The Synthesis of $Mg_3(PO_4)_2 \cdot 8H_2O$ and Its New Polymorphism

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Bobierrite, $Mg_3(PO_4)_2 \cdot 8H_2O$, could be synthesized from mixed solutions of Na_2HPO_4 and $MgSO_4$ at an initial pH of 6.4—7.0 with the addition of $Ca(NO_3)_2$, $CuSO_4$, $NiSO_4$, gelatin, or agar, by heating at 80—90 °C for 2—48 h. X-Ray studies indicated the coexistence of two kinds of lattice in each synthetic $Mg_3(PO_4)_2 \cdot 8H_2O$ crystal. One phase (Phase 1) is monoclinic, space group $P2_1/m$ or $P2_1$, with $a=10.08(2)$, $b=27.86(3)$, $c=4.656(7)$ Å, and $\beta=105.0(2)°$. The other phase (Phase 2) is monoclinic, space group C2/m, C2, or Cm, with $a=10.07(2)$, $b=13.38(2)$, $c=4.656(7)$ Å, and $\beta=105.0(2)°$. If a centrosymmetric space group C2/m is assumed for the latter, Phase 2 may be considered to be a new polymorph of $Mg_3(PO_4)_2 \cdot 8H_2O$, one belonging to the vivianite series. Newberyite, $MgHPO_4 \cdot 3H_2O$, was also formed in the above synthetic procedure. This phosphate was precipitated under slightly more acidic conditions than those where $Mg_3(PO_4)_2 \cdot 8H_2O$ was obtained.

Bobierrite, $Mg_3(PO_4)_2 \cdot 8H_2O$ (TMP8), has been found chiefly in guano deposits as minute crystals, associated with newberyite, $MgHPO_4 \cdot 3H_2O$ (DMP3), and several magnesium ammonium orthophosphates. TMP8 was first described by Bobierre in 1868;[1] X-ray and optical studies of this mineral were made by Barth in 1937.[2] According to Barth's determinations, TMP8 belongs to a different space group from that of the vivianite series ($A_3(XO_4)_2 \cdot 8H_2O$; A=Fe, Co, Ni, Zn, Mg: X=P, As), and the b-axis of the unit cell is doubled compared with the $8H_2O$ family. However, the crystal structure of TMP8 has not yet been determined at present. Therefore, we have investigated the crystal growth of TMP8 and its X-ray diffraction data in order to clarify the crystallographical relation between TMP8 and the vivianite group.

The preparations of TMP8 have been reported by de Schulten (1903),[3] Bassett and Bedwell (1933),[4] Frazier *et al.* (1963),[5] and the present authors (1974, 1976).[6-8] However, we have seen no reference to the crystal growth of this mineral. The present paper will deal with a new method of synthesizing TMP8 from mixed solutions of $MgSO_4$ and Na_2HPO_4 in an initial pH of 6.4—7.0 at 80—90 °C for 2—48 h by using inorganic and organic additives, and then additionally preparing the crystals in a suitable size for the X-ray Weissenberg method. The X-ray oscillation and Weissenberg photographs have indicated the coexistence of two monoclinic lattices (Phase 1 and Phase 2) in each synthesized TMP8 crystal, as will be described below.

Experimental

Preparation. Syntheses without Additives: A mixed solution of 4.1—8.3 g of $MgSO_4 \cdot 7H_2O$ and 4.0—8.0 g of $Na_2HPO_4 \cdot 12H_2O$ in 1500 ml of water was prepared. In each run, $MgSO_4 \cdot 7H_2O$ and $Na_2HPO_4 \cdot 12H_2O$ were mixed in the ratios given in Table 1. The pH of the mixture was then adjusted to 6.0—7.0 by adding HCl (about 2%) or acetic acid (HAc) (2%). The mixture thus prepared was heated in a water bath with a reflux at 90 °C for 2 h. The precipitates thus formed were filtered, washed with water, and dried in air and then in a silica gel desiccator for several days. The run products of the synthetic experiments are summarized in Table 1.

