

Cell determination of $\text{Na}_3\text{MgH}(\text{PO}_4)_2$, a Glaserite type structure, and the effect of partial substitution of calcium for magnesium

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Abstract

Magnesium sodium phosphate, $\text{Na}_3\text{MgH}(\text{PO}_4)_2$, crystallizes in the monoclinic cell $C2/m$, is isotypical to $\text{K}_3\text{CaH}(\text{PO}_4)_2$. The crystal morphology is related to the synthesis temperature and the evaporation rate. Partial calcium substitution for magnesium increases the cell symmetry.

1. Introduction

Alkaline and alkaline earth phosphates have been widely studied [1–5]. Because of the lack of data concerning hydrogenophosphates, we are interested in studying the magnesium–sodium hydrogenophosphate salt.

$\text{Na}_3\text{MgH}(\text{PO}_4)_2$ was prepared for the first time by Bassett and Bedwell [6]. The resultant precipitate slowly crystallized after standing in a stoppered flask at 55°C for 3 days.

A comparative study of $\text{Na}_3\text{MgH}(\text{PO}_4)_2$ and $\text{K}_3\text{CaH}(\text{PO}_4)_2$ powder patterns which was originally carried out by Frazier *et al.* [1] showed a close analogy between the two crystal structures and described the crystal morphology as plates that can be in the form of three-membered penetration twins to give the illusion of hexagonal symmetry. They concluded that the system symmetry was probably monoclinic. By comparing the two salts $\text{K}_3\text{CaH}(\text{PO}_4)_2$ and $\text{Na}_3\text{MgH}(\text{PO}_4)_2$, Frazier *et al.* noticed a volume decrease in the cell of the second salt.

The structure of $\text{K}_3\text{CaH}(\text{PO}_4)_2$ was solved by Takagi *et al.* [4]. They showed that it was the first example of a compound which is structurally related to a glaserite and contains an acidic phosphate group HPO_4^{2-} . $\text{K}_3\text{CaH}(\text{PO}_4)_2$ crystallizes in a monoclinic system having a centrosymmetric space group $C2/m$, with the following parameters: $a = 9.878 \text{ \AA}$, $b = 5.735 \text{ \AA}$, $c = 7.436 \text{ \AA}$, $\beta = 94.28^\circ$; $Z = 2$.

The Ca^{2+} , K^+ and PO_4^{3-} ions are packed in two types of columns along the [001] direction, one containing only the cations Ca^{2+} and K^+ (1), and the other both cations K^+ (2) and anions PO_4^{3-} . Each cation column is surrounded by six cation–anion columns and

in turn each cation–anion column is surrounded by three cation columns and three cation–anion columns alternately arranged. The arrangement of these columns in pseudo-hexagonal form is similar to that of glaserite, K_3NaSO_4 [7].

2. Cell parameters of $\text{Na}_3\text{MgH}(\text{PO}_4)_2$

The cell structure of $\text{Na}_3\text{MgH}(\text{PO}_4)_2$ was determined by the National Bureau of Standards using the Visser program [8]. It was indexed in triclinic symmetry $P1$, with the following parameters. $a = 5.2305 \text{ \AA}$, $b = 6.9224 \text{ \AA}$, $c = 5.1774 \text{ \AA}$, $\alpha = 91.563^\circ$, $\beta = 117.502^\circ$, $\gamma = 90.439^\circ$, $D_m = 2.88$ and $Z = 1$ [9]. The symmetry group $P1$ is not found in organic chemistry, which induced us to study this salt.

Many preparations were made under different conditions to synthesize the salt:

(1) using Bassett's method [6] with a standing period varying between 2 and 15 days, the crystal size never exceeded $20 \mu\text{m}$;

(2) at atmospheric pressure, a slow flow of a sodium hydroxide solution in phosphoric acid containing magnesium, or a flow of a phosphoric acid in hydroxide solution was tried unsuccessfully to increase the crystal size;

(3) finally, crystallization under controlled vapour pressure in the temperature range $40\text{--}150^\circ\text{C}$ during a period varying from a few days to two weeks; the size of the crystallite obtained was never adequate for structure determination using an automatic four-circle diffractometer.

