

The crystal structures of NaMgPO_4 , $\text{Na}_2\text{CaMg}(\text{PO}_4)_2$ and $\text{Na}_{18}\text{Ca}_{13}\text{Mg}_5(\text{PO}_4)_{18}$: new examples for glaserite related structures

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Abstract. Three phosphates with $(\text{NaM}^{\text{II}}\text{PO}_4)_x$ composition have been synthesized and characterized structurally. The low temperature modifications of NaMgPO_4 and $\text{Na}_2\text{CaMg}(\text{PO}_4)_2$ crystallize in the orthorhombic space group $P2_12_12_1$, and the monoclinic space group $P2_1/c$, respectively. The phase transitions at high temperature were investigated by thermal analysis and powder diffractometry. The high-temperature modification of $\text{Na}_2\text{CaMg}(\text{PO}_4)_2$ is isotypic with glaserite, $\text{K}_3\text{Na}(\text{SO}_4)_2$ as determined by Rietveld refinement. $\text{Na}_{18}\text{Ca}_{13}\text{Mg}_5(\text{PO}_4)_{18}$ crystallizes in the trigonal space group $R\bar{3}m$. The structures of all of these phosphates can be related to the arrangement of cations and phosphate tetrahedra in the glaserite structure.

Introduction

Whereas the crystal chemistry of silicates of alkaline and alkaline earth metals has extensively been studied the knowledge of the crystal structures of the corresponding phosphates is rather scarce. As some important biomaterials are based on phosphate glass ceramics this lack of information constitutes a considerable drawback for the further development of these materials (e.g. Vogel, Höland 1987; Schulz, Mieke, Fuess, Wange, Götz 1994; Alkemper, Fuess 1997). We therefore carried out a program to synthesize and to characterize relevant phases which may occur in phosphate glass ceramics.

In the system $\text{Na}_3\text{PO}_4\text{--Ca}_3(\text{PO}_4)_2$ only the structure of one ternary compound, NaCaPO_4 , was previously determined (Olsen, Bunch, Moore 1977; Ben Amara, Vlasse, Le Flem, Hagenmuller 1983a). In the system $\text{Na}_3\text{PO}_4\text{--Mg}_3(\text{PO}_4)_2$ three ternary phosphates were reported (Majling, Hanic 1976): $\text{NaMg}_4(\text{PO}_4)_3$, $\text{Na}_4\text{Mg}(\text{PO}_4)_2$ and NaMgPO_4 . Whereas the structure of the first is completely known (Ben Amara et al. 1983b), the others were only identified by their powder diffraction patterns. Indexing for $\text{Na}_4\text{Mg}(\text{PO}_4)_2$ indicated tetragonal system (Ghorbel, d'Yvoire, Dorémieux-Morin 1974) but failed for NaMgPO_4 . Using thermal analysis and high-temperature powder diffraction, up to five high-temperature

polymorphs of NaMgPO_4 were described (Kapralik, Potancok 1971; Majling 1973; Ust'yantsev, Tretnikova, Kellareva 1976).

Brianite, $\text{Na}_2\text{CaMg}(\text{PO}_4)_2$, the only intermediate phase in the system $\text{NaMgPO}_4\text{--NaCaPO}_4$ known by now, was first described by Fuchs, Olsen and Henderson (1967). Moore (1975) proposed isomorphism with merwinite ($\text{Ca}_3\text{Mg}(\text{SiO}_4)_2$). Ust'yantsev and Tretnikova (1976) detected a reversible phase transformation at 1113 K and an incongruent melting point at 1493 K.

$\text{Na}_4\text{Ca}_4\text{Mg}_{21}(\text{PO}_4)_{18}$, a quaternary oxide with a stoichiometry different from the general $\text{NaM}^{\text{II}}\text{PO}_4$ compounds, was synthesized and structurally characterized by Domanskii et al. (1982).

Experimental

A starting powder for the synthesis of NaMgPO_4 -crystals was obtained by heating an equimolar mixture of NaPO_3 and MgO to 1273 K, cooling to 873 K (5 K/min) and holding for 10 h. The powder contained $\alpha\text{-NaMgPO}_4$, the low-temperature modification, and a small amount of another phosphate, which could not be identified. This powder was then mixed with Na_2MoO_4 (1:1), heated to 1223 K and cooled slowly (10 K/h). After washing with water the powder contained platelike single crystals of $\alpha\text{-NaMgPO}_4$. Single phase powders could be obtained by riddling these crystals.