Syntheses with Inorganic Additives: A mixed solution of 4.1 g of $MgSO_4 \cdot 7H_2O$ and 4.0 g of $Na_2HPO_4 \cdot 12H_2O$ in 1500 ml of water was prepared. The solution was adjusted with HCl or HAc to each pH value given in Table 2. To this mixture, each inorganic additive ($Ca(NO_3)_2 \cdot 4H_2O$, $CuSO_4 \cdot 5H_2O$, $NiSO_4 \cdot 6H_2O$, $CoSO_4 \cdot 7H_2O$, $MnSO_4 \cdot 4H_2O$, and $ZnSO_4 \cdot 7H_2O$) in a molar ratio to $MgSO_4$ of about 1: 100, was then added. The mixture thus prepared was heated in the same manner as in the syntheses without additives.

Syntheses with Gelatin: The same procedure as in the syntheses with inorganic additives was carried out except for the replacement of inorganic additives with 10—50 g of

Table 1. Synthetic condition of TMP8 without additives

Run	Solutions: Starting materials (g/1500 ml of water) $Na_2HPO_4 \cdot 12H_2O$	Solutions: Starting materials (g/1500 ml of water) $MgSO_4 \cdot 7H_2O$	Initial pH of solution	Phases found[a] in products
1	8.0	8.3	6.0	DMP3, U
2	6.0	6.2	6.2	DMP3, U, TMP 8
3	8.0	8.3	6.2	U, TMP8
4	4.0	4.1	6.4	U, TMP8
5	4.0	4.1	6.6	U
6	4.0	4.1	6.8	U
7	4.0	4.1	7.0	U

a) DMP3=$MgHPO_4 \cdot 3H_2O$; TMP8=$Mg_3(PO_4)_2 \cdot 8H_2O$; U=unidentified crystalline material.

Table 2. Synthetic condition of TMP8 with inorganic additives

Additive	Solutions: Acid	Solutions: Initial pH	Phases found in products
$Ca(NO_3)_2 \cdot 4H_2O$	HCl	6.6—7.0	TMP8
	HAc[a]	6.4—7.0	TMP8
$CuSO_4 \cdot 5H_2O$	HCl, HAc	6.4—6.6	TMP8
$NiSO_4 \cdot 6H_2O$	HCl, HAc	6.4—6.6	TMP8
$CoSO_4 \cdot 7H_2O$	HCl	6.4—6.6	TMP8, U
$CoSO_4 \cdot 7H_2O$	HCl	6.8—7.0	U
$CoSO_4 \cdot 7H_2O$	HAc	6.4—7.0	U
$MnSO_4 \cdot 4H_2O$	HCl, HAc	6.4—7.0	U
$ZnSO_4 \cdot 7H_2O$	HCl, HAc	6.4—7.0	U

a) HAc=acetic acid.

gelatin, the narrowing of an initial pH region from 6.4—7.0 to 6.6—6.8, and the extension of a heating time from 2 h to 4—24 h.

Syntheses with Agar: First, a solution of 4.0 g of $Na_2HPO_4 \cdot 12H_2O$ in 1200 ml of water was prepared, and then 5—10 g of agar were added to the solution. The solution was then heated up to about 80 °C until the agar was dissolved. To this, a solution of 4.1 g of $MgSO_4 \cdot 7H_2O$ in 300 ml of water, adjusted to an acidic condition by adding an appropriate amount of HCl or HAc, which had been determined by experiments, was then stirred in. The mixture thus prepared was set aside to gel for several hours. The agar gel solution was heated by the same procedure as in the above syntheses at 80—90 °C for 4—48 h. The crystals thus obtained were washed by boiling them mildly in water, and dried in air and then in a silica gel desiccator for several days.

TABLE 3. CHEMICAL COMPOSITION OF SYNTHETIC TMP8[a)]

	MgO (%)	P_2O_5 (%)	H_2O (%)	Mg/P[b)]
Found	29.8	35.3	34.9[c)]	1.49
			36.4[d)]	
Calcd	29.7	34.9	35.4	1.5

a) Prepared by the addition of agar. b) Mole ratio. calculated by the use of this formula: $H_2O = 100 - (MgO + P_2O_5)$. d) Calculated from weight loss on heating.

