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Properties and composition of bredigite-structured phases

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Bredigite has an ideal composition close to $Ca_7Mg(SiO_4)_4$ and a structural formula indicating co-ordination numbers, $X^{[12]}X_2^{[9]}Y_4^{[10]}M^{[6]}[TO_4]_4$ (T = tetrahedrally co-ordinated ion). Experiments show that Ba or Sr can replace Ca in the large $X^{[12]}$ sites while Mg in the M site may be partially replaced by Mn^{2+}. When $X^{[12]}$ sites are occupied by two different ionic species, partial site ordering occurs. Bredigite-structured phases may occur in periclase refractories and high-Mg cement clinker. Ca–Mg bredigite reacts slowly with water; data on its hydration behaviour at 20 and 200° C are presented.

1. Introduction

Calcium silicates occur as important secondary phases in periclase (MgO) refractories; conversely, free MgO may occur in cement clinkers rich in calcium silicates. Therefore, the number and identity of compounds in the CaO–MgO–SiO_2 system has been the subject of numerous studies, on account of their technological importance.

The calcium–magnesium orthosilicates exhibit certain structural similarities, hence the number and formulae of these silicates have presented investigators with numerous difficulties. In particular, the existence of bredigite as a phase distinct from either $\alpha'Ca_2SiO_4$ or merwinite (ideally $Ca_3Mg(SiO_4)_2$) solid solutions and having a formula close to $Ca_{1.7}Mg_{0.3}SiO_4$ has only recently been established from mineralogical, crystal structure and phase equilibrium evidence: these data were reviewed earlier [1].

Bredigite has the ideal polyhedral formula $X^{[12]}X_2^{[9]}Y_4^{[10]}M^{[6]}[TO_4]_4$ where the figures in brackets are co-ordination numbers and $[TO_4]$ indicates an isolated tetrahedral group [2]. Because the $X^{[12]}$ and $M^{[6]}$ polyhedra occupy special positions, there are two non-symmetrically related sites of each type, spaced almost exactly $a/2$ apart along their respective diad axes. Moore and Araki used the notation X(11) and X(12) to differentiate the large $X^{[12]}$ sites and M(11) and M(12) for the two distinct octahedral sites. Si is the only cation thus far known to occupy the T sites and Mg, with some replacement by Mn, the octahedral M sites. The large X and Y sites are generally occupied by Ca, although some Ba can substitute in the $X^{[12]}$ site and some Mg in one of the $Y^{[10]}$ sites [2]. It is the ability of Mg to substitute for some of the Ca that is probably responsible for the range of Ca:Mg solid solutions that have been observed [1]. This report, an extension of our earlier work, explores further substitutions in these sites as well as investigating the hydration properties of bredigite.

2. Specimen preparations

2.1. Bredigite syntheses

All preparations were made from powdered quartz crystal (minus 100 mesh; 0.06% material nonvolatile with HF) and the appropriate dried 'Analar' grade carbonates or oxide (MgO) and nitrate ($Sr(NO_3)_2$). Weighed quantities of reactants in ~ 15 g batches were blended together under ethanol in an agate mortar, dried and heated in Pt crucibles to ~ 800° C for 8–12 h and reaction completed at 1000–1350° C. The kinetics of solid-state formation of bredigite are sluggish, so each mix was removed at 7 d intervals, reground and returned to the furnace. The progress of reaction was monitored by powder X-ray diffraction. Heating was continued until no further changes occurred and the powder pattern was characteristic of a single-phase bredigite.

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2.2. Compressive strength testing

For strength tests, bredigite of the composition $Ca_{1.7}Mg_{0.3}SiO_4$ was made into 6.35 mm cubes using the technique described by Imlach and Taylor [3]. The surface area of the bredigite was determined by Rigden's air permeability to be 0.14 $m^2 g^{-1}$. Since bredigite reacted only slowly with water, an activator (CaO) was also added. Two batches of cubes were made; the first was a 20:1 mixture by weight of bredigite and CaO, the second a 20:3 mixture of the same components. To both batches, sufficient boiled distilled water was added to produce a constant water: solid ratio of 0.35, and after mixing in CO_2-free conditions, cubes were fabricated at a pressure of 7 MN m^{-2}. For comparison, a separate set of cubes were fabricated from ordinary Portland cement made to B.S. 12; the surface area of this cement was determined to be 0.37 $m^2 g^{-1}$ (Rigden). These cubes were similarly pressed, but at a water:cement ratio 0.20. The fabricated cubes typically weighed about 0.6 g.