$\text{Na}_2\text{CaMg}(\text{PO}_4)_2$ single crystals were synthesized by mixing NaPO_3 , CaO and MgO in stoichiometric amounts with Na_2MoO_4 , heating to 1073 K and cooling slowly to 773 K (5 K/h). The Na_2MoO_4 was removed by washing with water. In this way a powder with hexagonal $\text{Na}_2\text{CaMg}(\text{PO}_4)_2$ - and rhombohedral $\text{Na}_{18}\text{Ca}_{13}\text{Mg}_5(\text{PO}_4)_{18}$ -crystals was obtained. Single phase powders resulted from riddling the larger $\text{Na}_2\text{CaMg}(\text{PO}_4)_2$ -crystals. A suitable crystal for structure determination had to be selected carefully because the plates were often twinned.

X-ray powder patterns were collected on a STOE powder diffractometer in transmission geometry using $\text{CuK}\alpha_1$ radiation. A position sensitive detector allowed fast measurements. Structure refinements were performed by

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Rietveld analysis using FULLPROF (Rodriguez-Carvajal 1990) for phases with supposed or known structure. Phase transformations were observed in-situ using a high temperature attachment with Debye-Scherrer geometry.

The data acquisition for single crystal structure determination was performed using a STOE-STADI-4 diffractometer with MoK α radiation (scan mode: $2\theta/\omega = 1/1$) at 293 K. Due to the small size of the crystals, long measuring times and limitations in $2\theta_{\max}$ were inevitable. The structure determination and the refinement were performed with SHELX-86 and SHELXL-93, respectively.

Phase transformation temperatures of powders were detected with heating rates of 5 K/min using a Setaram differential scanning calorimeter.

Results

The crystal structures of NaMgPO $_4$, Na $_2$ CaMg(PO $_4$) $_2$ and Na $_{18}$ Ca $_{13}$ Mg $_5$ (PO $_4$) $_{18}$

The details of the single crystal structure data collection and the structure determination are summarized in Table 1.

Table 1. Details and results of single crystal structure analysis of NaMgPO $_4$, Na $_2$ CaMg(PO $_4$) $_2$ and Na $_{18}$ Ca $_{13}$ Mg $_5$ (PO $_4$) $_{18}$.

	α -NaMgPO $_4$	α -Na $_2$ CaMg(PO $_4$) $_2$	Na $_{18}$ Ca $_{13}$ Mg $_5$ (PO $_4$) $_{18}$
Crystal	colorless prism	colorless hexagon	colorless rhombohedron
Crystal size	0.14 \times 0.20 \times 0.24 mm	0.20 \times 0.20 \times 0.07 mm	0.12 \times 0.18 \times 0.21 mm
μ	9.35 cm $^{-1}$	17.46 cm $^{-1}$	17.39 cm $^{-1}$
$2\theta_{\max}$	70 $^\circ$	70 $^\circ$	60 $^\circ$
$N(hkl)_{\text{unique}}$	3982	2792	1674
$N(\text{param})_{\text{refined}}$	190	128	135
Crystal system, SG	orthorhombic, $P2_12_12_1$ (No. 19)	monoclinic, $P2_1/c$ (No. 14)	trigonal $R\bar{3}m$ (No. 166)
a	8.828(2) Å	9.120(3) Å	15.811(3) Å
b	6.821(2) Å	5.198(2) Å	15.811(3) Å
c	15.250(4) Å	13.370(4) Å	21.499(4) Å
β	—	90.78 $^\circ$	—
V	918.3(4) Å 3	633.8(4) Å 3	4644(4) Å 3
Z	4	4	3
$R(F)$	0.049	0.040	0.039
$R_w(F^2)$	0.167	0.119	0.135

Table 2. Final atomic coordinates ($\cdot 10^4$) and displacement parameters (Å $^2 \cdot 10^3$) for α -NaMgPO $_4$.