TABLE 1. $\text{K}_3\text{CaH}(\text{PO}_4)_2$ and $\text{Na}_3\text{MgH}(\text{PO}_4)_2$ parameters

Compound	$a(\text{\AA})$	$b(\text{\AA})$	$c(\text{\AA})$	$\beta(^{\circ})$	Z	Space group
$\text{K}_3\text{CaH}(\text{PO}_4)_2$	9.878(1)	5.735(1)	7.436(1)	94.28(1)	2	$C2/m$
$\text{Na}_3\text{MgH}(\text{PO}_4)_2$	9.176(1)	5.240(1)	6.826(1)	93.12(1)	2	$C2/m$

Using Lou er's program [10], a monoclinic cell was obtained with the following parameters: $a = 9.176(1)$, $b = 5.240(1)$, $c = 6.826(1) \text{\AA}$, $\beta = 93.12(1)^{\circ}$, $D_x = 2.86(3)$ and $Z = 2$. These values agreed with the values expected by Frazeir *et al.* [1], see Table 1.

The relationships between monoclinic and triclinic cells are:

$$a_m = 2c_{\text{tri}} + a_{\text{tri}}$$

$$b_m = a_{\text{tri}}$$

$$c_m = b_{\text{tri}}$$

Systematic extinctions of hkl for $h + k = 2n + 1$ indicated the possible space groups $C2$, Cm and $C2/m$. The centrosymmetric space group $C2/m$ was chosen. The established contraction of all parameters is related to the difference between cation radii.

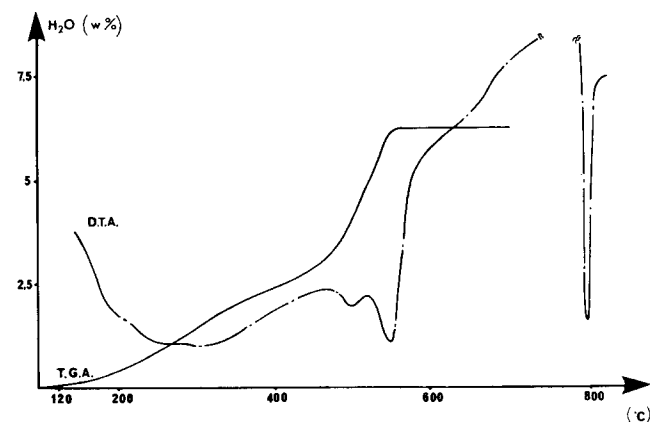


Fig. 1. Thermogravimetric and differential analysis of $\text{Na}_3\text{MgH}(\text{PO}_4)_2$.

That contraction is greater than 10%. Thus, we confirmed that $\text{Na}_3\text{MgH}(\text{PO}_4)_2$ is structurally related to $\text{K}_3\text{CaH}(\text{PO}_4)_2$. The structure of these two salts is glaserite type containing the hydrogenophosphate anion HPO_4^{2-} .

3. Synthesis and morphology of $\text{Na}_3\text{MgH}(\text{PO}_4)_2$

$\text{Na}_3\text{MgH}(\text{PO}_4)_2$ was prepared following an original method, by the evaporation of a concentrated solution of phosphoric acid containing magnesium hydroxide, $\text{Mg}(\text{OH})_2$, 0.5 mol l^{-1} , and neutralized by sodium hydroxide at pH 7. After evaporation under water vapour pressures ranging from 0.7 to 2.0 bar, a precipitation of $\text{Na}_3\text{MgH}(\text{PO}_4)_2$ was observed.

3.1. Centesimal analysis

Phosphor, sodium and magnesium were analysed using inductively coupled plasma atomic emission spectroscopy. The percentage of water was determined by thermal analysis. A Stanton Redcroft apparatus for simultaneous DTA/TGA was used (heating rate $5^{\circ} \text{ min}^{-1}$ see Fig. 1. Table 2 shows that, taking into account experimental errors, the water pressure does not seem to have any influence on this phase composition. In fact, this composition is constant and corresponds to the chemical compound $\text{Na}_3\text{MgH}(\text{PO}_4)_2$ [5–7], see Table 3.

