

Synthesis and properties of phosphate cancrinite (PO₄-CAN) a synthetic counterpart of depmeierite

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Phosphate cancrinite (PO₄-CAN) has been synthesized under mild hydrothermal conditions at 473 K using kaolin, sodium orthophosphate-dodecahydrate and strong alkaline conditions (8 M NaOH solution). Cancrinite crystals of rod-like habit and maximum lengths up to 2 μm were observed and characterized by X-ray powder diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDXS) and Fourier transform infrared spectroscopy (FTIR). Magic angle spinning nuclear magnetic resonance spectroscopy (MAS NMR) of the nucleus ³¹P, thermogravimetry (TG/DTG) and heating experiments under open conditions in a furnace were addition-

ally performed. The empirical formula Na₈[SiAlO₄]₆(PO₄)_{0.58}(CO₃)_{0.13}(H₂O)_{4.6} was calculated from EDXS analyses and TG data under consideration of a minor carbonate content, detected by FTIR spectroscopy. PO₄-CAN is stable up to 800 °C before thermal destruction rapidly occurs at 825 °C. The final product of TG analyses at 1000 °C is a mixture of a nepheline-like phase and the phosphate content of the initial cancrinite sample. XRD and FTIR results of the synthesis product are in good agreement with literature data of the rare mineral depmeierite.

Introduction

The minerals of the cancrinite family are porous tectosilicates with an ordered aluminosilicate framework with the alternating array of silicon and aluminum tetrahedra. In mineralogy cancrinites were included in the group of feldspathoids. In chemistry and material science cancrinites were assigned to the zeolite family and abbreviated by the IZA-code CAN.^[1] Most of the cancrinite members known up to now exhibit hexagonal symmetry, except the trigonal minerals hydroxycancrinite, franzinite and bystrite.^[2] Beside a framework with a Si:Al ratio of 1, found in most cancrinite species, even the Si-rich mineral cancrisilite is known, first described by Khomyakov et al. and later intensively characterized by Rastsvetaeva et al. and Ogorodova and coworkers.^[3–5] The extra-framework cations of cancrinites are Ca²⁺, Na⁺ and K⁺. These cations are widespread in nature and even a mixture of uni- and bivalent cations can contribute to the local charge balance of the cancrinite structure. Further extra-framework components are anion groups, enlarged inside the big channel of the cancrinite framework. Those space filling anions are mostly carbonate or sulfate-groups and in some cases also chlorine.

The cancrinite structure was first solved by Jarchow and can be described by a stacking of (Si, Al)O₄-layers, already proposed in the early work of Gossner and Musgnug.^[6–7] The layers are formed by single hexagonal rings of SiO₄ and AlO₄ tetrahedra, at which the rings not connected among each other. In the cancrinite structure the layers are stacked in AB sequence along [0001] direction. This stacking results in the formation of 11-hedral ε-cages in an array, forming a complete framework with a narrow channel system through the 6-ring opening of the ε-cages and a wide channel along c-axis. The latter has a 12-ring window of about 6 Å in diameter. The AB-stacking sequence is found within the half of the minerals of the cancrinite group whereas the other members exhibit variations in stacking of the (Si, Al)O₄-layers, for instance franzinite, with a ten-layer sequence.^[8–9] Eminent structural research on many of the cancrinite minerals was performed by the group of Bonaccorsi, Merlino and coworkers (Dept. of earth sciences, university Pisa) and an overview is given by these authors.^[10]

Beside structural variations of the cancrinite minerals even their crystal chemistry is manifold. An excellent overview on the crystal chemistry of cancrinites with AB-stacking sequence is given by the group of Pekov (Moscow State University) and Chukanov (Institute of Problems of Chemical Physics, Chernogolovska, Russia).^[11–12] These authors even observed and described many new cancrinite species in nature. In the case of the cancrinites with the AB-stacking the narrow ε-cages of seven mineral species are filled only with water molecules and sodium cations. The other members show exceptions, like davyne or microsommite, where the ε-cages are water free but contain chlorine and calcium cations.^[10–13] The large channels of the majority of the cancrinite minerals contain carbonate or sulphate and in a few cases chlorine anions or hydroxyl groups alone or as a mixture like sulphate and chlorine in davyne or sulfate and hydroxyl groups in allorite or only chlorine in quadridavyne.^[11–15] Beside those extra-framework anions the

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large channels are filled with water molecules and sodium or calcium or potassium cations even in mixture of two or all three cation types.