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Na(1)	1427(1)	2941(2)	5938(1)	8(1)	12(1)	9(1)	-2(1)	0(1)	-1(1)
Na(2)	1494(2)	2196(2)	2617(1)	12(1)	17(1)	7(1)	0(1)	-1(1)	-1(1)
Na(3)	1484(2)	2324(2)	-715(1)	11(1)	20(1)	9(1)	2(1)	0(1)	3(1)
Mg(1)	4867(1)	4529(1)	2604(1)	7(1)	6(1)	6(1)	-2(1)	-2(1)	0(1)
Mg(2)	4804(1)	415(1)	5960(1)	8(1)	11(1)	8(1)	2(1)	-3(1)	-2(1)
Mg(3)	4959(1)	247(1)	9218(1)	6(1)	13(1)	6(1)	3(1)	-2(1)	-2(1)
P(1)	3204(1)	2184(1)	992(1)	2(1)	5(1)	3(1)	0(1)	-1(1)	-1(1)
P(2)	3200(1)	2755(1)	7646(1)	3(1)	5(1)	2(1)	0(1)	0(1)	0(1)
P(3)	3163(1)	2559(1)	4332(1)	3(1)	10(1)	3(1)	2(1)	0(1)	0(1)
O(1)	3845(2)	3964(3)	1476(1)	12(1)	5(1)	5(1)	0(1)	-3(1)	-2(1)
O(2)	3559(2)	4435(3)	4835(1)	8(1)	11(1)	8(1)	-2(1)	-3(1)	-2(1)
O(3)	3839(2)	4581(3)	8093(1)	11(1)	9(1)	7(1)	-3(1)	-4(1)	-4(1)
O(4)	1439(2)	2294(3)	1016(1)	3(1)	13(1)	7(1)	1(1)	1(1)	2(1)
O(5)	3805(2)	2157(3)	49(1)	6(1)	14(1)	5(1)	-2(1)	1(1)	1(1)
O(6)	1439(2)	2861(2)	7665(1)	2(1)	5(1)	9(1)	0(1)	-1(1)	0(1)
O(7)	3782(2)	2581(3)	3388(1)	7(1)	17(1)	4(1)	1(1)	2(1)	0(1)
O(8)	1404(2)	2347(3)	4334(1)	3(1)	12(1)	7(1)	2(1)	1(1)	3(1)
O(9)	3677(2)	939(3)	8160(1)	11(1)	10(1)	10(1)	2(1)	-4(1)	3(1)
O(10)	3666(2)	327(3)	1490(1)	11(1)	5(1)	13(1)	1(1)	-6(1)	-1(1)
O(11)	3860(2)	817(3)	4810(1)	8(1)	13(1)	9(1)	4(1)	-3(1)	1(1)
O(12)	3812(2)	2688(3)	6693(1)	6(1)	13(1)	6(1)	-2(1)	2(1)	1(1)

The final atomic coordinates and displacement parameters are collected in Tables 2–4¹.

α -NaMgPO $_4$ crystallizes in the orthorhombic space group $P2_12_12_1$. The phosphate tetrahedra are nearly regular. Mg is coordinated quadratically by five oxygen atoms with distances 1.97 Å–2.18 Å. A sixth oxygen atom is shifted to a distance of 2.48 Å–2.97 Å. The structure is closely related to that of maricite, NaFePO $_4$ (Le Page, Donnay 1977), but there the Fe coordination is slightly distorted but centrosymmetric octahedral. This is the main reason for the symmetry reduction from $Pnma$ in the case of NaFePO $_4$ to the subgroup $P2_12_12_1$ of NaMgPO $_4$.

α -Na $_2$ CaMg(PO $_4$) $_2$ is isotypic with merwinite, Ca $_2$ CaMg(SiO $_4$) $_2$ as suggested by Moore (1975). Although

¹ Additional material to this paper can be ordered referring to the no. CSD 408374 (NaMgPO $_4$), CSD 408373 (Na $_2$ CaMg(PO $_4$) $_2$) and CSD 408372 (Na $_{18}$ Ca $_{13}$ Mg $_5$ (PO $_4$) $_{18}$), names of the authors and citation of the paper at the Fachinformationszentrum, Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany. The list of F_o/F_c -data is available from the author up to one year after the publication has appeared.

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₂₃	<i>U</i> ₁₃	<i>U</i> ₁₂
Na(1)	4e	5812(1)	2786(2)	3986(1)	16(1)	13(1)	12(1)	-2(1)	-1(1)	-1(1)
Na(2)	4e	835(1)	7774(2)	4101(1)	15(1)	13(1)	9(1)	-2(1)	-1(1)	1(1)
Ca(1)	4e	2373(1)	3149(1)	2494(1)	24(1)	10(1)	7(1)	0(1)	0(1)	1(1)
Mg(1)	4e	2526(1)	2542(1)	5018(1)	6(1)	7(1)	4(1)	1(1)	0(1)	0(1)
P(1)	4e	4137(1)	7727(1)	3695(1)	5(1)	5(1)	4(1)	0(1)	-1(1)	0(1)
P(2)	4e	9185(1)	2707(1)	3654(1)	6(1)	5(1)	3(1)	-1(1)	0(1)	0(1)
O(11)	4e	4024(2)	6723(3)	2633(1)	25(1)	19(1)	8(1)	-7(1)	-2(1)	2(1)
O(12)	4e	9236(2)	1951(3)	2558(1)	27(1)	15(1)	4(1)	-3(1)	0(1)	3(1)
O(21)	4e	3348(2)	341(3)	3811(1)	15(1)	7(1)	8(1)	0(1)	2(1)	3(1)
O(22)	4e	8319(2)	5215(3)	3812(1)	13(1)	8(1)	8(1)	0(1)	3(1)	4(1)
O(31)	4e	758(2)	3052(3)	4068(1)	8(1)	15(1)	14(1)	4(1)	-5(1)	-1(1)
O(32)	4e	5752(2)	8028(3)	4014(1)	8(1)	15(1)	15(1)	4(1)	-6(1)	-1(1)
O(41)	4e	3410(2)	5746(3)	4386(1)	15(1)	10(1)	17(1)	6(1)	4(1)	-3(1)
O(42)	4e	8455(2)	505(3)	4242(1)	14(1)	9(1)	13(1)	4(1)	2(1)	-3(1)