The cubes were cured at 100% r.h. in a sealed system, to which "Carbosorb" had been added to ensure a CO_2-free atmosphere. Cubes were removed for compressive strength tests at intervals of 7, 28 and 91 d. In addition, 10 cubes of the 20:1 bredigite:CaO mix were allowed to set for 24 h at 100% r.h. and subsequently autoclaved under saturated steam conditions for 48 h at 200° C.

3. Experimental results

3.1. Chemical substitutions in bredigite

Previous studies of the replacement of Mg in bredigite by other ions were somewhat inconclusive; although Zn, Co and Ni could not be substituted for Mg at 1300–1350° C [1] and are not reported to occur in natural or slag bredigites, Mn does substitute in slag bredigites where 20% replacement of Mg by Mn has been observed [2].

The choice of an appropriate reaction temperature is difficult; CaMg bredigite decomposes above 1372 ± 2° C [4] and the substitution of other ions for Mg has, at least at the outset of the investigation, an unknown effect on the upper limit of thermal stability of the notional bredigite solid solution. Moreover, the kinetics of bredigite formation entirely by solid-state reaction at lower temperatures are known to be sluggish. Therefore, reactions to determine the extent of bredigite solid solution were generally undertaken at lower temperatures (1000–1100° C) such that no liquid developed, but lengthy annealing periods ranging between 70 and 125 d were required. Under these conditions, Co^{2+} (radius 7.45 nm) appear not to substitute for Mg (7.2 nm) despite the similarity in size. The only change observed upon prolonged annealing was that, at ambient, the proportion of $\gamma:\beta$ Ca_2SiO_4, when cooled from 1100° C, was greater than when cooled from 1300° C. It also proved impossible to synthesize Mn bredigite. The results of prolonged annealing of this composition were virtually identical to those of the attempted Co bredigite, yielding Ca_2SiO_4 and merwinite solid solutions.

In the type specimen [2] 36% of the M(11) site is occupied by Mn, compared with only 7% Mn in the M(12) site [2]. As this raises the possibility that transition elements can fill the M(11) site but not occupy the M(12) site to any significant extent, synthesis of the composition $Ca_{14}MgMn(SiO_4)_8$ was attempted. This gave a single phase, the diffractometer trace of which could be indexed as a bredigite pattern*. It was stable between 1000 and 1300° C but at 800° C the green Mn–Mg bredigite transformed to a fine, pale brown powder which was a mixture of bredigite and γ-Ca_2SiO_4 type solid solutions.

The existence of large, 12-co-ordinated sites in bredigite suggests the possibility of Sr and Ba substitution; The crystal-structure refinement [2] of the type slag mineral indicated that Ba was concentrated in the X(11) site. To test these and other possibilities, attempts were made to synthesize compounds with both large sites [X(11) and X(12)] filled with Sr and Ba. The cell parameters of six bredigite-structured compositions are compared in Table I, while other physical data are given in Table II.

These cell parameters, together with the fractional co-ordinates given by Moore and Araki [2], were used to generate calculated diffractometer traces, as described in the previous study [1]. These computer-synthesized diffractometer traces were superimposed on the actual traces and the extent of misfit, if any, noted. Slight misfits between the traces for the Ba–Ca and Ba–Sr bredigite were attributed to traces of merwinite solid solution persisting as a minority phase in the sintered product. A further potential source of

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*The phase at $Ca_{14}MgMn(SiO_4)_8$ has $a = 10.928$ (4), $b = 18.426$ (7), $c = 6.786$ (2): (e.s.ds in brackets). An indexed powder pattern will be submitted to the *Powder Diffraction File*.

