X-ray investigation of bredigite.

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INTRODUCTION.

THE X-ray work described below has been done on crystals of bredigite obtained from two different sources, the natural mineral from Scawt Hill, County Antrim, and the synthetic mineral from spiegel-eisen slags. Both types of material have been fully described by Tilley and Vincent (1948). Their analysis shows that the slag mineral is a calcium orthosilicate in which Ca is partly replaced by Mg, Mn, and Ba, the extent of the replacement being represented by the formula $(Ca_{1.59}Ba_{0.08}Mg_{0.31}Mn_{0.09})SiO_4$. Tilley and Vincent conclude that this ortho-rhombic (pseudo-hexagonal) phase is identical with the high-tempera-ture form α' of pure Ca_2SiO_4, the existence of which was suggested by Bredig (1943a), and confirmed by Trömel (1949) using a high-tempera-ture powder camera. Bredig (1943a) also suggests, on the basis of a comparison of X-ray powder patterns, that the crystal structure of α'-Ca_2SiO_4 is similar to that of β-K_2SO_4. The present single-crystal work was originally undertaken in order to investigate the structure of α'-Ca_2SiO_4 more fully.

UNIT-CELL DETERMINATION, AND RELATIONSHIP BETWEEN BREDIGITE AND PURE α'-Ca_2SiO_4.

The orthorhombic (pseudo-hexagonal) symmetry of bredigite was confirmed, and the cell dimensions found for the natural and the syn-thetic minerals were the same within the limits of experimental error.[2] These are quoted in table I, together with the cell dimensions given by Bredig (1950) for pure α'-Ca_2SiO_4 at 700° C., and also the cell dimen-sions of β-K_2SO_4. It will be seen that, allowing for the larger ionic radius of K^+ compared with Ca^{2+}, the cell dimensions of β-K_2SO_4 correspond with those reported by Bredig for α'-Ca_2SiO_4, but that the

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[2] The crystals obtained from rock sections were too imperfect for anything but an approximate determination of cell dimensions, and all further work was done on the slag mineral.

a and b dimensions found for bredigite are approximately twice those reported by Bredig for pure α'-Ca_2SiO_4.

TABLE I. Orthorhombic unit-cell dimensions.

Phase.	Cell dimensions in Å.			b/a.	Content of unit cell.
	a.	b.	c.		
Bredigite (Scawt Hill) ...	$10\cdot93\pm0\cdot05$	$18\cdot41\pm0\cdot07$	$6\cdot75\pm0\cdot02$	$1\cdot69$	16
Bredigite (slag)	$10\cdot91\pm0\cdot03$	$18\cdot41\pm0\cdot05$	$6\cdot76\pm0\cdot02$	$1\cdot69$	
α'-Ca_2SiO_4 at 700° C. ... (Bredig, 1950)	$5\cdot30$	$9\cdot55$	$6\cdot78$	$1\cdot80$	—
β-K_2SO_4	$5\cdot73$	$10\cdot01$	$7\cdot42$	$1\cdot75$	4
α'-Ca_2SiO_4 at 750° C. ...	$11\cdot08\pm0\cdot05$	$18\cdot55\pm0\cdot07$	$6\cdot76\pm0\cdot02$	$1\cdot68$	—

The latter discrepancy may arise, not from any real difference between bredigite and α'-Ca_2SiO_4, but because the dimensions for bredigite were obtained from single-crystal photographs, while those for α'-Ca_2SiO_4 were obtained from powder photographs taken by Trömel. The single-crystal photographs show that the intensities of reflections with h and/or k odd (for the large unit cell) are in general weaker than those with h and k even, and thus powder lines corresponding to the former reflections might not have been detected. In an attempt to resolve this point, high-temperature photographs of pure α'-Ca_2SiO_4, taken by Trömel and kindly loaned to the author, were examined, and it was not found possible to assign indices to all the observed lines on the basis of the cell dimensions given by Bredig. A fairly satisfactory interpretation was obtained using the cell dimensions given in the last line of table I, in which it will be seen that the a and b dimensions are approximately, but not exactly, twice those given by Bredig. At least six weak lines cannot be indexed at all if these a and b dimensions are halved.