Table 3. Final atomic coordinates ($\cdot 10^4$) and displacement parameters ($\text{\AA}^2 \cdot 10^3$) for α -Na₂CaMg(PO₄)₂.

Table 4. Final atomic coordinates ($\cdot 10^4$) and displacement parameters ($\text{\AA}^2 \cdot 10^3$) for α -Na₂CaMg(PO₄)₂.

Atom	Site	Occupancy	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₂₃	<i>U</i> ₁₃	<i>U</i> ₁₂
Mg(1)	6c	0.1667	0	0	3605(1)	12(1)	12(1)	12(1)	0	0	6(1)
Mg(2)	3b	0.0833	0	0	5000	10(1)	10(1)	8(1)	0	0	5(1)
Mg(3)	6c	0.1667	0	0	1609(1)	11(1)	11(1)	15(1)	0	0	6(1)
Ca(1)	3a	0.0833	0	0	0	63(1)	63(1)	7(1)	0	0	32(1)
Ca(2)	18f	0.5000	3091(1)	0	0	19(1)	23(1)	17(1)	9(1)	4(1)	12(1)
Na(3)	18g	0.3750	3192(1)	0	5000	19(1)	27(1)	21(1)	15(1)	7(1)	14(1)
Ca(3)	18g	0.1250	3192(1)	0	5000	19(1)	27(1)	21(1)	15(1)	7(1)	14(1)
Na(4)	18h	0.2000	2157(1)	-2157(1)	2654(1)	19(1)	19(1)	14(1)	2(1)	-2(1)	4(1)
Ca(4)	18h	0.3000	2157(1)	-2157(1)	2654(1)	19(1)	19(1)	14(1)	2(1)	-2(1)	4(1)
Na(5)	18h	0.5000	1073(1)	-1073(1)	1052(1)	27(1)	27(1)	20(1)	-2(1)	2(1)	14(1)
Na(6)	18h	0.4250	2163(1)	-2163(1)	-1193(2)	43(1)	43(1)	56(2)	-3(1)	3(1)	27(1)
Ca(6)	18h	0.0750	2211(3)	-2211(3)	-462(5)	32(3)	32(3)	70(7)	2(2)	-2(2)	16(3)
P(1)	18h	0.5000	2217(1)	-2217(1)	991(1)	9(1)	9(1)	13(1)	0(1)	0(1)	6(1)
O(1)	18h	0.5000	2779(1)	-2779(1)	1019(1)	23(1)	23(1)	15(1)	1(1)	-1(1)	19(1)
O(2)	18h	0.5000	1983(1)	-1983(1)	1640(2)	29(1)	29(1)	21(1)	-5(1)	5(1)	18(1)
O(3)	36i	1.0000	2877(2)	4117(2)	667(1)	22(1)	21(1)	29(1)	-5(1)	2(1)	15(1)
P(2)	18h	0.5000	1110(1)	-1110(1)	-724(1)	12(1)	12(1)	17(1)	-2(1)	2(1)	5(1)
O(4)	18h	0.5000	1205(1)	-1205(1)	26(2)	34(1)	34(1)	19(2)	4(1)	-4(1)	13(2)
O(5)	18h	0.5000	564(1)	-564(1)	-862(2)	25(1)	25(1)	36(2)	3(1)	-3(1)	16(1)
O(6)	36i	1.0000	2682(2)	2138(2)	1002(1)	39(1)	16(1)	37(1)	-10(1)	-16(1)	11(1)
P(3)	18h	0.5000	4329(1)	-4329(1)	-709(1)	14(1)	14(1)	12(1)	-1(1)	1(1)	6(1)
O(7)	18h	0.5000	3972(1)	-3972(1)	-157(2)	40(2)	40(2)	18(2)	-3(1)	3(1)	31(2)
O(8)	18h	0.5000	4034(2)	-4034(2)	-1301(2)	165(6)	165(6)	15(2)	1(1)	-1(1)	133(6)
O(9A)	36i	0.3000	5849(9)	5308(7)	474(4)	76(8)	18(4)	26(5)	5(4)	27(5)	21(5)
O(9B)	36i	0.7000	6224(4)	5450(3)	760(2)	50(3)	15(2)	44(3)	1(2)	24(2)	14(2)