TABLE I Cell parameters of bredigite-structured phases, $XYCa_{12}Mg_2(SiO_4)_8$

X	Y	a (nm)	b (nm)	c (nm)	V (10^3 nm^3)
Ca	Ca	109.06(2)†	183.82(6)	67.57(2)	1354.60
Sr	Ca	109.16(3)	184.00(5)	67.61(2)	1358.08
Sr	Sr	109.21(3)	184.97(5)	67.87(2)	1371.03
Ba	Ca	109.61(4)	184.78(7)	67.75(2)	1372.29
Ba	Sr	109.34(4)	185.43(6)	67.92(2)	1376.79
Ba	Ba*	109.01(3)	184.58(6)	135.97(5)	2 × 1367.93

*Space group *Cmcm*, the others are *P2nn*.

†Values in () are the standard deviation of the last significant figure.

error is that the fractional atomic co-ordinates of an essentially Ca–Ca bredigite become progressively less reliable when applied to isostructural phases containing increasing quantities of larger-sized replacement ions.

The X-ray powder patterns also provide evidence concerning the distribution of cations in X(11) and X(12) sites. The intensity of the 110 reflection is rather sensitive to the difference between ordered and disordered arrangements. The observed intensity values of 110 may be compared with calculated values, assuming different site population distributions, in Table III. The observed values of the 110 reflections indicate that some ordering of the cations has taken place in the $X^{[12]}$ sites.

Similar calculations, made for $Ca_{14}MgMn(SiO_4)_8$, disclose that the intensity of the 110 reflection is < 1 for a disordered Mg–Mn distribution, while $I = 3$ and 5 for ordering of Mg on the M(11) and M(12) sites, respectively. The diffractometer trace gives $I = 2.5 \pm 1$, indicating the probability that some ordering of Mg and Mn occurs. Unfortunately, the 110 reflection is relatively weak and, moreover, occurs at high d-spacings: it is thus difficult to measure its intensity accurately and thereby determine the quantitative extent of site ordering.

TABLE II Density of bredigite-structured phases–$XYCa_{12}Mg_2(SiO_4)_8$

X	Y	Formula weight	Calculated	Measured†
Ca	Ca	1346.4	3.30	3.32
Sr	Ca	1393.9	3.41	3.39
Sr	Sr	1441.5	3.49	3.46
Ba	Ca	1443.7	3.49	3.48*
Ba	Sr	1491.2	3.60	3.55*
Ba	Ba	1540.9	3.74	3.72*

*Contains traces of merwinite impurity, by X-ray diffraction

†Determined by density bottle; measured values are ± 0.03; density units are g cm^{-3}.

3.2. Phases related to bredigite

The Ba–Ba "bredigite" could not be satisfactorily indexed using a bredigite-type cell. Moreover, the general fit of intensities between observed and calculated patterns, using a bredigite model, was markedly less satisfactory relative to other examples, particularly at low angles. Moore and Araki [2] note that the low-angle reflections are "sensitive to cation ordering and short-range distortions". Consequently, a study of the crystallography of this phase has been undertaken; while closely related structurally to bredigite, it is apparent that the phase has a centred cell with doubled c. Full details and an indexed powder pattern will be reported elsewhere [5]. Further support is provided by a comparison of densities, shown in Fig. 1. The densities of the five bredigite-structured phases listed in Table II lie, within experimental error, on a linear trend whereas the calculated density for the Ba–Ba phase lies about 0.04 g cm^{-3} above the position indicated by simple extension of the trend line. Apparently the atomic arrangement in the Ba–Ba phase represents a more efficient packing than is achieved in the bredigite structure.

3.3. Hydration of Ca–Mg bredigite

The results of compressive strength measurements on bredigite–CaO cubes may be contrasted with

TABLE III Relative intensities of the 110 reflections of phases $XYCa_{12}Mg_2(SiO_4)_8$

Site assignment		Calculated*		Observed†	
X	Y	O	D	diff.	Guinier
Sr	Ca	8	< 1	–	3
Ba	Ca	25	< 1	6	10
Ba	Sr	9	< 1	~ 2	6

*O and D refer to an ordered and disordered population distribution, respectively.

†Observed intensities from diffractometer and Guinier (film recording), respectively.

