undertaken to obtain data on the decomposition of C<sub>3</sub>S.<sup>d</sup> DTA experiment.<sup>e</sup> Comparable experiments made using quartz instead of silicic acid, contained residual quartz.

CC, calcium carbonate.

BH, boric acid.

SH, silicic acid.

S, silica (quartz)-minus 160 BS mesh.

at subsolidus temperatures. The second principal difference concerns the additional data obtained in the title study on the stability relationships between Ca<sub>2</sub>SiO<sub>4</sub> polymorphs and the extent and mechanism of boron solid solution in Ca<sub>2</sub>SiO<sub>4</sub>.

Data on ternary compositions, on the pseudobinary join, including the ternary compound, together with those in the literature, have been used to revise the liquidus phase diagram for the high CaO portions of this system: Fig. 7 shows the results: quenching data which elucidate subsolidus compatibilities are given in Table IV. The disposition of liquidus features is much affected by subsolidus compatibilities. Of the four calcium silicates (CaSiO<sub>3</sub>, Ca<sub>3</sub>Si<sub>2</sub>O<sub>7</sub>, Ca<sub>3</sub>SiO<sub>5</sub> and Ca<sub>2</sub>SiO<sub>4</sub>) only Ca<sub>2</sub>SiO<sub>4</sub> forms a significant range of boron-containing solid solutions, the direction of which is shown to be coincident with the join extending towards Ca<sub>3</sub>B<sub>2</sub>O<sub>6</sub>. Neither Ca<sub>3</sub>SiO<sub>5</sub> nor CaO forms solid solutions with B<sub>2</sub>O<sub>3</sub>, but the rather delicate balance of free energies between Ca<sub>3</sub>SiO<sub>5</sub> and Ca<sub>2</sub>SiO<sub>4</sub> is much affected by solid solution which results in an enhancement of the stability of the dicalcium silicate type phase. Two additional two-phase regions are created, one of Ca<sub>3</sub>SiO<sub>5</sub> plus Ca<sub>2</sub>SiO<sub>4</sub> solid solution, the other of CaSiO<sub>3</sub> and Ca<sub>2</sub>SiO<sub>4</sub> solid solution. Therefore, with increasing B<sub>2</sub>O<sub>3</sub> content the first ternary three-phase regions to be encountered depending on Ca:Si ratio are (Ca<sub>3</sub>Si<sub>2</sub>O<sub>7</sub>, CaSiO<sub>3</sub>, and Ca<sub>2</sub>SiO<sub>4</sub> solid solution) and (Ca<sub>3</sub>SiO<sub>5</sub>, CaO, and Ca<sub>2</sub>SiO<sub>4</sub> solid solution). The latter region is of special relevance to cement making; thermodynamic stabilization of dicalcium silicate by solid solution results in the amount of potential Ca<sub>3</sub>SiO<sub>5</sub> formed at conventional clinkering temperatures (1400–1550 °C), decreasing very rapidly as boron is added. This, coupled with the progressive contraction of the range of thermal stability of Ca<sub>3</sub>SiO<sub>5</sub>, results in its rapid disappearance from the liquidus surface. Ca<sub>3</sub>SiO<sub>5</sub> is shown

as persisting from its incongruent melting point to a liquidus peritectic at > 1700 °C, but this interpretation is based on incomplete evidence. Indeed, we have not found definite evidence that Ca<sub>3</sub>SiO<sub>5</sub> has any stability field at liquidus temperatures: what is proven is that Ca<sub>2</sub>SiO<sub>4</sub> solid solutions and CaO coexist with melt along a univariant boundary curve and that this curve appears at the liquidus at some temperature > 1700 °C and terminates at a lower temperature bound at a liquidus peritectic at 1400 °C. At this peritectic, lime and Ca<sub>2</sub>SiO<sub>4</sub> coexist with Ca<sub>11</sub>(SiO<sub>4</sub>)<sub>4</sub>(BO<sub>3</sub>)<sub>2</sub> and liquid. This peritectic point is only slightly lower, by 20 °C, than the thermal maximum which marks the incongruent melting of Ca<sub>11</sub>(SiO<sub>4</sub>)<sub>4</sub>(BO<sub>3</sub>)<sub>2</sub> itself.

