Electron Microscopic Study of the Dehydration of Brucite and the Recrystallization of Periclase upon Further Heating

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A number of investigators have studied the transformation of brucite to periclase through dehydration. Büssem and Köberich[1] showed that the periclase crystallites produced from brucite by dehydration were oriented in such a way that (111) of the periclase is parallel with (0001) of the brucite. Goodman[2] investigated the transformation process with an electron microscope. He decomposed the brucite crystals by electron bombardment and took sets of an electron micrograph and a corresponding diffraction photograph at various stages of the bombardment. He concluded that, in the decomposition process, the small shrinkage in the basal plane of the brucite took place first, and then the collapse of the planes downward to the original [0001]. Ball and Taylor[3] proposed the existence of a spinel-like intermediate phase, $Mg_3(OH)_2O_2$, between brucite and periclase after an X-ray analysis of natural brucite. In order to explain the spinel-formation process, he suggested an inhomogeneous dehydration, instead of a homogeneous dehydration. Recently Anderson and Horlock[4] investigated the dehydration process of natural brucite and found that the dehydration proceeded from the edge of the crystal toward the center, that no spinel-like intermediate was found, and that similar lattices of magnesium hydroxide and magnesium oxide-like intermediate, with only slightly different sizes, could be recognized.

In the present work the brucite crystals obtained by the hydrothermal treatment of chemically-pure magnesium hydroxide will be used to get rid of as much effect of impurities as possible.

Experimental

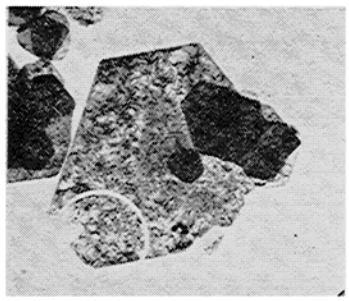
The Preparation of the Brucite Crystals. — In order to take an electron diffraction photograph of a single crystal, the brucite crystals must be thin enough to transmit electrons but be at least 0.5 μ across so as to be separated from one another. Brucite crystals satisfying the requirements and still free from impurities were obtained by the following procedures. Chemically-pure magnesium hydroxide was put in an autoclave with water and kept at an appropriate temperature (with reference to the magnesium oxide water phase equilibrium[5]) for several hours. Different amounts of water and of magnesium hydroxide and various treating temperatures and heating periods were employed. Properly-crystallized brucite was obtained by treating 2 g. of chemically-pure magnesium hydroxide in a 30 cc. autoclave with 15 cc. water at 350°C for 24 hr.

Heating and Examination Methods.—The brucite crystals were heated in the following two different methods and were examined with an electron microscope operated at 80 kV.

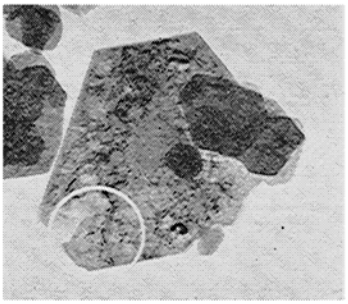
Heating in the Electron Microscope with a Specimen-heating Attachment.—The crystals were first laid on a Pt-mesh and heated at the heating rate of about 10°C per min. up to 400°C with a heating attachment in the electron microscope. Choosing one crystal, a series of electron micrographs and corresponding diffraction photographs were taken at various stages of heating in order to pursue the crystal transformation through the dehydration. Next the crystals were heated further at a heating rate of about 30°C per min. up to 900°C, and the graphs were also taken at various stages of heating in order to observe any change after the dehydration. More than ten crystals were examined by these procedures.

Heating by Electron Bombardment. — The crystals were heated by electron bombardment in the electron microscope. The beam intensity was gradually increased, and at successive stages of bombardment, pairs of electron micrographs and corresponding diffraction photographs were taken. The maximum temperature rise as a result of the extensive electron bombardment was checked by the behavior of metal powder particles of various kinds (aluminum, copper, manganese, nickel, iron and chromium) in the bombardment. Only chromium particles remained undecomposed. From the standpoint of the melting points, the maximum temperature was estimated to be somewhere between 1453°C and 1535°C. In a high vacuum condition, however, the evaporation of metals cannot be disregarded so the temperature might be lower.

