

On the oriented transformation of $\text{Ca}(\text{OH})_2$ to CaO

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SUMMARY. The conversion of $\text{Ca}(\text{OH})_2$ to CaO has been studied by X-ray diffraction techniques. When $\text{Ca}(\text{OH})_2$ crystals are heated *in vacuo* the conversion is oriented, but not when they are heated at atmospheric pressure. This difference is attributed to the lowering of the decomposition temperature *in vacuo* and consequent lower thermal vibration.

THE reaction mechanism of solid-state decomposition of trigonal alkaline earth hydroxides to the corresponding cubic oxides is a fascinating subject studied by many workers. Garrido (1936, 1951), for example, studied the dehydration of naturally occurring $\text{Mg}(\text{OH})_2$ to MgO by X-ray diffraction techniques and observed a high degree of topotaxy. Ball and Taylor (1961) reinvestigated the dehydration of brucite and proposed an inhomogeneous reaction mechanism to explain the observed topotaxy. Brett and Anderson (1967) showed that the spinel reflections on which Ball and Taylor based their postulate of an intermediate phase were due to impurity. West (1934) studied the dehydration of $\text{Ca}(\text{OH})_2$ and reported that only a low degree of topotaxy was preserved. Chatterji and Jeffery (1966) observed by electron diffraction the dehydration of $\text{Ca}(\text{OH})_2$ to CaO . In this case the crystals were heated inside an electron microscope by concentrating the electron beam. For comparison they also studied the dehydration of $\text{Mg}(\text{OH})_2$ under similar conditions and observed only slightly closer orientation relationships. They were of the opinion that the difference between X-ray and electron diffraction results might be due to the lowering of decomposition temperature of $\text{Ca}(\text{OH})_2$ under high vacuum (Mayers, 1942). To test this hypothesis and to find out the orientational relationship a systematic X-ray diffraction investigation was carried out on the $\text{Ca}(\text{OH})_2$ to CaO transformation.

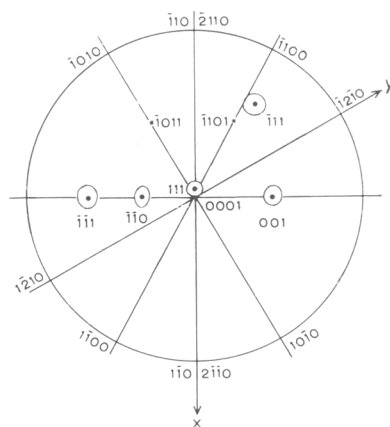
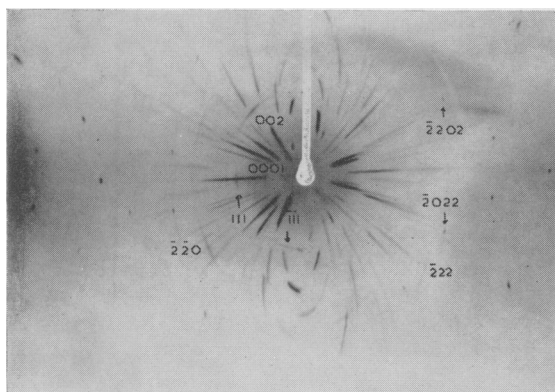
Single crystals of $\text{Ca}(\text{OH})_2$ were grown from a paste of Portland cement (water to cement ratio 0.60). The set cement pastes were stored under distilled water in glass beakers, these beakers were in their turn stored in a desiccator containing $\text{Ca}(\text{OH})_2$ in aqueous suspension and were left in a vibration-free place for 3–4 weeks by which time single crystals of $\text{Ca}(\text{OH})_2$ suitable for X-ray work had grown. $\text{Ca}(\text{OH})_2$ crystals grown from cement paste are very pure (Mikhail, Brunauer, and Copeland, 1965).

The crystals were heated in a cylindrical vacuum furnace (pressure 10^{-4} mm Hg) provided with a thermostatic control. A calibrated 'Chromel-Alumel' thermocouple connected to a potentiometer was used for measuring temperature. Some of the same batch of crystals were also heated at atmospheric pressure. The dehydrated crystals were coated with Bostik A thinned in dry benzene on removal from the furnace, in order to prevent rapid rehydration, and X-ray oscillation photographs were taken on a 3.0-cm radius Unicam camera using Cu-radiation. Several runs were made with different single crystals of approximately equal size. The observed results are summarized in table I.