Measurements. The run products were identified by X-ray powder diffractometry (Cu $K\alpha$, Ni filter), refractive index measurement (the immersion method), optical microscopy, and chemical analysis. Chemical analysis was performed on TMP8 grown in an agar-containing solution; the magnesium was determined by the chelatometric titration method; the phosphorus, by molybdovanadate colorimetry, and the water contents, as loss on ignition to about 800 °C. The chemical compositions of the synthetic TMP8 are shown in Table 3. The lattice constants of the synthetic TMP8 were obtained by the least-squares calculation on the basis of the results of the Weissenberg method (Cu $K\alpha$, Ni filter, and Si standard). Weissenberg photographs were taken with regard to zero-, first-, and second-layer lines about the c-axis, and the zero-layer line about the a- and b-axes.

Results and Discussion

General Remarks. As is shown in Table 1, no pure phase of TMP8 was precipitated on syntheses of this compound from a mixed solution of Na_2HPO_4 and $MgSO_4$ without additives. In this case, only a small amount of TMP8 appeared in the products. Under the syntheses without additives, it seemed rather diffcult to form. Therefore, we investigated tentatively the effects of inorganic and organic additives on the TMP8 formation, and then the influence of those additives on the size and morphology of the crystals. Inorganic additives ($Ca(NO_3)_2 \cdot 4H_2O$, $CuSO_4 \cdot 5H_2O$, or $NiSO_4 \cdot 6H_2O$) and organic additives (gelatin or agar) were found to be effective on the formation of TMP8. The habits of the synthetic TMP8 crystals obtained both with and without additives were plates, with (010) being the dominant forms and elongated along the c-axis. The size of the TMP8 crystals obtained inclined to increase as the initial pH of the mixture was lowered and as the heating temperature and time increased. The pH of the mixture was observed to be lowered after the precipitation of crystals.

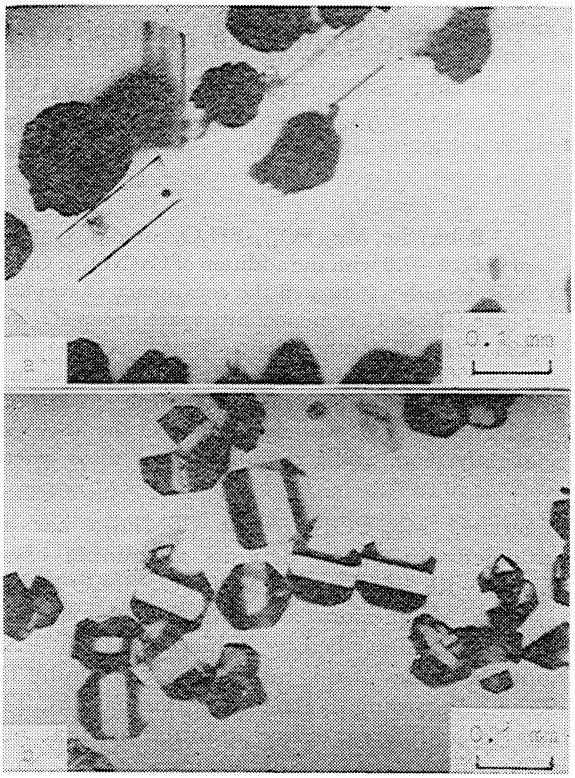

Fig. 1. Photographs of TMP8, DMP3, and U obtained without additives.
a) TMP8 and U obtained at initial pH 6.2 using HCl. TMP8=parallelepiped platy crystals. U=spherically aggregated materials. b) DMP3 obtained at initial pH 6.0.

Crystals from the Solution without Additives. In the syntheses without additives, TMP8 was found in only small amounts in the products at initial pH values of the mixture of 6.2—6.4, as is shown in Table 1. Figure 1-a shows TMP8 crystals coexisting with unidentified crystalline materials (U). Under slightly more acidic conditions, namely, at the initial pH 6.0, sometimes DMP3 (Fig. 1-b) containing U was obtained, while U was precipitated at the initial pH values of the mixture of 6.6—7.0.

Crystals from the Solutions with Inorganic Additives. The run data of the synthetic experiments with inorganic additives are given in Table 2. Below the initial pH value of 6.2, no precipitate was formed. Above each initial pH shown in Table 2, U tended to be precipitated predominantly.