This system still contains a number of features which require further investigation. From the standpoint of crystal chemistry, the most important is the influence of borate on the polymorphism and crystal structures of the Ca<sub>2</sub>SiO<sub>4</sub> polymorphs. The high-temperature α and α' phases of dicalcium silicate are believed to have simple, salt-like structures, resembling K<sub>2</sub>SO<sub>4</sub>. But in practice, and despite many attempts, their crystal structures have never been fully elucidated. Moreover, powder X-ray data can be a misleading indicator of structure type. All the high-temperature dicalcium silicate structures have X-ray powder patterns which are similar; this, together with the rapidity of some of the phase transformations implies, but does not prove, that close structural similarities exist. Yet in a technological context, phase transformations between the polymorphs are important; with their large attendant volume changes, they make it impractical to use Ca<sub>2</sub>SiO<sub>4</sub> in dimensionally stable refractories. The largest volume change occurs when one of the structurally related phases in the (α, α'/β) family transforms to γ, the olivine-structured polymorph. Although B<sub>2</sub>O<sub>3</sub> is a good stabilizer for



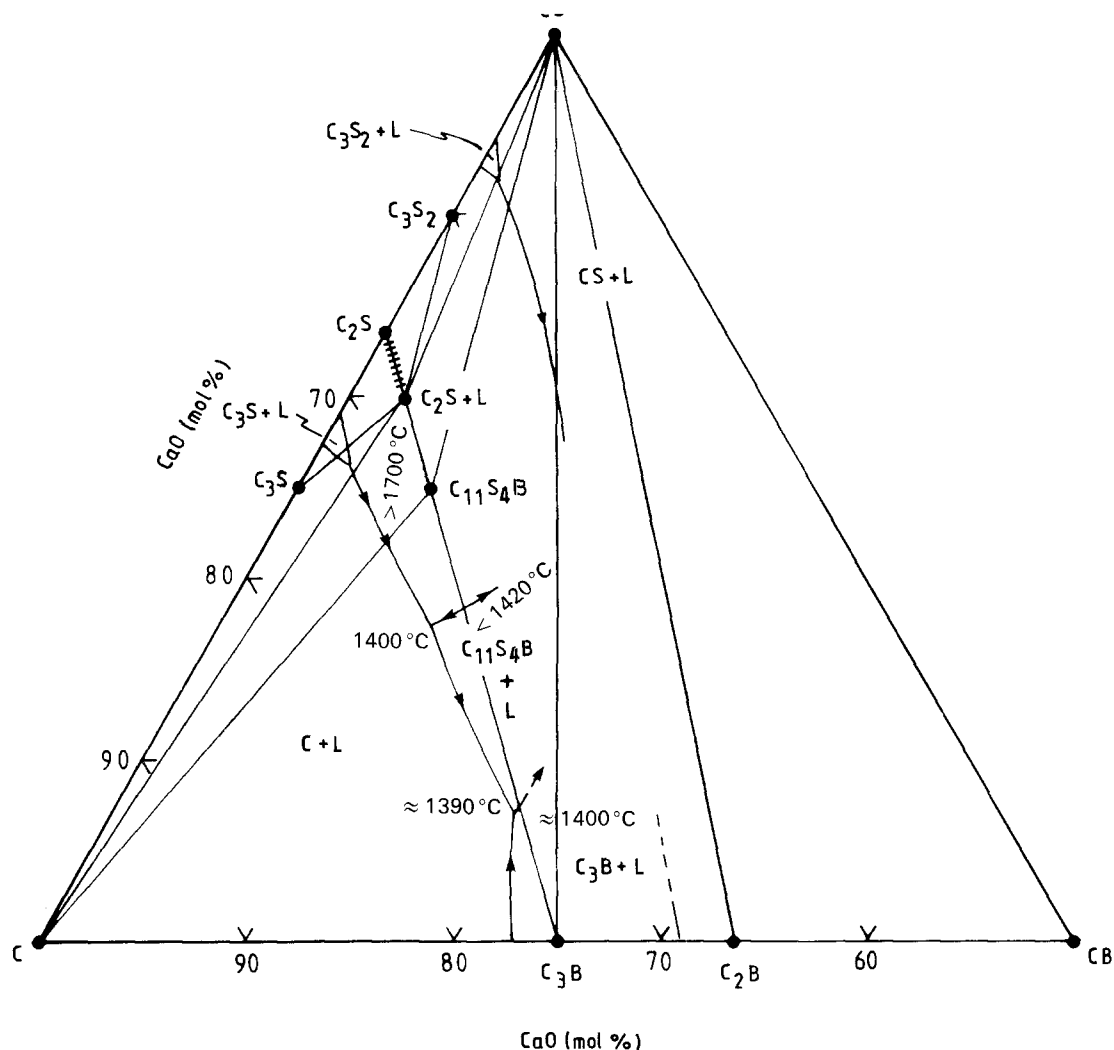


Figure 7 Ternary liquidus relationships of part of the CaO-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> system.

alpha-type structures, where it suppresses temperature-induced polymorphic transformations, it may be somewhat volatile, particularly in reducing atmospheres and those containing water vapour. Boric oxide is also a good flux, greatly lowering solidus temperatures of complex oxide mixtures. On that account it may be an unacceptable constituent of a refractory. Nevertheless, there may exist scope for exploring the refractory potential of boron-stabilized dicalcium silicate solid solutions.

The mechanism of solid solution of boric oxide in Ca<sub>2</sub>SiO<sub>4</sub> is also unusual, inasmuch as few authenticated examples of solid solutions amongst silicates which require formation of cationic defects have been reported. The electrical and ion-conduction properties of these solid solutions might warrant further investigation.