This observation, however, does *not* establish the identity of bredigite and α'-Ca_2SiO_4, since visual comparison of the two powder photographs shows some marked differences in the two patterns. It seems unlikely that this is due purely to differential thermal expansion, since Trömel's photographs show that little change takes place in the pattern of α'-Ca_2SiO_4 between 750° C. and 1000° C. It is more probable that there is a real, though probably a small, structural difference between bredigite and the α'-Ca_2SiO_4 prepared by Trömel. This structural difference, if it exists, is probably not due to the presence of metallic elements other than Ca in bredigite, since powder photographs of synthetic Ca_2SiO_4 prepared and quenched from 1790° C. by Rait and Goldschmidt (1945) are practically identical with the bredigite pattern. It is there-

fore concluded that the exact relationship between bredigite and the phases occurring in the pure Ca_2SiO_4 system is not yet definitely established, and that this point requires further investigation, which the author hopes to be able to undertake.

Number of atoms per unit cell.—The observed density of the slag mineral is $3·40 \pm 0·02$ gm./c.c. (Tilley and Vincent, 1948), and the number of formula units per unit cell is 16. This result is in agreement with the predicted relationship to the β-K_2SO_4 structure for which the number of formula units is 4 (see table I).

Space-group.—Systematic absences among the X-ray reflections show that the lattice is primitive, and that there is a diagonal glide-plane perpendicular to the z-axis. The first crystal to be examined, extracted from the vugs of the slag, appeared to have a pseudo-diagonal glide-plane perpendicular to the y-axis, that is, there were only a few $h0l$ reflections for which $(h+l)$ was odd, the strongest being 401. Later, evidence was found that these reflections were due, at least in part, to the presence of an extra phase in these bredigite crystals. Crystals afterwards obtained from sections appeared to be free from this extra phase, and a Weissenberg photograph showed that $(h+l)$ was even for all observed $h0l$ reflections except for 401 which was extremely weak. The appearance of this reflection may be due to the presence of a trace of the extra phase, or it may be a real effect, for which an explanation must be sought when the structure analysis has been carried farther.

For the purposes of the structure determination it will be assumed for the present that the glide-plane perpendicular to the y-axis is real, and that the space-group is therefore either *Pmnn* or *P2nn*. If the space-group is *Pmnn* all zones of reflections will be centric, whereas if the space-group is *P2nn* the $h0l$ and $hk0$ zones of reflections will be acentric. Application of the distribution method (Howells, Phillips, and Rogers, 1950) to the observed $hk0$ reflections indicates that this zone is centric (see fig. 1), and thus there is a strong probability that the space-group is *Pmnn*. As the structure analysis proceeds this question will be examined more fully.

The space-group for β-K_2SO_4 is *Pmcn*. Taken in conjunction with the doubling of the a and b dimensions, the difference between the space-groups for bredigite and β-K_2SO_4 indicates a difference between the structures which must involve more than slight displacements of corresponding atoms.

Preliminary work on the structure of bredigite.—An $(hk0)$ Patterson projection has confirmed the similarity of the array of Ca and Si atoms

in bredigite and the K, Na, and S atoms in glaserite. It also indicates two possible arrangements of the oxygen atoms, one of which resembles the arrangement in glaserite. Further work to determine the exact nature of the structure is now proceeding.