The maximum size of the crystals obtained by the addition of $Ca(NO_3)_2 \cdot 4H_2O$ and $CuSO_4 \cdot 5H_2O$ were as large as 2.8 by 1.4 and 2.2 by 1.2 mm, respectively, while that of the crystals obtained by the addition of $NiSO_4 \cdot 6H_2O$ was relatively small (about 0.12 by 0.08 mm). The dimension in the direction of b-axis was usually below about 0.02 mm. The synthetic TMP8 crystals are shown in Figs. 2-a, b, and c. On the other hand, U was precipitated from the mixture to which $MnSO_4 \cdot 4H_2O$ or $ZnSO_4 \cdot 7H_2O$ had been added, under the synthetic conditions studied here, and both TMP8 and U were precipitated from a mixture to which

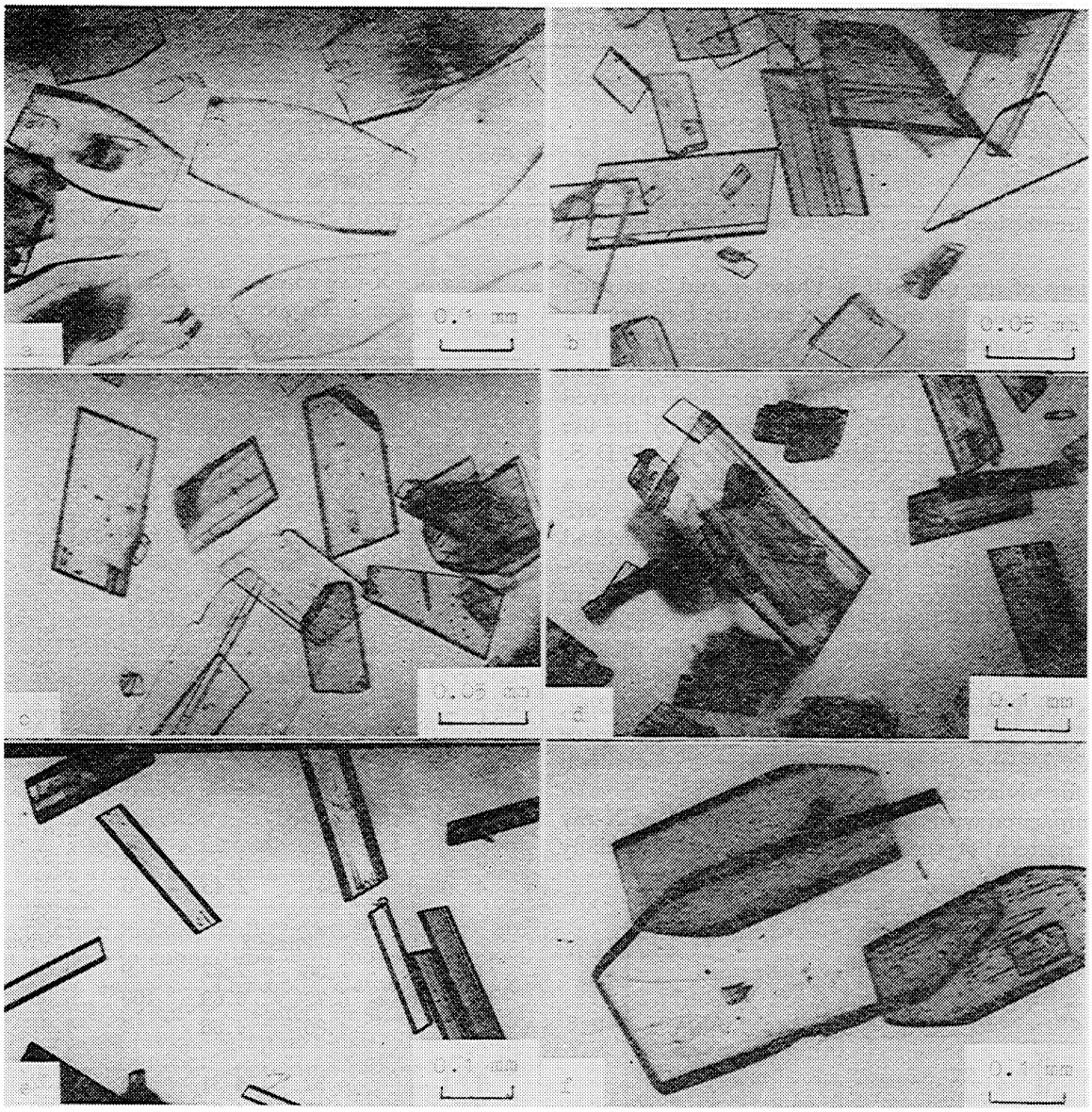

Fig. 2. Photographs of TMP8 obtained with additives at initial pH 6.6 using HCl.
a) $Ca(NO_3)_2 \cdot 4H_2O$, b) $CuSO_4 \cdot 5H_2O$, c) $NiSO_4 \cdot 6H_2O$, d) gelatin (10 g/1500 ml), e) gelatin (45 g/1500 ml), f) agar.

$CoSO_4 \cdot 7H_2O$ was added at an initial pH of about 6.4—6.6. These results might be interpreted as follows: since Mg ions in the TMP8 structure are inferred to be octahedrally coordinated in all their sites,[9] the presence of Cu^{2+} and Ni^{2+}, which tend to prefer octahedral coordination,[10] will be effective on the stabilization of those cation sites of TMP8 and, as a result, on the promotion of its nucleation and crystal growth.

Crystals from the Solutions with Organic Additives. The TMP8 crystals grown in the gelatin solution heated for 6 h were in the form of colorless and transparent fragments. The crystals were plates about 0.1 mm long as a maximum. When the heating time ranged to 24 h, the crystals with a maximum length of about 0.3—0.4 mm were obtained (Fig. 2-d). In this case, the smoothness of the surfaces of the crystals was generally inferior to that of the crystals obtained from the mixtures heated for 6 h described above. As the concentrations of gelatin were increased (40—50 g/1500 ml), the crystals obtained were more elongated along the c-axis and altered from a plate-like shape into a needle-like appearence (Fig. 2-e).