the space group is $P2_1/c$, the structure is nearly C -centered. The reflections $h + k = 2n$ contribute with about 1–5% of the overall medium intensity only. The phosphate tetrahedra are almost regular. The Mg-coordination however differs significantly from NaMgPO₄. The oxygen octahedra are only slightly distorted ($d_{\text{Mg-O}} = 2.08 \pm 0.04 \text{ \AA}$, $\angle_{\text{O-Mg-O}} = 90 \pm 7^\circ$).

Na₁₈Ca₁₃Mg₅(PO₄)₁₈ crystallizes in the trigonal space group $R\bar{3}m$ with a relatively large unit cell. The composition was fixed under the assumption of two cationic positions per phosphorous atom leading to the general formula NaM^{II}PO₄.

Furthermore, only magnesium was located in the octahedral oxygen-coordinated sites ($d_{\text{Mg-O}} = 1.98 \text{ \AA} - 2.21 \text{ \AA}$). The remaining more irregular coordinated positions are occupied by sodium and calcium. Due to their similar ionic radii, it is impossible to distinguish exactly between them and we assume, that they share sites. The final structure refinement was carried out using fixed idealized site occupancies based on the previous refinement with fixed dis-

placement parameters. The cationic positions Na(6) and Ca(6) have a distance of 1.5 Å from each other and so only one of them can be occupied. This leads to disordered phosphate tetrahedra around P(3) with relatively high displacement parameters and a splitted position O(9).

High-temperature polymorphs of NaMgPO₄ and Na₂CaMg(PO₄)₂

Thermal analysis of NaMgPO₄ in the range of 300 K to 1173 K shows one endothermic and one exothermic effect on heating and cooling respectively (e.g. heating: 1001 K, cooling: 924 K at a rate of 5 K/min). These effects belong to the reversible, but kinetically hindered phase transition of NaMgPO₄ at 690(15) K. This was confirmed by high-temperature X-ray diffraction. Above about 1200 K decomposition is observed. Fig. 1 shows the room temperature diffraction pattern of α -NaMgPO₄ (compared with ICDD 32-1119) and the pattern of β -NaMgPO₄ at 1193 K (ICDD 32-1120). At 1243 K additional reflections are ob-

Fig. 1. In-situ powder diffraction patterns of the phase transitions and the decomposition of NaMgPO_4 . The lines marked by arrows are caused by the platinum support.