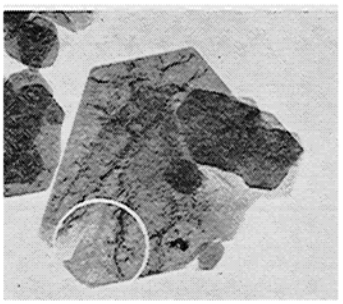
1) W. Büssem and F.Köberich, *Z. physik. Chem.*, **B, 17**, 310 (1932).
2) J. F. Goodman, *Proc. Roy. Soc.*, **A247**, 346 (1958).
3) M. C. Ball and H. F. W. Taylor, *Miner. Mag.*, **32**, 754 (1961).
4) P. J. Anderson and R. F. Horlock, *Trans. Faraday Soc.*, **58**, 1993 (1962).
5) D. M. Roy, R. Roy and E. F. Osborn, *Am. J. Sci.*, **251**, 337 (1953).



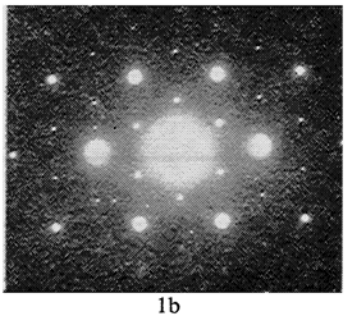
1a



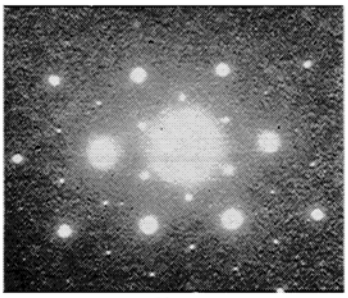
2a



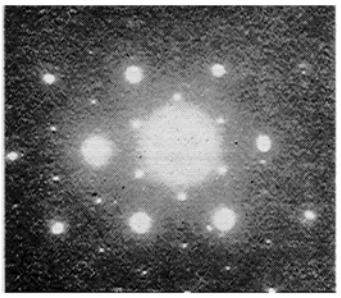
3a



1b

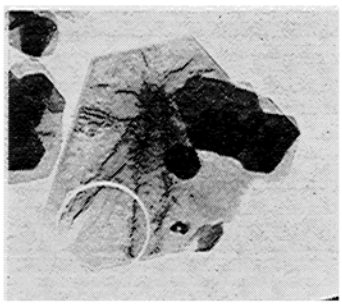


2b

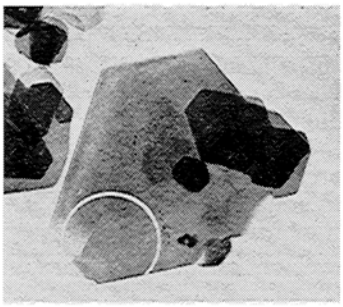


3b

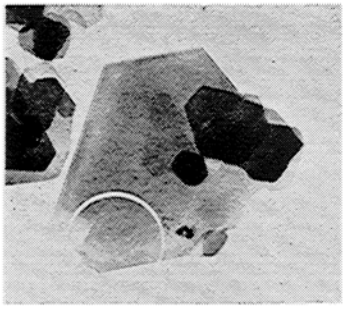
Fig. 1a. Brucite crystal before heating (×30000).
Fig. 1b. Diffraction pattern from the area in a circle in Fig. 1a.
Fig. 2a. Brucite crystal heated 10°C per minute up to 250°C with a heating attachment (×30000).
Fig. 2b. Diffraction pattern from the area in a circle in Fig. 2a.
Fig. 3a. Brucite crystal heated 10°C per minute up to 270°C with a heating attachment (×30000).
Fig. 3b. Diffraction pattern from the area in a circle in Fig. 3a.