The crystals grown in the agar solution heated for 6 h were about 0.08 mm long as a maximum. Heat treatment for 24—48 h yielded crystals as large as $0.5 \times 0.25 \times 0.04$ mm in maximum size (Fig. 2-f). The surface smoothness of TMP8 crystals grown in the agar solution were, in general, superior to that of crystals in the gelatin solution microscopically. This is probably due to the difference in the stability of gel between the gelatin and agar solutions at 80—90 °C.

A New Crystal Phase of TMP8. Each crystal examined here showed the coexistence of two monoclinic lattices (Phase 1 and Phase 2), judging from the results of the oscillation and Weissenberg photographs. Table 4 shows the lattice constants and possible space groups of Phase 1 and Phase 2 in comparison with those of the natural TMP8 and vivianite, respectively. The axial

TABLE 4. CRYSTALLOGRAPHIC DATA FOR PHASE 1 AND PHASE 2

	a/Å	b/Å	c/Å	β/°	Space group
Phase 1	10.08 (2) [a]	27.86 (3)	4.656 (7)	105.0 (2)	$P2_1/m$, $P2_1$
Bobierrite	9.946[b]	27.654	4.639	104.02	$P2_1/c$[1]
Phase 2	10.07 (2)	13.38 (2)	4.656 (7)	105.0 (2)	C2/m, C2, Cm
Vivianite	10.08	13.43	4.70	104.50	$C2/m$[13]

a) Parenthesized figures represent the estimated standard deviation(esd); 10.08 (2) indicates an esd of 0.02. b) *kX*.

orientations of the unit cell of Phases 1 and 2 in each crystal are parallel to each other, and the b-dimension of Phase 1 is approximately twice that of Phase 2. The lattice constants for Phase 1 are slightly larger than those determined by Barth. Those dimensions observed by us agree rather well with those obtained by the use of the indexed powder data described in the J. C. P. D. S. File.[11] The systematic absences for Phase 1 lead to a space group of $P2_1/m$ or $P2_1$ because of the presence of a weak reflection of $h0l$ with both h and l odd, instead of the $P2_1/c$[1] assigned to natural TMP8. In this synthetic crystal, however, there are a number of extra extinctions that are beyond the criteria demanded by those space groups. The lattice dimensions for Phase 2 are very similar to those of vivianite, and the systematic absences for Phase 2 indicate a space group of C2/m, C2, or Cm. If we assume the centrosymmetric space group C2/m, the space group for Phase 2 is identical to that for vivianite series.