Orientation of the Indicatrix.—Tilley and Vincent (1948) suggested an arbitrary definition of the optic axial plane as (100) and the prismatic cleavages as (110), thus making $b \backsimeq \sqrt{3}a$, which is in accordance with the
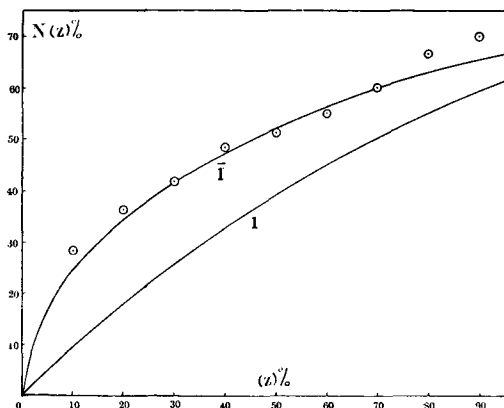

FIG. 1. Intensity distribution curve for the $hk0$ reflections from bredigite. (z) = intensity of a reflection expressed as a percentage of the average intensity, $N(z)$ = percentage of reflections having intensities $\leqslant (z)$. Curve marked $\bar{1}$ is the calculated distribution for a centric zone, and that marked 1 is the calculated distribution for an acentric zone. ⊙ experimental points.

unit cell of table I. However, direct comparison of the optical and X-ray results from several crystals (both single and twinned) showed that the optic axial plane is in fact (010) (acute bisectrix parallel to z). The cleavage plane thus becomes (130), and the common form of twinning is on (110) not on (130). The latter is also in accordance with X-ray observations, since, of the four twinned crystals examined, all were twinned on (110).

THE EXTRA PHASE PRESENT IN CRYSTALS OF THE SLAG MINERAL.

Several bredigite crystals were extracted from vugs in the slag. A number of these proved to be single crystals of the orthorhombic phase, but X-ray photographs, particularly Weissenberg photographs, showed the presence of a few extra reflections, fainter and broader than those

of the main pattern, and always in the same position with respect to the latter.

It was not possible to interpret these extra reflections in terms of either of the twin laws observed by Tilley and Vincent (1948). To confirm this, two twinned crystals were extracted from slag sections, and both gave X-ray patterns which could be interpreted on the basis of twinning on (110). Comparison of (hk0) Weissenberg photographs of these and the crystals from the vugs showed that while the pattern from the major component of the twinned crystal matched exactly the main pattern from the 'single' crystal, the reflections from the minor component of the twinned crystal did not coincide with the broad extra reflections. Although no crystals showing twinning on (130) were obtained, so that a similar direct test was impossible, calculation showed that the extra reflections were not due to twinning on this plane.

The possibility that the extra reflections were due to the presence of one of the other phases found in the slag, monticellite (orthorhombic), melilite (tetragonal), and calcium sulphide (cubic), was also considered, but in no case did the positions of the reflections accord with the published X-ray data.

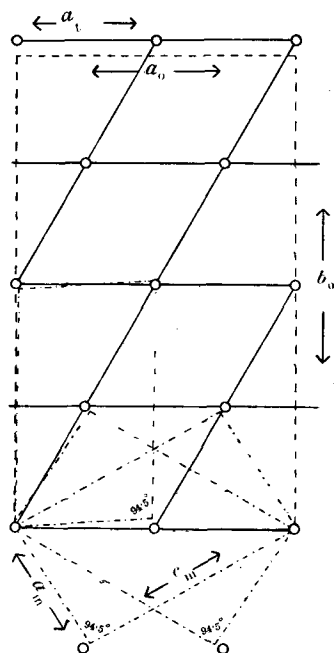FIG. 2. Relative orientations of the trigonal, orthorhombic, and monoclinic lattices.
—— Trigonal lattice $\perp$ c-axis,
– – – Orthorhombic lattice $\perp$ c-axis,
–·–·– Monoclinic lattice $\perp$ b-axis,
○ Pairs of cations which overlap in this projection in all three structures.

