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FURTHER STUDIES ON $6\text{CaO}\cdot 3\text{SiO}_2\cdot \text{H}_2\text{O}^*$ LESLEY DENT GLASSER AND DELLA M. ROY, *The Pennsylvania State University, University Park, Pennsylvania*

INTRODUCTION

In the course of studies in the system $\text{CaO-SiO}_2\text{-H}_2\text{O}$ (1), several new calcium silicate hydrates were prepared. One of these, C_2SH_x ,[†] termed "Phase Y" by Roy, was found to be in equilibrium with α' - C_2S and water above 800°C . at about 1000 atm. water vapor pressure. Determination of weight loss on heating to 1250°C . gave the formula $\text{C}_6\text{S}_3\text{H}$.

Small single crystals have been obtained, and the unit cell determined. The powder data have been indexed, and in addition dehydration and D.T.A. curves have been obtained.

UNIT CELL

The compound crystallizes in small prisms. Rotation and oscillation photographs about all axes, together with $Ok\bar{l}$, $1k\bar{l}$, $2k\bar{l}$, $h0\bar{l}$, and $hk0$ Weissenbergs were taken. They showed the unit cell to be triclinic; the cell constants, refined by comparison with the powder data, are given in Table 1. Both real and reciprocal spacings are quoted, since the latter are often the more useful. The prism axis is a . Evidence was found of twinning on (010).

The powder data were indexed by direct comparison of rotation and

TABLE 1. UNIT CELL PARAMETERS FOR $6\text{CaO}\cdot 3\text{SiO}_2\cdot \text{H}_2\text{O}$

Real cell		Reciprocal cell ($\lambda = 1.542 \text{ \AA}$)	
a	6.84 \AA (all $\pm .02$)	a^*	.2297 r.u. (all $\pm .0005$)
b	6.94	b^*	.2244
c	12.89	c^*	.1206
α	$90^\circ 45'$ (all $\pm 10'$)	α^*	$88^\circ 10'$ (all $\pm 3'$)
β	$97^\circ 22'$	β^*	$82^\circ 27'$
γ	$98^\circ 16'$	γ^*	$81^\circ 33'$

$$V = 601 \text{ \AA}^3 \quad G = 2.94. \quad Z = 1.99.$$

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† Standard cement chemical nomenclature ($\text{C} = \text{CaO}$, $\text{S} = \text{SiO}_2$, $\text{H} = \text{H}_2\text{O}$) will be used throughout.

powder photographs taken on the same 6cm. diameter camera, and the indices assigned were checked against a list of the strongest intensities found on the Weissenberg photographs. Once the indices of most lines had been fixed by this method, the cell parameters were refined to give the best agreement with accurate d values; these were obtained using a Norelco wide range diffractometer with filtered copper radiation and 1° slit. The instrument had been calibrated against a silicon standard.

It was considered impracticable to carry the indexing below about $d=2 \text{ \AA}$, since at such small spacings it is difficult to obtain unambiguous indices. Down to this point the indexing is satisfactory, and the agreement between observed and calculated d values is good.

D.T.A. CURVES

A differential thermal analysis was made on two samples dried at 110° C. ; quartz was used as reference standard and the rate of heating was $5^\circ/\text{min.}$ In each case, one large endothermic peak was found, at 700° C.

DEHYDRATION CURVES

Dehydration curves were determined by heating the sample in a horizontal furnace regulated by a temperature controller; the temperature was measured by a chromel-alumel thermocouple placed immediately above the sample. Nitrogen was passed through tubes freshly packed with soda-lime and silica gel and then through the furnace to provide an inert atmosphere. About 100 mg. of sample was contained in a 300 mg. Pt microboat. This was heated to successively higher temperatures and weighed, at intervals of 12 hours, to essentially constant weight (within about 0.1 mg.). Extra sample was placed in the furnace, to permit portions to be removed and examined at various stages.