A 15° oscillation X-ray photograph showing spots both from Ca(OH)_2 and CaO is shown in fig. 1. CaO reflections were drawn out to form arcs of constant θ . All the reflections on the photograph could be attributed either to Ca(OH)_2 or CaO ; no extra spots were present.

TABLE I. *Single crystals of Ca(OH)_2 heated in vacuo; the 'time' column gives the time the maximum temperature was maintained*

Max. temp.	Time	Observation
350 °C	20 hours	Sharp drawn-out spots of CaO . No Ca(OH)_2 single crystal spots
260	20	Sharp drawn-out spots of CaO , together with some Laue streaks. No Ca(OH)_2 single crystal spots
260	8	Sharp single crystal spots of Ca(OH)_2 . No CaO spots
260	12	A few drawn-out spots of CaO together with sharp Laue streaks. Only the 100 and 101 spots of Ca(OH)_2 appeared on some of the Laue streaks
260	10	Sharp drawn-out spots of CaO together with single crystal spots of Ca(OH)_2



FIGS. 1 and 2: Fig. 1 (left). A 15° oscillation X-ray pattern of Ca(OH)_2 single crystal heated in vacuum at 260°C for 10 hours. The indices of the types $hkil$ and hkl correspond to Ca(OH)_2 and CaO reflections respectively. Fig. 2 (right). The stereographic representation of the observed orientational relationship between Ca(OH)_2 and CaO structures. The poles 0001 of the trigonal Ca(OH)_2 and 111 of the cubic CaO are at the centre of the stereogram.

Stereographic projections (Henry, Lipson, and Wooster, 1961) were used to find the orientational relationship between the Ca(OH)_2 and CaO structures. Fig. 2 shows the observed orientational relationship between Ca(OH)_2 and CaO . For CaO X-ray reflections, which had no associated Laue streaks, an area of 'possible angular error' was drawn for each reflection indicating the uncertainty involved in locating a particular reciprocal lattice vector with respect to the rotation axis of the crystal and the direction of the X-ray beam.

The observed orientational relationship between the structures of Ca(OH)_2 and CaO is $\text{Ca(OH)}_2[0001] \parallel \text{CaO}[111]$ and $\text{Ca(OH)}_2a \parallel \text{CaO}[1\bar{1}0]$.

Ca(OH)_2 crystals that were heated to decomposition at atmospheric pressure gave a normal powder diagram of CaO, i.e. they preserved a poor degree of orientation as was observed by West (1934) under similar conditions.

It is known that at atmospheric pressure Ca(OH)_2 decomposes to CaO between 450 and 500 °C depending on the size of the crystal. It seems probable that the higher temperature necessary to decompose Ca(OH)_2 at atmospheric pressure also leads to disorientation of CaO crystallites due to the higher thermal vibration. This inference is consistent with the observations of Chatterji and Jeffery (1966) for Ca(OH)_2 and Goodman (1958) for Mg(OH)_2 that heating after complete conversion of hydroxide to oxide leads to powder diagrams.

After this work had been completed the authors became aware of a paper by Brett (1969) on the same subject. Brett also observed an unoriented conversion of Ca(OH)_2 when heated at atmospheric pressure but an oriented one *in vacuo*. He also observed that the amount of topotaxy is rather poor with Ca(OH)_2 . Brett suggested that his results can be explained as due to the differences in the rates of nucleation and recrystallization of CaO in different conditions.

Though both investigations are in general agreement, there are some divergences in results and interpretation. Fig. 2 of the present paper shows a high degree of topotaxy. The difference between this result and that of Brett may be attributed to the re-formation of Ca(OH)_2 and the consequent disruption of the CaO structure in his case. Brett used a water-base adhesive, Seccotine, to mount his crystals.

The earlier observation of Chatterji and Jeffery (1966), which has been further confirmed in this investigation, that further heating after complete conversion of Ca(OH)_2 to CaO leads to complete loss of topotaxy, even in high vacuum, is rather difficult to explain from the nucleation and recrystallization mechanism suggested by Brett. Further work is in hand to develop a reaction mechanism consistent with all the above observations.

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