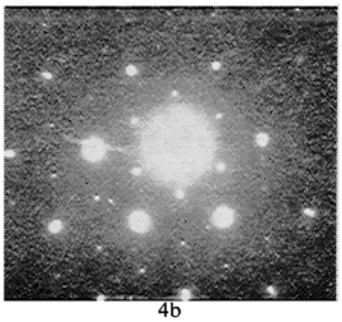
4a



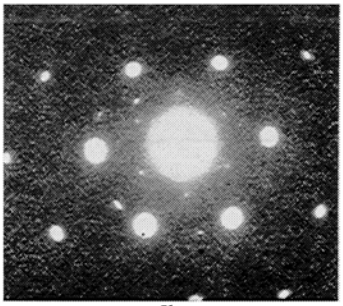
5a



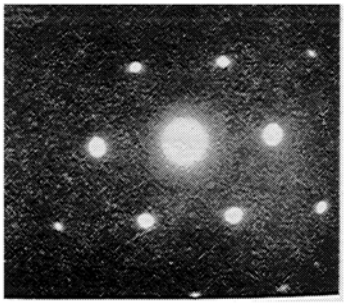
6a



4b

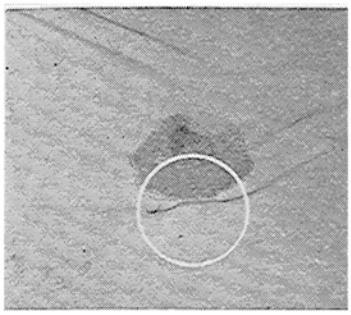


5b

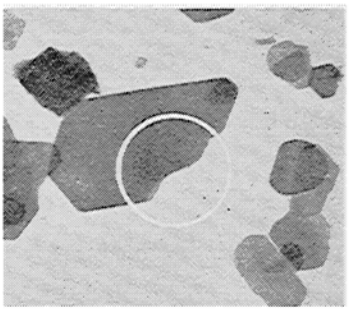


6b

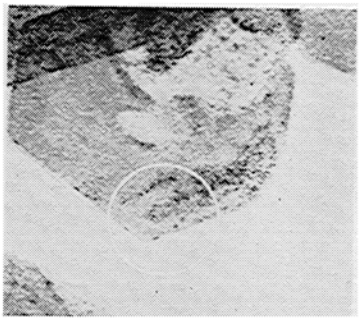
Fig. 4a. Brucite crystal heated 10°C per minute up to 290°C with a heating attachment (×30000).
Fig. 4b. Diffraction pattern from the area in a circle in Fig. 4a.
Fig. 5a. Brucite crystal heated 10°C per minute up to 310°C with a heating attachment (×30000).
Fig. 5b. Diffraction pattern from the area in a circle in Fig. 5a.
Fig. 6a. Brucite crystal heated 10°C per minute up to 330°C with a heating attachment (×30000).
Fig. 6b. Diffraction pattern from the area in a circle in Fig. 6a.



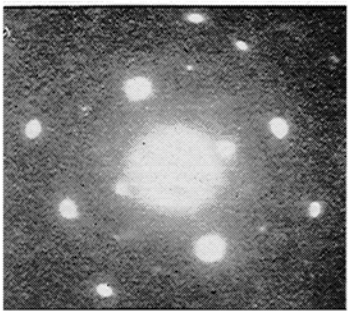
7a



8a



9a



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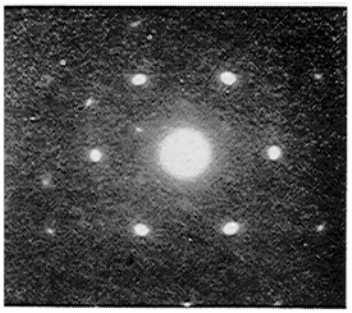
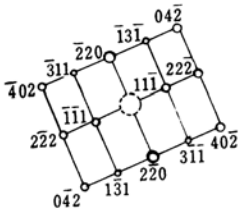