Runs were made on two samples (Fig. 1), both of which had previously been dried at 100° C. In each case there was a loss at about 550° C. and a second, larger, loss at about 650° C. After complete dehydration, the product was $\beta\text{-C}_2\text{S}$. The loss at 650° was the same for both samples, and agrees with the water content as originally determined by Roy. It presumably corresponds with the 700° D.T.A. peak and is not inconsistent with the data of Roy (1) for the equilibrium hydrothermal decomposition of Phase Y. The loss at 550° was much greater in sample A than in sample B; a portion of A was withdrawn at the point P in Fig. 1, and its diffraction trace showed that it was still essentially Phase Y. This confirms Roy's formula, but leaves the earlier loss unexplained. Examination of the diffraction patterns of the starting materials showed that sample A had two lines with pronounced intensity differences as compared with the

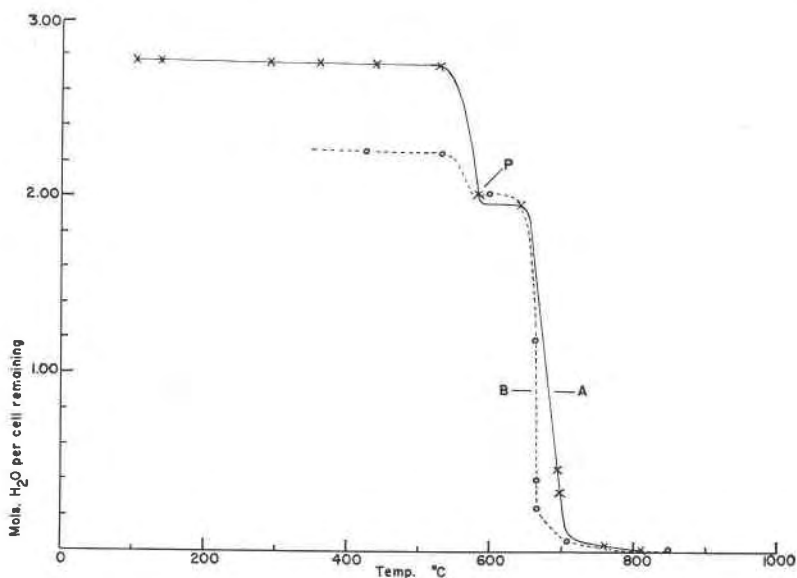


FIG. 1. Dehydration curves for samples A and B (see text). Principal weight-loss at about 650° corresponds to dehydration of Phase Y. Sample removed at P is essentially unchanged.

standard pattern for Phase Y; these lines are indicated with an asterisk in Table 2. In the sample withdrawn at point P, the intensity of these lines was normal, and a new line had appeared at about 3.12 \AA . Sample B before heating also showed this intensity difference, but to a much smaller degree. The correlation between intensity variation and water loss at 550° suggested that a small amount of some other phase might be present. Re-examination of diffraction traces from the earlier work revealed that slight intensity differences had occasionally shown up before, and that once or twice the line at 3.12 \AA had been found. In all cases the effects had been very small, and, since they had not been consistent, had been regarded as spurious. The extra lines did not appear to correspond to any of the known calcium silicates, hydrous or anhydrous, or to lime or calcite.

Optical examination of the initial material showed that a small amount of a fibrous substance was present. Some of this was sorted out by hand, and a powder photograph was taken. The pattern obtained, which showed strong preferred orientation effects, was similar to that of hillebrandite. This is consistent with the observed dehydration temperature, 550° . The two lines noted above in the diffractometer pattern might conceivably correspond to those noted at 3.33 and 3.02 \AA in natural

TABLE 2. POWDER DATA AND INDICES FOR $6\text{CaO}\cdot 3\text{SiO}_2\cdot \text{H}_2\text{O}$