The only satisfactory interpretation of the extra reflections which could be found was that they were due to a small amount of a trigonal phase in fixed orientation relative to the main orthorhombic crystal. The cell dimensions of this phase compared with those of bredigite are $c_t = c_o = 6\cdot76$ Å., $a_t = a_o/2 = 5\cdot46$ Å., and $\sqrt{3}\, a_t = 9\cdot46$ Å., where $b_o = 9\cdot21$ Å., the subscripts t and o denoting the trigonal and orthorhombic phases respectively. The relative orientations of the two lattices are such that $a_t \| a_o$ and $c_t \| c_o$ (see fig. 2). Examination of the $hk0$, $hk1$, $hk2$,

and $hk3$ Weissenberg photographs suggests that the Laue symmetry of
the extra phase is $\bar{3}m$, and the association of the extra reflections with
the strongest of the $hk0$ reflections from bredigite indicates that there
is probably a strong resemblance between the two structures when
projected along the z-axis (this is not surprising considering the strongly
pseudo-hexagonal nature of the z-axis of bredigite). These observations
suggest that the extra phase is in fact the α-form of Ca_2SiO_4. High-tem-
perature powder investigations by Trömel (1949) and Van Valkenburg
and McMurdie (1947) have shown that this phase has a trigonal unit
cell, and according to Bredig (1941, 1942) it has a trigonal structure
identical with that of glaserite, $K_3Na(SO_4)_2$. The Laue symmetry of
glaserite is $\bar{3}m$, and the projections along z of structures of this mineral
and of bredigite have been shown to be probably very similar (see below).

The trigonal phase was not observed optically by Tilley and Vincent
either in the original investigation (1948) or in a re-examination of
crystals which had been used in this X-ray work. However, detection
of this phase would be difficult owing to the close similarity of the opti-
cal properties of the trigonal and orthorhombic phases (see table III),
and the uniaxial character of the trigonal phase may be masked by
stresses present in the bredigite crystal. In addition, the relative inten-
sities of the X-ray reflections show that only a small amount of the
trigonal phase is present. What little there is may be in the form of
particles which, though in parallel orientations, are very small and are
distributed throughout the specimen. This assumption of small particle
size (or of inhomogeneous strain, see above) is supported by the observed
broadening of the X-ray reflections.

No trigonal phase was detected in five crystals extracted from sections
of the slag, whereas no crystal extracted from a vug failed to show the
extra X-ray reflections characteristic of the trigonal phase. Some
suggestions may be made to account for the apparent difference in
trigonal phase content in the vugs and in the main body of the slag. It
may be due to differences in composition which could influence the
phases stable at room-temperature in two ways, first by affecting the
nature of the phase in equilibrium at a constant high temperature,
and second by altering the rate of inversion on cooling (cf. Bredig,
1950). It could also be due to different rates of cooling in the two parts
of the slag, or to a combination of the two effects.

The cell dimensions of the trigonal phase associated with bredigite
are compared in table II with those reported by other workers for the
α-Ca_2SiO_4 phase either at high temperature or stabilized by the addition

of various oxides. It will be seen that the a dimension agrees reasonably well with the other reported values, but c and hence c/a differ from the rest by about 5%.

This difference is of the same order as reported by Bredig (1943b) for the discontinuous change in the c/a ratio on heating trigonal $KNaSO_4$. Bredig attributes this increase in c/a for $KNaSO_4$ (and also the thermal effects observed by other workers) to the onset of rotation of the SO_4 group. For this compound there is no change in crystal system when the axial ratio changes, but Bredig suggests that for several other compounds, including Ca_2SiO_4, rotation of the anion group starts simultaneously with the transition from the orthorhombic to the trigonal form. He further remarks that no obvious explanation can be given for the observation that c/a is the same for pure α-Ca_2SiO_4 at 1500° C. (in which the anions are presumed to rotate) and for the stabilized α-phase at room-temperature (in which the anions would not be expected to rotate). It follows that the most direct interpretation of the differences in c and c/a, which are seen in table II, is that in the trigonal phase

TABLE II. Trigonal unit-cell dimensions.