8b

9b



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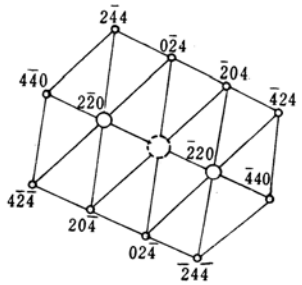
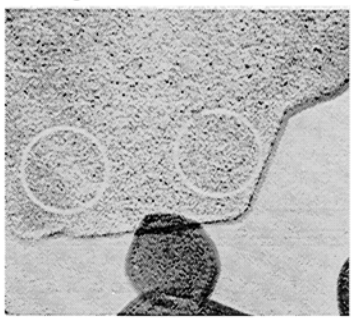
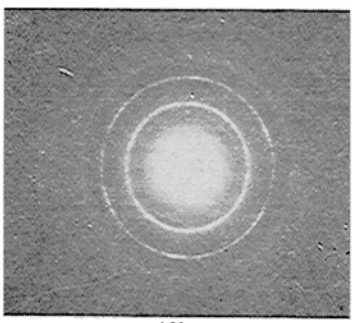


9c

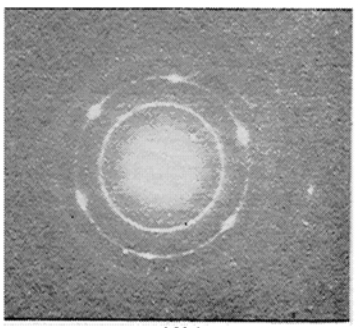
Fig. 7a. Brucite crystal heavily bombarded by electrons (×15000).
Fig. 7b. Diffraction pattern from the area in a circle in Fig. 7a.
Fig. 7c. An indexing of the diffraction pattern shown in Fig. 7b.
Fig. 8a. Brucite crystal heated 10°C per minute up to 600°C with a heating attachment (×15000).
Fig. 8b. Diffraction pattern from the area in a circle in Fig. 8a.
Fig. 9a. Brucite crystal heavily bombarded by electrons (×30000).
Fig. 9b. Diffraction pattern from the area in a circle in Fig. 9a.
Fig. 9c. An indexing of the diffraction pattern shown in Fig. 9b.



10a



10b



10b′

Fig. 10a. Brucite crystal heavily bombarded by electrons (×30000).
Fig. 10b. Diffraction pattern from the area in the left circle in Fig. 10a.
Fig. 10b′. Diffraction pattern from the area in the right circle in Fig. 10a.

TABLE I. RELATIONS OF THE ORIENTATIONS BETWEEN THE PERICLASE AFTER FURTHER HEATING AND THE ORIGINAL BRUCITE

Type	Corresponding faces in orientation: Periclase	Corresponding faces in orientation: Original brucite	Occurrence	Heating method	Fig. No.
1	(111) (220)	(0001) $(11\bar{2}0)$	almost always	A, B	same as 6a, 6b
2	(112) (220)	(0001) $(11\bar{2}0)$	rarely	A, B	7a, 7b, 7c
2′	(112) (220)	(0001) $\{(11\bar{2}0), (1\bar{2}10), (\bar{2}110)$ in three directions	rarely	A	8a, 8b
3	(221) (220)	(0001) $(11\bar{2}0)$	rarely	A, B	9a, 9b, 9c
4	Random orientation		rarely	B	10b