Both research groups, mentioned above, described many interesting new mineral species within the last years. Two of them exhibit unusual anion groups inside their large channels. These are the minerals kyanoxalite with extra framework oxalate anions and depmeierite, the first member of the cancrinite family with extra-framework PO_4^{3-} groups, i.e. trivalent anions inside the large channels beside carbonate.^[16–17]

Both new cancrinite species, the oxalate cancrinite as well as the PO_4 -cancrinite depmeierite could recently be obtained as synthesis product^[18–19] and both materials are of particular interest.

The trivalence of the phosphate anions enlarged in the wide channel of the cancrinite framework requires a lower degree of anion fillings for charge balance. Modified physico-chemical properties of such a phosphate cancrinite were expected which can lead to technical applications of “synthetic depmeierite”. External molecules indeed cannot enter the internal pore system of cancrinite because it is blocked by the extra-framework ions but nevertheless external species can be adsorbed on the outer surface of the crystals. Thus it was already shown that cancrinite can adsorb bile acid or antacid acid on the outer surface of the particles and an insertion in pharmacy seems possible.^[20–21] Beside surface adsorption the ion exchange effect of cancrinites is in the focus of applied mineralogy as recently demonstrated by an incorporation of hazardous cations Cd^{2+} , Pb^{2+} and Ni^{2+} via ion exchange in cancrinite.^[22]

In this sense synthetic depmeierite could be of interest for future applications like adsorption of large species on the external surface of the cancrinite particles or for ion exchange procedures. Furthermore a simple synthesis procedure of PO_4 -cancrinite depmeierite on the basis of widespread educts and mild reaction conditions at low temperature and low pressure is already known.^[19]

Beside the cancrinite minerals manifold synthetic species with cancrinite structure were obtained via synthesis up to now, as alumosilicates or with the substitution of the framework atoms as well as with diverse non-framework constituents. Synthesis of cancrinites already started nearly 150 years ago with the early research of Lemberg followed by many others.^[23] In the 20th century Barrer and co-workers continued synthesis work on cancrinites and feldspathoids on large scale before further new species were synthesized with the aim of applications of cancrinite in industry and techniques up to the present time.^[24–29]

Beside these extensive studies on synthesis of cancrinites with extra-framework monovalent or divalent anions, only one experimental study of the synthesis of Depmeierite, i.e. of a cancrinite species with trivalent anions, is known up to now.^[19] Thus the present paper reports on a further synthesis in order to obtain more information on the properties of phosphate cancrinite (PO_4 -CAN) with the aim to synthesize material of improved quality with a chemical composition in the direction of ideal depmeierite, as a formula $\text{Na}_8[\text{SiAlO}_4]_6(\text{PO}_4)_{0.66}(\text{H}_2\text{O})_3$ was

proposed by Pekov et al.^[17] Mild hydrothermal conditions were employed as in^[19] and the educts kaolin and sodium orthophosphate-dodecahydrate as well as sodium hydroxide solution were inserted too.^[19] This use of the widespread and cheap clay rock kaolin, almost consisting of the pure mineral kaolinite, is known as a suitable Si–Al source to obtain cancrinites.^[27–29]

Whereas the synthesis, described in^[19] was performed using only a 0.8 M NaOH solution under addition of 1.7 g Na_3PO_4 , the present study uses much stronger alkaline conditions of 8 M NaOH and an excess of 4 g sodium orthophosphate-dodecahydrate to improve the conversion of the educts and to observe material of improved crystal quality. Therefore even a larger reaction period of 48 h was employed instead of 10 h of the early synthesis experiment.^[19]

As the chemical composition, the X-ray powder pattern and the FTIR spectrum of synthetic depmeierite were already given in^[19] the aim of the present study is to compare the product of the stronger reaction conditions with the data of^[19] and to investigate further properties like crystal size and morphology, structural features of the extra-framework PO_4 anions and the thermal behaviour of PO_4 -CAN. Our synthesis product was therefore characterized by X-ray powder diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX-analysis), Fourier transform infrared spectroscopy (FTIR) and ^{31}P Magic angle spinning nuclear magnetic resonance spectroscopy (MAS NMR). Thermogravimetry (TG/DTG) and further heating experiments were performed in a muffle furnace under open conditions to study the thermal decomposition behaviour of PO_4 -CAN.