In comparison with the J. C.P. D. S. File,[11] the X-ray powder pattern of the synthetic TMP8 is especially characteristic in the presence of the prominent peak at 13.1—13.2° in 2θ. This can be explained as the strongest reflexion (020) of Phase 2. Figure 3 shows the X-ray diffraction patterns of TMP8 obtained by the addition of inorganic and organic compounds. The TMP8 obtained by adding $NiSO_4$ gives, in general, well-defined X-ray peaks of Phase 2 (Fig. 3-e). The X-ray powder diffraction data were indexed, using the lattice

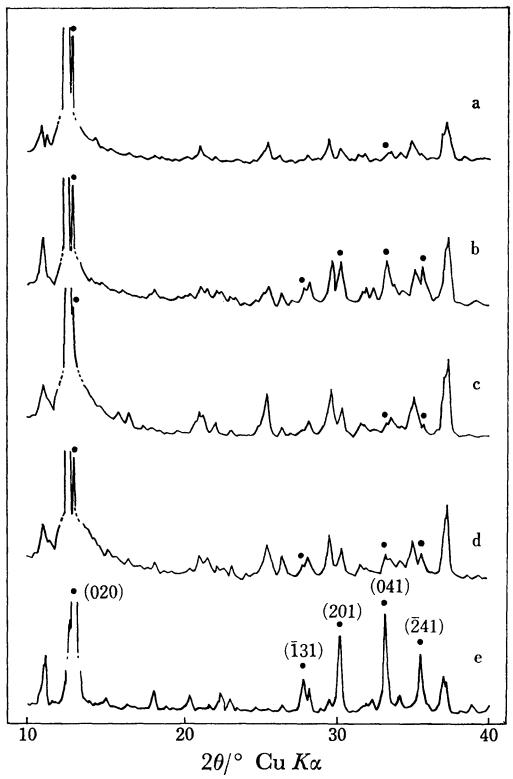

Fig. 3. X-ray diffraction patterns of TMP8 obtained with additives.
a) Agar, b) gelatin, c) $Ca(NO_3)_2 \cdot 4H_2O$, d) $CuSO_4 \cdot 5H_2O$, e) $NiSO_4 \cdot 6H_2O$. Marks (●) show relatively strong diffraction peaks of Phase 2.

TABLE 5. X-RAY POWDER DIFFRACTION DATA OF PHASE 1 AND PHASE 2 COMPARED WITH THOSE OF BOBIERRITE AND VIVIANITE RESPECTIVELY

h	k	l	d_{obsd}	d_{calcd}	I/I_0	d_{obsd}	I/I_0
			Phase 1			Bobierrite	
0	2	0	13.87	13.93	2		
1	2	0	7.96	7.98	4	8.04	18
0	4	0	6.96	6.97	100	6.96	100
2	0	0	4.86	4.87	1	4.87	2
1	6	0	4.18	4.19	1	4.19	6
$\bar{1}$	3	1	4.09	4.09	1	4.11	4
2	4	0	3.97	3.99	1	4.00	4
						3.81	2
0	8	0	3.47	3.48	2	3.48	8
3	2	0	3.15	3.16	1	3.16	4
$\bar{1}$	7	1	3.00	3.00	4	3.02	10
2	1	1	2.93	2.93	3	2.94	25
2	8	0	2.81	2.83	1	2.81	14
						2.66	4
						2.61	6
0	9	1	2.56	2.55	3	2.57	10
4	0	0	2.41	2.43	6	2.41	12
						2.35	4
			Phase 2			Vivianite	
1	1	0	7.88	7.87	9	8.00	27
0	2	0	6.72	6.69	100	6.80	100
2	0	0	4.86	4.86	2	4.91	40
						4.50	13
$\bar{1}$	1	1	4.32	4.31	5	4.32	4
1	3	0	4.05	4.05	1	4.09	13
2	2	0	3.93	3.93	3		
$\bar{2}$	0	1	3.83	3.83	3	3.84	40
						3.65	5
0	4	0	3.35	3.35	2	3.33	3
$\bar{1}$	3	1	3.19	3.19	7	3.20	53
3	1	0	3.13	3.15	4		
2	0	1	2.95	2.94	12	2.97	67
0	4	1	2.69	2.68	15	2.71	67
3	3	0	2.62	2.62	2	2.64	8
$\bar{2}$	4	1	2.52	2.52	11	2.52	33
4	0	0	2.41	2.43	6	2.42	40
						2.31	27
2	4	1	2.21	2.21	4	2.23	20