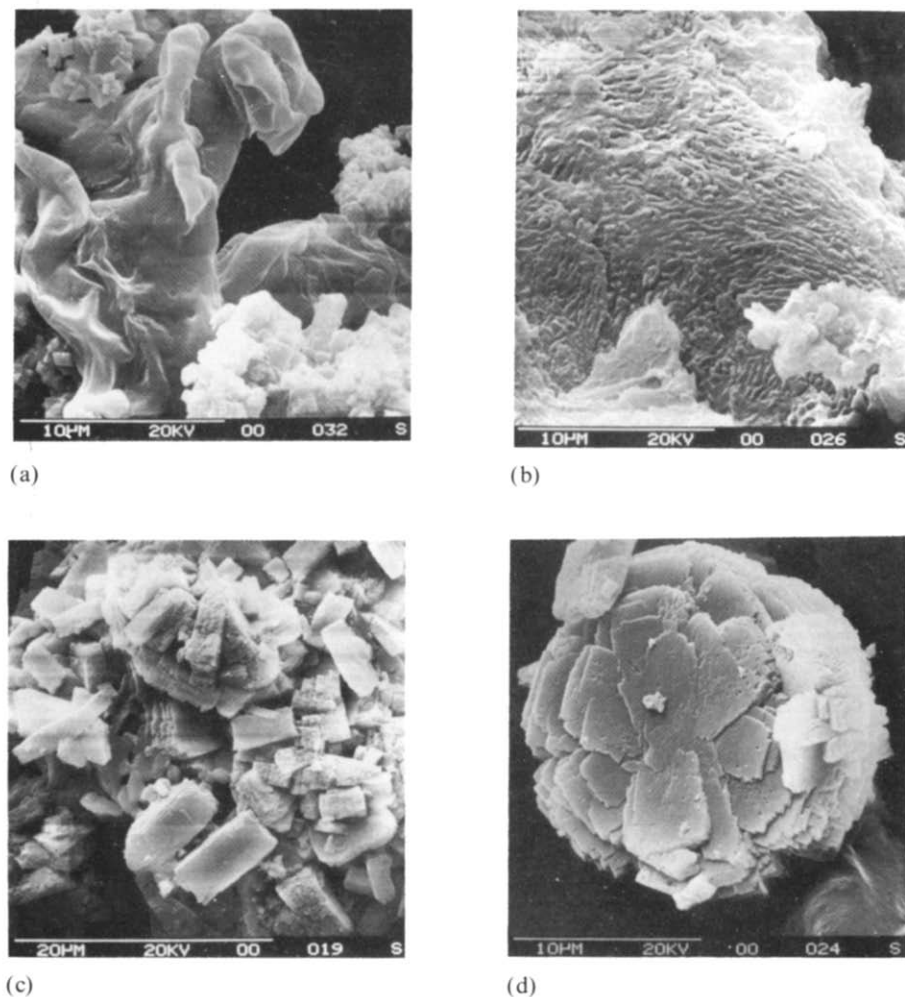
The morphology of the crystallites is related to the conditions of preparation. At low temperature (0.7 bar), $\text{Na}_3\text{MgH}(\text{PO}_4)_2$ was precipitated as a gelatinous compound [7], (Figs. 2(a) and 2(b)). Evaporation

TABLE 2. Centesimal analysis of the precipitate

Pressure (bar)	PO_4 (wt.%)	Na (wt.%)	Mg (wt.%)	H_2O (wt.%)	$[\text{Na}]/[\text{P}]$	$[\text{Mg}]/[\text{P}]$
0.7	66.6	22.4	8.3	4.0	1.40	0.49
0.8	65.8	22.6	7.5	4.1	1.42	0.45
0.9	67.1	23.3	7.8	4.0	1.44	0.46
1.0	66.6	23.0	7.5	4.3	1.43	0.44
1.2	65.9	23.8	7.4	4.0	1.48	0.44
1.4	66.2	21.5	9.4	3.9	1.34	0.56
1.6	65.8	23.9	7.4	4.0	1.50	0.44
2.0	65.9	22.7	8.5	4.1	1.42	0.51