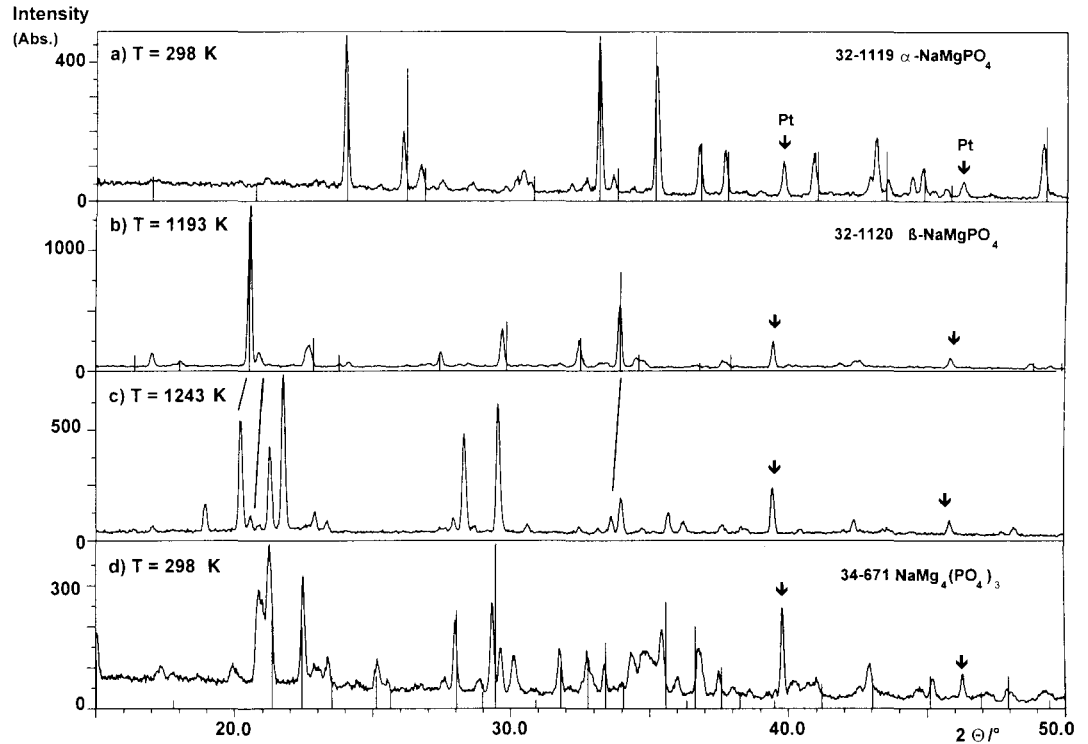


Fig. 2. Result of RIETVELD-refinement of the powder pattern of $\beta\text{-Na}_2\text{CaMg}(\text{PO}_4)_2$ ($T = 1093 \text{ K}$). Reflections marked with arrows are caused by a second phase.

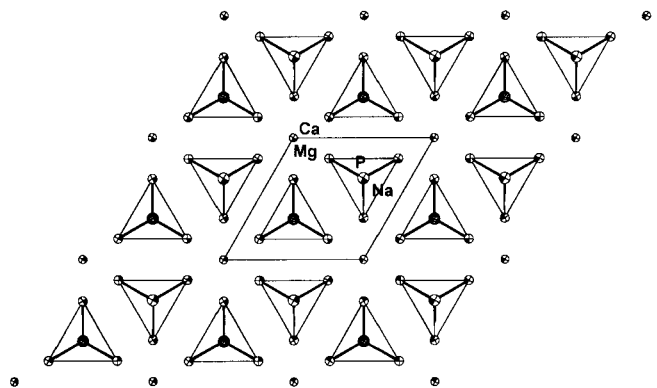
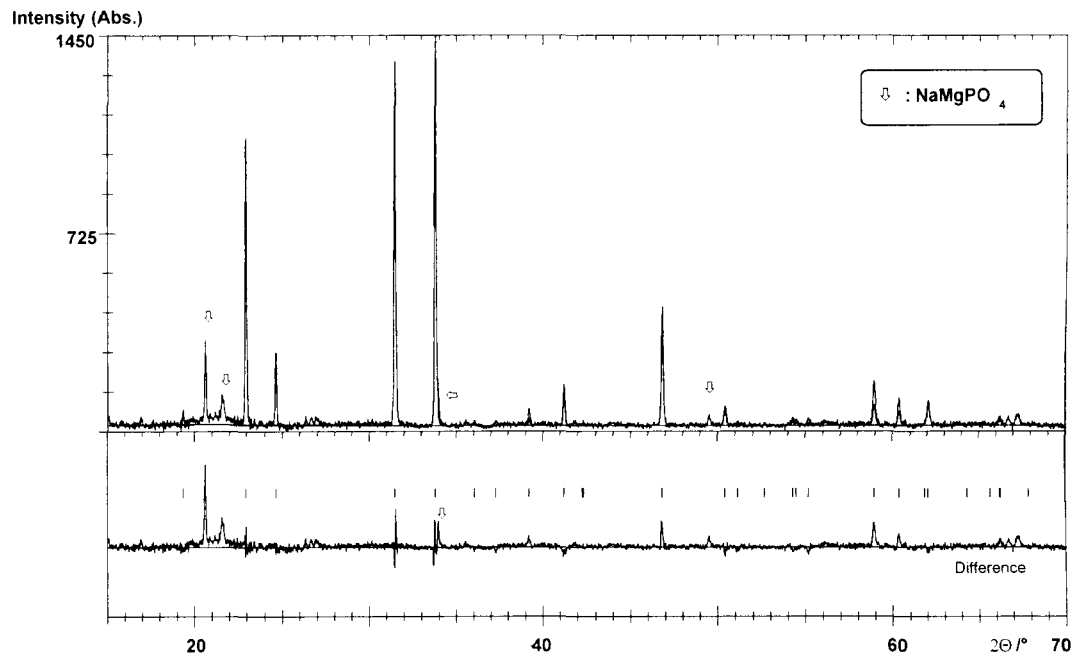


Fig. 3. Structure of $\beta\text{-Na}_2\text{CaMg}(\text{PO}_4)_2$ (glaserite structure, projection on (001)).