Boron-substituted  $\alpha$ -type Ca<sub>2</sub>SiO<sub>4</sub> is reactive with water, and forms cementitious composites. While the reactivity of boron-doped Ca<sub>2</sub>SiO<sub>4</sub> does not appear to be as good as that of Ca<sub>3</sub>SiO<sub>5</sub>, particularly with respect to early strength gain, experimental cement clinkers containing mainly boron-doped Ca<sub>2</sub>SiO<sub>4</sub> do achieve good 7, 28 and 365 day strengths. Boron is known to be a powerful retarder for cement hydration but, when incorporated into a clinker based on

$\alpha$  modifications of dicalcium silicate, it does not significantly affect strength gain beyond about 7 days, relative to belitic clinkers formulated with more conventional stabilizer combinations.

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### References

1. G. A. RANKIN and F. E. WRIGHT, *Amer. J. Sci.* **31** (1915) 1.
2. A. MUAN and E. F. OSBORN, "Phase Equilibria Among Oxides in Steelmaking", American Iron and Steel Institute, New York (Addison Wesley, Reading, MA, 1965) Library of Congress, 64-25807.
3. R. W. NURSE, in "The Dicalcium Silicate Phase", Proceedings of the Third International Symposium on the Chemistry of Cement, London (1952) pp. 56-90.
4. J. WELCH and W. GUTT, *J. Amer. Ceram. Soc.* **42** (1959) 11.
5. E. T. CARLSON, *J. Res. Nat. Bur. Stand.* **9** (1932) 825.
6. E. P. FLINT and L. S. WELLS, *ibid.* **17** (1936) 727.
7. K. SUZUKI, H. KAZUTAKA and J. HIDEO, *J. Ceram. Soc. Jpn* **79** (1971) 199.

8. A. A. COLVILLE and P. A. COLVILLE, *Amer. Mineral.* **62** (1977) 1003.
9. J. V. SMITH, I. L. KARLE, H. HAPTMAN and J. KARLE, *Acta Crystallogr.* **13** (1960) 454.
10. R. F. KEVTSOVA and N. V. BELOV, *Sov. Phys. Crystallogr.* **5** (1961) 659.
11. F. P. GLASSER and K. MOHAN, *Cement Conc. Res.* **7** (1977) 1.
12. E. G. SHAME and F. P. GLASSER, *Brit. Ceram. Trans. J.* **86** (1987) 13.
13. K. SUZUKI and I. HIRA, *J. Ceram. Soc. Jpn* **78** (1970) 189.

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