Heating methods: A, heating attachment B, electron bombardment

Results

Crystal Changes upon Dehydration. — The brucite crystals were laid flat on carbon film, which was put on a Pt-mesh by spattering, since (0001) was perpendicular to the electron beam. Like the natural brucite crystals used by Goodman, the present ones had complex patches on the surface (Fig. 1a) which might come from the internal-disordered structures, as Goodman suggested. The changes in the diffraction patterns through the dehydration were the same in the two different ways of heating. The crystals were heated in a heating attachment at the heating rate of about 10°C per min., and electron micrographs and corresponding diffraction photographs of one crystal of each of them were taken at 250°C, 270°C, 290°C, 310°C and 330°C. These graphs are shown in Figs. 1a, 1b, 2a, 2b, 3a, 3b, 4a, 4b, 5a, 5b, 6a and 6b. The original reflections of the brucite first diffused outward, and then the reflections of the periclase appeared. In Figs. 2b and 3b, it can be observed that the original reflections have diffused outward. In the dehydrating stage, a_0 of the brucite is calculated to cover a range from 3.11 Å to 3.03 Å in Fig. 2b, and from 3.11 Å to 3.01 Å in Fig. 3b, while the a_0 of the original brucite is 3.11 Å. In Fig. 4b reflections from the periclase have appeared distinctly apart from the diffused ones. In Fig. 5b, all the reflections belong to the periclase except the six patterns nearest the center. These six reflections belong to a hexagonal lattice. Other corresponding reflections cannot be detected, perhaps because they are too vague and too near those of the periclase. From these six reflections, a_0 is calculated to be 2.99 Å. This fact shows that a_0 of the brucite shrinks to 2.99 Å through the dehydration. In Fig. 6b the dehydration has been completed. Figure 6b shows that (111) of the periclase is parallel with (0001) of the original brucite and that (220) of the periclase is parallel with $(11\bar{2}0)$ of the original brucite.

Crystal Changes upon Further Heating after Complete Dehydration.—The changes in diffraction patterns caused by further heating after complete dehydration were also almost identical in the two methods of heating. Upon further heating, the patterns of many crystals remained as they were. In a few crystals, however, the patterns were changed into several other types, as Table I shows; type 1 was sometimes mixed slightly into the other types.

Discussion

Dehydration Process. — Although Goodman has observed only one intermediate shrinked lattice (a_0=2.99 Å), the results in the present work show that the brucite lattice shrinks gradually as the water molecules are expelled. No information could be obtained about the dimension of the C-axis. Judging from the crystal structure of the brucite, however, the shrinkage will be more extensive in the C direction. Each region where the shrinkage takes place is supposed to be 40~50 Å across, because the periclase crystallites produced from the brucite at 300°C are known to be about this size.[6] Water molecules possibly escape at the sites where defects exist and then through the cracks caused by the lattice shrinkage. Through the shrinkage, slight slips between oxygen layers are required to produce the periclase, because oxygens are hexagonal-closed packing in the brucite, whereas in the periclase they are cubic-closed packing. Thus the dehydration seems to take place in two steps. The gradual shrinkages of the lattice

6) W. R. Eubank, *J. Am. Cer. Soc.*, **34**, 225 (1951).

with the escape of the water molecules first take place, and then the slips between oxygen layers or the crystallizations take place.

The Changes in the Diffraction Patterns Caused by Further Heating After Complete Dehydration.—Goodman noticed a change in the diffraction patterns after the complete dehydration by extensive bombardment. The patterns partially became rings, which shows random orientation. He referred this to a bulk movement of the solids under the influence of the thermal stress. In the present work, the changes in the orientation upon further heating took place in the several ways shown in Table I. It seems that the structure immediately after complete dehydration is so defective that the recrystallization upon further heating sometimes takes place with a slight movement of the orienting direction, and also in rare cases with an extensive movement of the structure, which causes the random orientation. A strict interpretation of the mechanism of this phenomenon, however, has not yet been established.

Summary

1) The hexagonal plate crystals of the brucite, about 1 μ across, have been obtained by the hydrothermal treatment of chemically-pure magnesium hydroxide.

2) The brucite crystals transformed themselves upon dehydration into aggregates of the minute periclase crystallites oriented in such a way that (111) is parallel with (0001) of the original brucite crystal and (220) is parallel with (11$\bar{2}$0).

3) The dehydration seems to take place in two steps. The escape of water molecules and the gradual shrinkage of the lattice take place at the first step of the dehydration. The slip of the oxygen layers and the crystallization take place at the second step.

4) Upon further heating after complete dehydration, the orientation of the crystallites remained unchanged in many crystals. In a few crystals, however, the orientation changed in the several ways shown in Table I. This phenomenon is a kind of sintering in the grain.

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