TABLE 3. Average experimental values and calculated values

	PO_4 (wt.%)	Na (wt.%)	Mg (wt.%)	H_2O (wt.%)	[Na]/[P]	[Mg]/[P]
Experimental value	66.5	23.0	7.8	4.0	1.45	0.46
Calculated value	67.10	24.10	8.55	3.17	1.50	0.5

Fig. 2. Influence of water pressure on the $\text{Na}_3\text{MgH}(\text{PO}_4)_2$ crystal morphology: (a) 0.7 bar, (b) 0.8 bar, (c) 1.0 bar, (d) 2.0 bar.

at high temperature ($125\text{ }^\circ\text{C}$) (2.0 bar), gives well developed crystallites whose size varies between 10 and $20\text{ }\mu\text{m}$ (see Figs. 2(c) and 2(d)). These crystallite plates are gathered into rows giving the illusion of hexagonal symmetry. These observations show the noticeable influence of temperature on the nucleation rate and growth rate of $\text{Na}_3\text{MgH}(\text{PO}_4)_2$ crystallites.

3.2. Partial substitution of magnesium by calcium

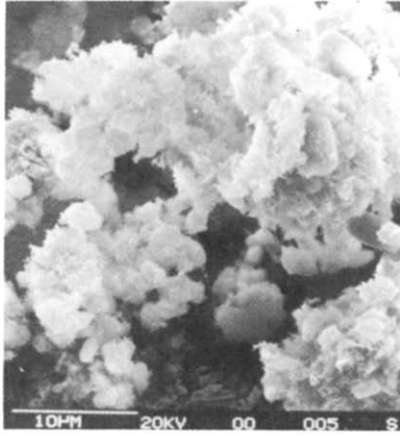
We substituted 5–10 at.% of magnesium with calcium using the same preparation method. A centesimal analysis of the precipitate was carried out under the same conditions (Table 4).

Important modifications in the crystallite morphology and in the powder pattern of this compound are observed.

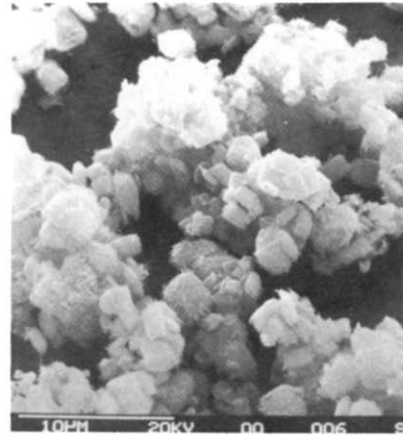
Substituting for magnesium with calcium influenced the crystallite's morphology. This substitution disturbed the crystal growth during precipitation. The plates previously observed are less developed in the presence of calcium. The crystal morphology became square or even rounded, as illustrated in Fig. 3. At the same time, an important change in the powder pattern is observed; the number of reflections decreased, indicating a higher symmetry. These results are illustrated in Fig. 4. The reflections (hkl) and ($hk\bar{l}$) are merged,

TABLE 4. Centesimal analysis of precipitate

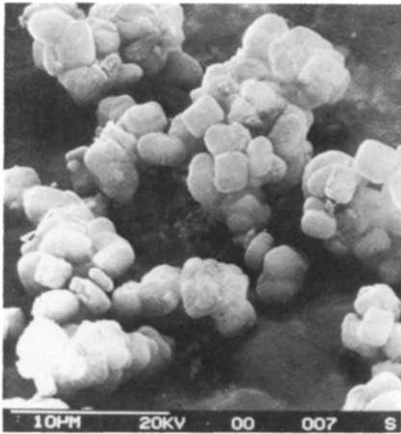
Pressure (bar)	PO_4 (wt.%)	Na (wt.%)	Mg (wt.%)	Ca (wt.%)	[Na]/[P]	[Mg]/[P]	[Ca + Mg]/[P]
0.6	66.7	24.4	7.7	1.7	1.51	0.45	0.51
0.8	66.2	24.6	7.5	1.7	1.53	0.44	0.50
1.0	64.5	24.1	7.4	1.6	1.54	0.45	0.50
1.2	66.1	24.5	6.3	1.6	1.53	0.37	0.43
1.6	66.7	24.8	6.3	1.6	1.53	0.37	0.43
2.0	67.1	25.2	6.2	1.6	1.55	0.36	0.42