Phase.		Cell dimensions in Å.			Reference.
		a.	c.	c/a.	
α-Ca_2SiO_4 at 1500° C. ...	... 5·45		7·18	1·32	Bredig, 1950
α-Ca_2SiO_4 at 1500° C. ...	... 5·47**		7·19**	1·31	Van Valkenburg & McMurdie, 1947
Ca_2SiO_4 containing Al_2O_3 and Na_2O	... 5·45*		7·03*	1·29	
Ca_2SiO_4 containing Fe_2O_3 and Na_2O	... 5·41*		7·01*	1·30	Greene, 1944
$7CaO.P_2O_5. 2SiO_2$ ...	... 5·39*		7·11*	1·32	Bredig, 1943a
Phase associated with bredigite	5·46±0·02		6·76±0·02	1·24	—

* Calculated on the assumption that the original figures are given in kX.
** Recalculated from Van Valkenburg and McMurdie's data.

associated with bredigite crystals the anions are not rotating, but have taken up positions in accordance with the space-group symmetry. By contrast, it would appear that in the other stabilized α-Ca_2SiO_4 structures at room-temperature the anions, though not actually rotating, occupy statistically the positions corresponding to rotation, and so the c/a ratio does not change from its value at high temperatures. All these suggestions must, however, remain very tentative until accurate X-ray intensity data are available, from which definite conclusions can be drawn about the positions of the atoms.

The relationship between the α, α', and β structures.

Detailed information is available for only one of the structures of Ca_2SiO_4, that of the β-form, larnite, which has been solved by Mrs. Midgley (1952). O'Daniel and Tscheischwili (1942) have shown that the γ-form has an olivine-type structure, while Bredig has predicted structural similarity between α-Ca_2SiO_4 and $K_3Na(SO_4)$, and between α'-Ca_2SiO_4 and β-K_2SO_4. The preliminary structure work described in this paper is in agreement with these predictions. On the basis of the knowledge so far available, it thus seems very probable that the structures of the trigonal (α), orthorhombic (α'), and monoclinic (β) forms of Ca_2SiO_4 are very similar to one another, while the transition to the γ-form involves a considerable rearrangement of the atoms. Optical data and measurements of cell dimensions support this view (see table III).

TABLE III. Physical characters of the modifications of calcium orthosilicate.

		α-Ca_2SiO_4.	α'-Ca_2SiO_4.	β-Ca_2SiO_4.	γ-Ca_2SiO_4.
Mineral name...	...	—	Bredigite	Larnite	Calcio-olivine
Crystal system	...	Trigonal	Orthorhombic	Monoclinic	Orthorhombic
Refractive indices α ...		1·724 ⎫	1·713 ⎫	1·707 ⎫	1·642 ⎫
β ...		1·724 ⎬ 1	1·717 ⎬ 2	1·715 ⎬ 3	1·645 ⎬ 4
γ ...		1·738 ⎭	1·732 ⎭	1·730 ⎭	1·654 ⎭
Optic axial angle 2V...		0	~ 30°	~ 74°	60°
Cell dimensions in Å. a		5·46 ⎫	10·91 ⎫	5·48 ⎫	5·06 ⎫
b		— ⎬	18·41 ⎬	6·76 ⎬ 5	11·28 ⎬ 6
c		6·76 ⎭	6·76 ⎭	9·28 ⎭	6·78 ⎭
β		—	—	94·5°	—
Volume in Å.^{3}	...	$\frac{1}{2}$(346)	4(339)	344	387
Contents of unit cell...		Ca_2SiO_4	$16Ca_2SiO_4$	$4Ca_2SiO_4$	$4Ca_2SiO_4$

[1] Beliankin and Lapin, 1946. Data obtained from $(Ca_{1·58}Mg_{0·32}Fe_{0·10})SiO_4$.
[2] Tilley and Vincent, 1948. Data obtained from $(Ca_{1·59}Ba_{0·08}Mg_{0·31}Mn_{0·09})SiO_4$.
[3] Tilley, 1929. Data obtained from Ca_2SiO_4 containing only a trace of Al_2O_3, FeO, and MgO.
[4] Quoted by Tilley, 1929. Data obtained from synthetic Ca_2SiO_4.
[5] Midgley, 1952.
[6] O'Daniel and Tscheischwili, 1942.