Table 6. Refractive indices of TMP8 synthesized by the addition of inorganic and organic compounds

Additive	α	β	γ	Reference
$Ca(NO_3)_2 \cdot 4H_2O$	1.512 (3) [a]	—	1.548 (4)	This work
$CuSO_4 \cdot 5H_2O$	1.512 (4)	—	1.549 (4)	This work
$NiSO_4 \cdot 6H_2O$	1.523 (3)	—	1.561 (3)	This work
Gelatin	1.508 (4)	—	1.539 (4)	This work
Agar	1.514 (3)	—	1.548 (4)	This work
Synthetic	1.501 (2)	1.513 (2)	1.536 (2)	Frazier *et al.*[5]
Synthetic	1.510	—	1.543	Barth[2]
Natural	1.510	1.520	1.543	Gruner *et al.*[1]

a) Parenthesized figures indicate the error in the final decimal places.

parameters shown in Table 4 and comparing the data with those of the Weissenberg photographs. The calculated and prominently observed interplaner spacings and indices of Phases 1 and 2 are shown in Table 5, compared with those of TMP8 and vivianite, respectively, in the J. C. P. D. S. File.[12] The reflexions of *h0l* in Phases 1 and 2 overlap each other completely. Therefore, the apparent intensities of the reflexions of each phase were measured on the basis of the X-ray diffraction data of TMP8, in which the intensities of the diffraction lines of Phase 1 or Phase 2 are relatively predominant. The indices and the intensities of each reflexion of Phase 2 correspond with those of each reflexion of vivianite. Phase 2 is considered to be a polymorph of TMP8 and is supposed to be isomorphous with vivianite. The calculated densities are 2.14 for Phase 1 and 2.23 for Phase 2, assuming a formula weight of 4 per unit cell for Phase 1 and a formula weight of 2 per unit cell for Phase 2.

The refractive indices of the synthetic TMP8 are shown in Table 6 in comparison with those determined by some other authors. The optic elasticity axis, Z, in the synthetic crystal is oriented in a direction of about 30° with the crystallographic c-axis. The optical properties measured by us approximate those reported by Barth, and Gruner *et al.*[1] The discrepancies among the refractive indices observed by us may be attributed to the coexistence of Phases 1 and 2 in each synthetic TMP8. The presence of two lattices in the crystal is probably due to the superposition of the thermodynamically stable regions of each phase and to the fact that there is hardly any difference in the potential energies between those phases.

Conclusion

From the studies of the synthetic conditions of $Mg_3(PO_4)_2 \cdot 8H_2O$ (TMP8) and the results of the X-ray single crystal method of the octahydrate, the following conclusions were obtained:

1) TMP8 was synthesized from the mixed solutions of Na_2HPO_4 and $MgSO_4$ at 80—90 °C for 2—24 h, in an initial pH of 6.4—7.0, with the addition of $Ca(NO_3)_2 \cdot 4H_2O$, $CuSO_4 \cdot 5H_2O$, $NiSO_4 \cdot 6H_2O$, gelatin, or agar.

2) Two phases (Phase 1 and Phase 2) of TMP8 were found by means of the X-ray Weissenberg technique to coexist in each synthesized crystal particle.

3) The above Phase 2 is considered to be a new polymorph of TMP8.

4) Newberyite, $MgHPO_4 \cdot 3H_2O$, was also formed in the synthetic procedure of TMP8. This phosphate was precipitated under slightly more acidic conditions than those where TMP8 was obtained.

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