Table 5. Atomic coordinates of $\beta\text{-Na}_2\text{CaMg}(\text{PO}_4)_2$ obtained by RIETVELD-refinement.

		SG: $P\bar{3}m1$ (No. 164)			$T = 1093 \text{ K}$	
		$a = 5.309(2) \text{ \AA}$			$c = 7.237(1) \text{ \AA}$	
		$R = 6.7$			$R_B = 16.5$	
Atom	Site	x	y	z	B (fixed)	
Mg	1a	0	0	0	0.8	
Ca	1b	0	0	$1/2$	1.0	
Na	2d	$1/3$	$2/3$	0.766(4)	1.0	
P	2d	$1/3$	$2/3$	0.249(4)	0.4	
O1	2d	$1/3$	$2/3$	0.029(4)	1.0	
O2	6j	0.176(4)	-0.176(4)	0.31(1)	1.0	

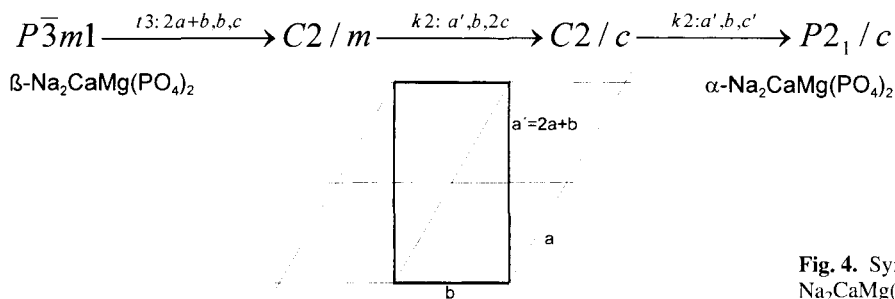


Fig. 4. Symmetric relations between the polymorphs of $\text{Na}_2\text{CaMg}(\text{PO}_4)_2$.

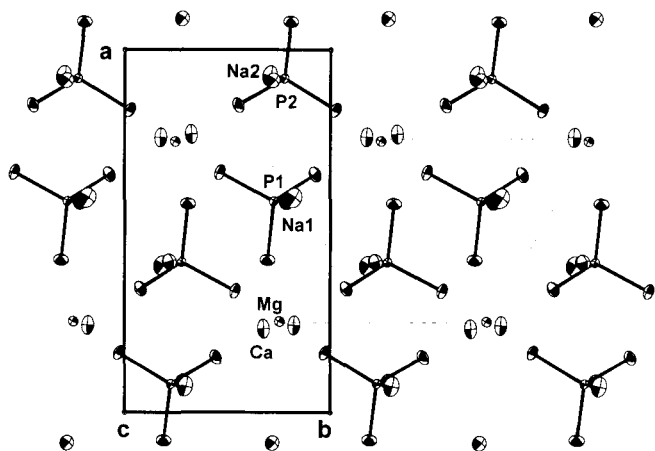


Fig. 5. Structure of $\alpha\text{-Na}_2\text{CaMg}(\text{PO}_4)_2$ (projection on (001), $0 < z < 0.5$).

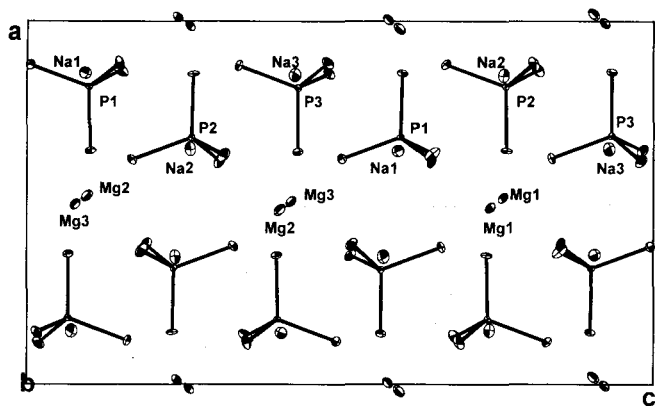


Fig. 6. Structure of $\alpha\text{-NaMgPO}_4$ (projection on (010)).