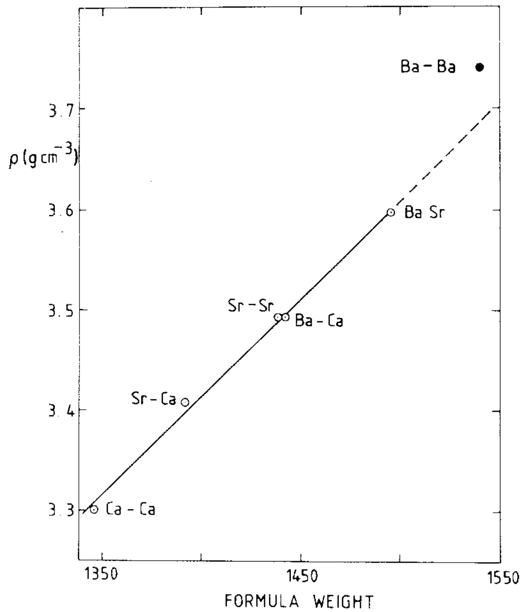

Figure 1 Densities and formula weights of five bredigite-structured phases (open circles; see Table I for cell contents). The extension of the trend line (dashed) whose best fit equation is $\varphi = 2.05 \times 10^{-3}$, formula weight + 0.568, does not include the value for the Ba–Ba phase, which is believed to represent a different structural variant.

those obtained on Portland cement in Table IV. After 7 d cubes made from a 20 : 1 bredigite : CaO mixture were too weak to be tested. The results given in Table IV are the mean of the four highest values obtained in replicate determinations. Being weak, the cubes generally failed by crumbling whereas the strength of the neat cement cubes were such that they shattered.

Fragments of broken cubes were examined by powder X-ray diffraction. The 20 : 1 mix contained unaltered bredigite and $Ca(OH)_2$, together with traces of $CaCO_3$, after 7 d. The X-ray diffraction patterns obtained after 7 and 28 d from the 20 : 3 mix contained these phases together with an, as yet, incompletely characterized phase having its most conspicuous reflections at 49 and 26.2 nm; in addition a third reflection at 19.3 nm probably overlaps a bredigite reflection, thereby contributing to its anomalously strong intensity. Whatever phase contributed to these reflections seemed to be essentially absent after 91 d curing.

TABLE IV Cube compressive strength (MN m^{-2})

Material*	Hydration Duration at 20° C (d)		
	7	28	91
20 : 1	–	1.2	3.7
20 : 3	1.4	2.2	4.5
OPC	100	140	178

*Ratios are weight of Ca-bredigite: lime. OPC = ordinary Portland cement to B.S. 12.

Bredigite and $Ca(OH)_2$ had completely disappeared from the autoclaved cubes which consisted of mixtures of brucite ($Mg(OH)_2$) and $Ca_8Si_5O_{18}$. The autoclaved cubes were barely coherent and had essentially zero strength.

5. Discussion and conclusions

Large cations can replace Ca in the $X^{[12]}$ sites where they, apparently, preferentially occupy the X(11) sites. Complete replacement occurs with Sr as the substituting cation, while Ba replacement appears to be restricted to about 50%. However, further work is required to determine the preferred site occupancies and the exact extent of Ba solid solutions. Complete replacement of Ca by Ba in the $X^{[12]}$ sites results in a new, bredigite-related structure.

A bredigite structure may be formed by replacing up to half the Mg ions by Mn. This limit probably occurs because Mn can occupy the M(11) site but not, to any extent, the M(12) site. This may also be true for other transition elements and is a further area requiring more detailed investigation.

Bredigite hydrates at a slow, but appreciable rate at 20° C in an alkaline environment. However, after 91 d the compressive strength of lime-activated bredigite cubes is too low to consider that bredigite has much potential as a desirable constituent of cement clinker, although undoubtedly preferable to free MgO in this respect. Although bredigite hydrates rapidly at 200° C, its high-temperature hydration products are incoherent. Thus, bredigite is unlikely to prove to be a desirable constituent either of cement clinker of periclase refractories where it is potentially liable to react with hot H_2O vapour.

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