(a)



(b)



(c)



(d)

Fig. 3. Precipitate morphology of $\text{Na}_3\text{Mg}_{1-x}\text{Ca}_x\text{H}(\text{PO}_4)_2$: (a) 0.8 bar, (b) 1.0 bar, (c) 1.6 bar, (d) 2.0 bar.

inducing evolution from a monoclinic system to an orthorhombic or hexagonal system. The (002) reflection is not changed, indicating conservation of the c direction.

4. Discussion

The crystal morphology is related to the synthesis temperature and the evaporation rate. The nucleation

rate B^0 and the growth rate G are influenced by the temperature. The growth and nucleation rates are frequently represented by the following power-law models [11, 12]

$$G = K_g s^a$$

$$B^0 = K_n s^b M_i^c$$

where M_i is the suspension density and s the supersaturation of the solution. The rate constants follow an

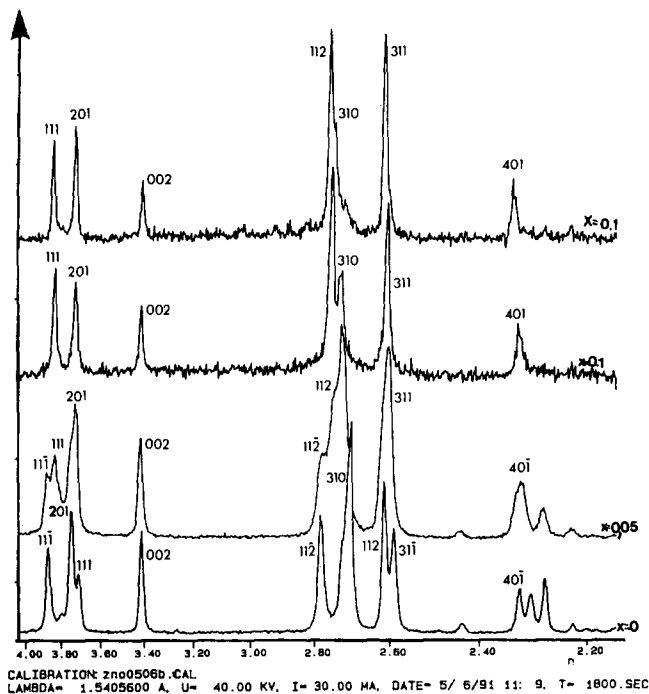


Fig. 4. Powder pattern modification of $\text{Na}_3\text{Mg}_{1-x}\text{Ca}_x\text{H}(\text{PO}_4)_2$.

Arrhenius type of temperature dependency:

$$K_g = K_1 \exp(-\Delta E_g/RT)$$

$$K_n = K_2 \exp(-\Delta E_n/RT)$$

ΔE_g and ΔE_n are respectively the activation energy for crystal growth and the activation energy for nucleation. The supersaturation is a function of the ratio $\Delta E_n/\Delta E_g$ and the temperature [13, 14]. The evaporation rate depends on temperature and water pressure. The rates of nucleation and growth are related to the evaporation rate.

At lower water pressure (less than or equal to 0.3 bar), the solution temperature is 60 °C, and a high evaporation rate is recorded. Under these conditions no

precipitation occurred, since the nucleation rate is not sufficient. In fact, it is lower than the evaporation rate. When the water pressure increases, the temperature increases and crystals with a size of about 10 μm are obtained.

The substitution of magnesium by calcium influenced the crystal morphology and increased the system symmetry. This is probably due to the disorder introduced by the substitution in the system.

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