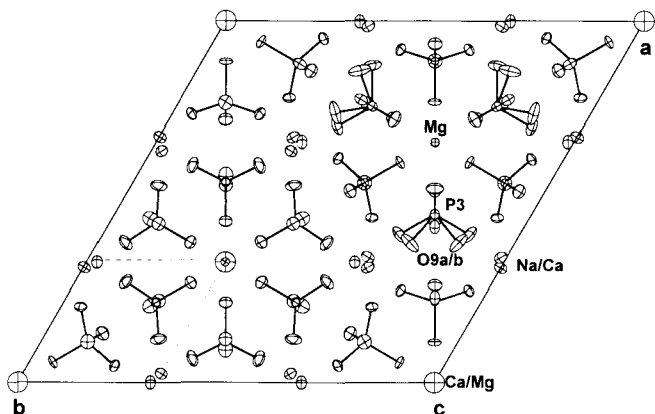


Fig. 7. Structure of $\text{Na}_{18}\text{Ca}_{13}\text{Mg}_5(\text{PO}_4)_{18}$ (projection on (001), $0 < z < 1/3$). Additional sodium and calcium sites lie above and below the phosphate tetrahedra.

served. As no reflections of $\alpha\text{-NaMgPO}_4$ were observed after cooling, they can be assigned to a decomposition product. In the resulting powder only $\text{NaMg}_4(\text{PO}_4)_3$ could be identified definitely. Thermal analysis also becomes more complex after heating above 1200 K.

$\alpha\text{-Na}_2\text{CaMg}(\text{PO}_4)_2$ undergoes a reversible phase-transition at $808(\pm 5)$ K. The powder pattern of the high-temperature modification can be simulated on the basis of the structure of glaserite, $\text{K}_3\text{Na}(\text{SO}_4)_2$ (Eysel 1973). Measured and calculated pattern and their difference are shown in Fig. 2. The reflections marked with an arrow can not be simulated and belong to a byproduct, which is not observed at room temperature. The results of the refinement are summarized in Table 5. The displacement parameters were fixed to avoid too many degrees of freedom with only the limited information available.

Discussion

The crystal structures presented can all be related to the one with highest symmetry, e.g. to the glaserite structure type. A plot of the structure of $\beta\text{-Na}_2\text{CaMg}(\text{PO}_4)_2$ on the (001)-plane is shown in Fig. 3. All phosphate tetrahedra are equivalent. Magnesium and calcium are coordinated octahedrally (000) and icosahedrally ($00\frac{1}{2}$) respectively. The octahedra ($d_{\text{Mg-O}} = 2.04 \pm 0.01$) are very regular. Sodium, situated on the threefold axis, is coordinated by ten oxygen atoms. A detailed description of the glaserite structure was given by Moore (1973). It is closely related to other phosphate structures, for example apatite.

The symmetry reduction from $\beta\text{-Na}_2\text{CaMg}(\text{PO}_4)_2$ to $\alpha\text{-Na}_2\text{CaMg}(\text{PO}_4)_2$ can be explained by a complete sequence of supergroup-subgroup relations. The types of symmetry reduction and the change of lattice constants is shown in Fig. 4. The relation between the polymorphs can best be seen from a projection on (001) (Fig. 5). The dotted cell can be compared directly with the unit cell of $\beta\text{-Na}_2\text{CaMg}(\text{PO}_4)_2$. Whereas the Mg atoms still are coordinated nearly octahedrally ($d_{\text{Mg-O}} = 2.08 \pm 0.04$ Å, $\angle_{\text{O-Mg-O}} = 90 \pm 7^\circ$), the icosahedral coordination of calcium is broken. The tetrahedra are slightly tilted breaking the threefold symmetry.

The structural details of $\alpha\text{-NaMgPO}_4$ and its relation to $\beta\text{-Na}_2\text{CaMg}(\text{PO}_4)_2$ can best be seen from a projection on (010) (Fig. 6). The dotted cell again allows the comparison of the atomic arrangements. The phosphate tetrahedra are tilted and no longer related to each other by a threefold symmetry axis. The main reason for the symmetry reductions seems to be the fivefold coordination of magne-

sium, however. Fivefold coordination is well known for magnesium containing phosphates and seems to be the main reason for the relatively low symmetries compared with other $\text{NaM}^{\text{II}}\text{PO}_4$ (e.g. NaCaPO_4 , Olsen et al. 1977; NaMnPO_4 , Moore 1972; NaFePO_4 , Le Page, Donnay 1977).

$\text{Na}_{18}\text{Ca}_{13}\text{Mg}_5(\text{PO}_4)_{18}$ again reflects the arrangement of the glaserite like $\text{NaM}^{\text{II}}(\text{PO}_4)$ structures (Fig. 7). Here the threefold crystal symmetry is conserved but all the unit axes are tripled. The disruption due to magnesium results in the overall reduction of symmetry and a slight disorder of some of the phosphate tetrahedra.

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