$d_{\text{obs.}}$	Int.	$d_{\text{calc.}}$	hkl	$d_{\text{obs.}}$	Int.	$d_{\text{calc.}}$	hkl
6.90	25	$\begin{cases} 6.87 \\ 6.71 \end{cases}$	$\begin{cases} 010 \\ 100 \end{cases}$	2.736	10	2.747	$2\bar{1}2$
				2.718	20	$\begin{cases} 2.717 \\ 2.710 \end{cases}$	$\begin{cases} 02\bar{3} \\ 2\bar{1}\bar{3} \end{cases}$
4.61	10	4.61	012	2.634	15	$\begin{cases} 2.633 \\ 2.630 \end{cases}$	$\begin{cases} 023 \\ 12\bar{3} \end{cases}$
						$\begin{cases} 2.632 \\ 2.599 \end{cases}$	$\begin{cases} 114 \\ 2\bar{2}0 \end{cases}$
3.435	70	3.435	020	2.594	2	2.599	$2\bar{2}0$
*3.349	25	3.356	$\begin{cases} 20\bar{1} \\ 200 \end{cases}$	2.556	25	2.556	005
3.293	20	3.291	021	2.488	2	2.483	$20\bar{4}$
3.258	25	3.258	120	2.473	2	2.475	$22\bar{2}$
3.209	5	3.207	$2\bar{1}0$	2.290	100	$\begin{cases} 2.291 \\ 2.290 \end{cases}$	$\begin{cases} 105 \\ 030 \end{cases}$
*3.067	50	3.067	$02\bar{2}$			$\begin{cases} 2.275 \\ 2.272 \end{cases}$	$\begin{cases} 21\bar{4} \\ 130 \end{cases}$
2.986	40	2.986	022	2.270	5	$\begin{cases} 2.272 \\ 2.255 \end{cases}$	$\begin{cases} 130 \\ 30\bar{1} \end{cases}$
2.890	25	2.891	120	2.243	2	2.255	$30\bar{1}$
2.860	15	$\begin{cases} 2.863 \\ 2.864 \end{cases}$	$\begin{cases} 21\bar{1} \\ 122 \end{cases}$	2.135	5	$\begin{cases} 2.159 \\ 2.134 \end{cases}$	$\begin{cases} 301 \\ 032 \end{cases}$
		2.823	35			2.823	$\begin{cases} 20\bar{3} \\ 202 \end{cases}$

hillebrandite (2), although it has been pointed out (2) that the synthetic material usually shows shorter, rather than longer, spacings. Preferred orientation could account for the apparent absence of the rest of the pattern in the diffractometer trace. On the whole, the evidence is not too satisfactory on this point, but it seems fair to assume that the extra phase is a hillebrandite-like material. If the extra phase is assumed to have a water content similar to that of hillebrandite, recalculation of the water content of Phase Y raises it to 2.1–2.2 mols. per cell, which does not materially alter the conclusion regarding the formula.

CELL CONTENTS

It was felt that it would be hopeless to attempt to determine the density of such tiny crystals by conventional methods. The density was therefore calculated from the refractive indices of the crystals, using the adaptation of the Lorentz-Lorenz equation derived by Howison and Taylor (3), which usually gives values correct to within $\pm 2\%$. This gives a value of 2.94; on this basis $Z=1.99$, and the cell contents are $12\text{CaO}\cdot 6\text{SiO}_2\cdot 2\text{H}_2\text{O}$.

The conditions of formation and dehydration suggest that the water may be present as hydroxyl groups not attached to silicon. Gard and

Taylor (4) point out that calcium silicates containing water as molecules, or as hydroxyl attached to silicon, such as afwillite (5) or tobermorite (6), tend to be formed hydrothermally, and to dehydrate, at much lower temperatures. The temperature of dehydration of Phase Y is much more nearly comparable to those of xonotlite (7) and foshagite (4) which are considered to contain water as hydroxyl groups not attached to silicon. For xonotlite, this has been established by a structure determination (8). If Phase Y really does contain its water as hydroxyl not attached to silicon, the constitution (for the unit cell contents) is $\text{Ca}_{12}\text{Si}_6\text{O}_{22}(\text{OH})_4$, which implies the presence of Si_2O_7 groups, together with either SiO_4 groups or oxide ions. Such a mixture of groupings has been reported for epidote and zoisite (9), and it might well account for the awkwardly shaped unit cell. On the other hand, the prism axis, a , (6.84 Å) is similar in length to b (6.76 Å) for $\beta\text{-C}_2\text{S}$ (or c , the prism axis of $\alpha'\text{-C}_2\text{S}$). Together with the high refractive indices, this suggests a possible similarity in structure. However, examination of the pseudomorphs formed by dehydrating the original material gave no evidence of preservation of order, implying that there is no simple relationship. Without further work, it is not possible to make even a guess at the structure.

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