Mrs. Midgley (1952) has described the relatively small atomic movements involved in transitions from one to another of these three similar structures. This proposed mechanism of phase change would lead one to expect certain relative orientations between any two phases where they exist in conjunction.

The relative orientation of the trigonal and orthorhombic lattices, determined directly from X-ray photographs as described above, agrees with that predicted from the structures (see fig. 2). The relative orienta-

tion of the monoclinic and orthorhombic lattices could not be found directly, since no single crystal was available in which the monoclinic phase was present in conjunction with another phase. Instead, the relative orientation was found indirectly in the following manner. First the optic axial plane of larnite was found, by X-ray and optical observation of the same crystal, to be near (100), according to Midgley's (1952) choice of axes, and γ is parallel to the y-axis. The prominent twin lamellae were shown to be parallel to (100). These results are in agreement with those reported by Tilley (1929). Tilley and Vincent (1948) find several examples of larnite associated with bredigite in the Scawt Hill mineral, and give drawings showing the relative orientation of the twin lamellae of larnite and the optic axial plane of bredigite. In one case twin lamellae are at $\pm 30°$ to the optic axial planes of the two portions of a twinned bredigite crystal, and in another case the twin lamellae are at $90°$ and $\pm 30°$ to the bredigite optic axial plane. In all cases the acute bisectrices for larnite and bredigite were parallel, that is the y-axis of larnite is parallel to the z-axis of bredigite. In a plane at right angles to this direction the above data indicate that there are three possible orientations of the monoclinic relative to the orthorhombic lattice, and these are shown in fig. 2. They are in accordance with the postulated mechanism of phase change. The circles indicate the pairs of cations which overlap or partially overlap in this projection of all three structures. The anions and other cations are omitted in order not to confuse the diagram.

The fact that bredigite has been found in conjunction with larnite, and also apparently with the trigonal phase, is in agreement with Trömel's findings that for pure Ca_2SiO_4 and for Ca_2SiO_4 containing 10% $(Na_2O + Al_2O_3 + CaO)$ the trigonal phase is stable at high temperatures, the orthorhombic phase stable at intermediate temperatures, and the monoclinic phase metastable at low temperatures (Trömel and Möller, 1950). However, it is perhaps surprising to find three orientations of the monoclinic phase if this has, in fact, been formed from the orthorhombic phase, since two of these orientations are equivalent, but the third requires slightly different atomic shifts. The three orientations are, however, exactly equivalent if the monoclinic phase forms directly from the trigonal phase (cf. Tilley and Vincent, 1948, p. 262). On the evidence presented in this paper it is unfortunately impossible to decide whether the trigonal α-phase has formed from the orthorhombic α'-phase on cooling, or vice versa.

It would therefore appear (see also Greene, 1944, and Bredig, 1950)

that the equilibrium and metastable states of Ca_2SiO_4, especially when other cations are present, require a considerable amount of further investigation.

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Summary.—Preliminary work has been done on the structure of the mineral bredigite, and it has been shown that while the structure is similar to, it is not identical with, that of β-K_2SO_4. The X-ray investigation has shown the presence in some bredigite crystals of a small quantity of a trigonal phase which could not be detected optically. The optic axial plane, twin planes, and cleavage plane have been determined unambiguously. The relative orientations of the trigonal, orthorhombic, and monoclinic phases are discussed in relation to their structures.

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[1] I am indebted to Mrs. Midgley for allowing me to see her paper prior to publication.