Experimental Section

Synthesis conditions

For synthesis 1 g of kaolin (FLUKA 60609, a fine powdered natural raw material, almost consisting of very pure kaolinite with only few traces of muscovite, iron oxide and rutile) and 4 g of sodium orthophosphate-dodecahydrate (Sigma Aldrich 71911) and 20 ml of 8 M NaOH (Merck 1.06467) were filled into a 50 ml Teflon lined steel autoclave and heated at 200 °C and 48 hours. The product PO_4 -CAN was washed with 150 ml of distilled water and dried at 80 °C in a cabinet dryer over night.

Analytical methods

The as synthesized product and the products of the heating experiments as well as the TG-residue were analysed by X-ray powder diffraction using a Philips PW-1800 diffractometer with Bragg-Brentano geometry and $\text{CuK}\alpha$ radiation. The diffractograms were taken at a 2 Theta range 5°–85° and a step width of 0.02° with 2 sec measuring time per step. The data were processed with the WinXPow software (Stoe & Chi GmbH, Darmstadt) and the X'Pert Highscore software (PANalytical, Almelo, NL).

The FTIR spectrum of PO_4 -CAN was taken on a Bruker AXS Vertex 80v spectrometer using the KBr pellet technique (1–2 mg sample and 200 mg KBr). The spectrum was measured in the MIR range (400 to 4000 cm^{-1}).

SEM images of the sample were taken on a JEOL JSM-6390A scanning electron microscope at an acceleration voltage of 30 kV. EDX-Analyses were performed with a QUANTAX-EDX-spectrometer and the Bruker XFlash M410 EDX detector, combined with the SEM.

The PO_4 -cancrinite was further analysed by ^{31}P MAS NMR spectroscopy to get more information on the local structure of the extra-framework anions in the cancrinite channel. The sample was measured on a Bruker Avance Neo 400WB spectrometer equipped with a 4 mm MAS double air bearing probehead. The spectrum was recorded at a frequency of 162.06 MHz with 3 μs pulse duration and 30 s pulse delay. 240 scans were accumulated at a spinning rate of 12.5 kHz. NaH_2PO_4 was used as secondary standard for ^{31}P chemical shift.

A Setaram Setsys evolution 1750 thermobalance was inserted to measure the water content of the sample by thermogravimetry (TG) and the dehydration characteristics at elevated temperature by differential thermogravimetry (DTG). The sample was therefore heated up to 1000 °C under flowing synthetic air atmosphere (80 Vol% N_2 , 20 Vol% O_2 ; 20 ml/min. flow rate, heating rate 5 °/min and 10 minutes holding time at T_{max}).

Further heating experiments were performed under open conditions at 800 °C, 825 °C and 850 °C to study the thermal destruction of the cancrinite framework and the resulting high temperature products. A muffle furnace Naber L 08/14 equipped with a Nabertherm C250 temperature controller was therefore used (heating rate 5 °/min and 30 min holding time at T_{max}).

Results and discussion

Synthesis, X-ray powder diffraction and FTIR

The product appeared as a white polycrystalline powder. The X-ray powder pattern is given in Figure 1. The diffractogram shows the typical signals of cancrinite and the hexagonal cell parameters $a_0 = 12.757(5)$ Å and $c_0 = 5.191(1)$ Å were refined (SG $P6_3$). These values are somewhat larger, compared with the cell constants of the depmeierite sample, described in^[19] but the cell volume of the members of the cancrinite family is known to react very sensitive on the degree of channel fillings with extra-framework species and water molecules.^[11–12]

The FTIR spectrum of PO_4 -CAN is shown in Figure 2.

The spectrum is in good agreement with the literature data, given for depmeierite.^[12,17, 19] The O–H stretching vibrations of the water molecules by H-bonds are responsible for the bands at 3600 cm^{-1} , 3525 cm^{-1} and 3431 cm^{-1} . The vibration at 1636 cm^{-1} denotes the bending mode of water molecules. The weak bands at 1470 cm^{-1} and 1380 cm^{-1} are the stretching vibrations of carbonate impurities of the sample. Those impurities are well known and were always found in cancrinites or sodalites, synthesized under strong alkaline conditions. Traces of carbonate in the NaOH solution, inserted for synthesis, are therefore responsible. The band at 1147 cm^{-1} and the strong signals at 1096 cm^{-1} and at 995 cm^{-1} (strongest band)

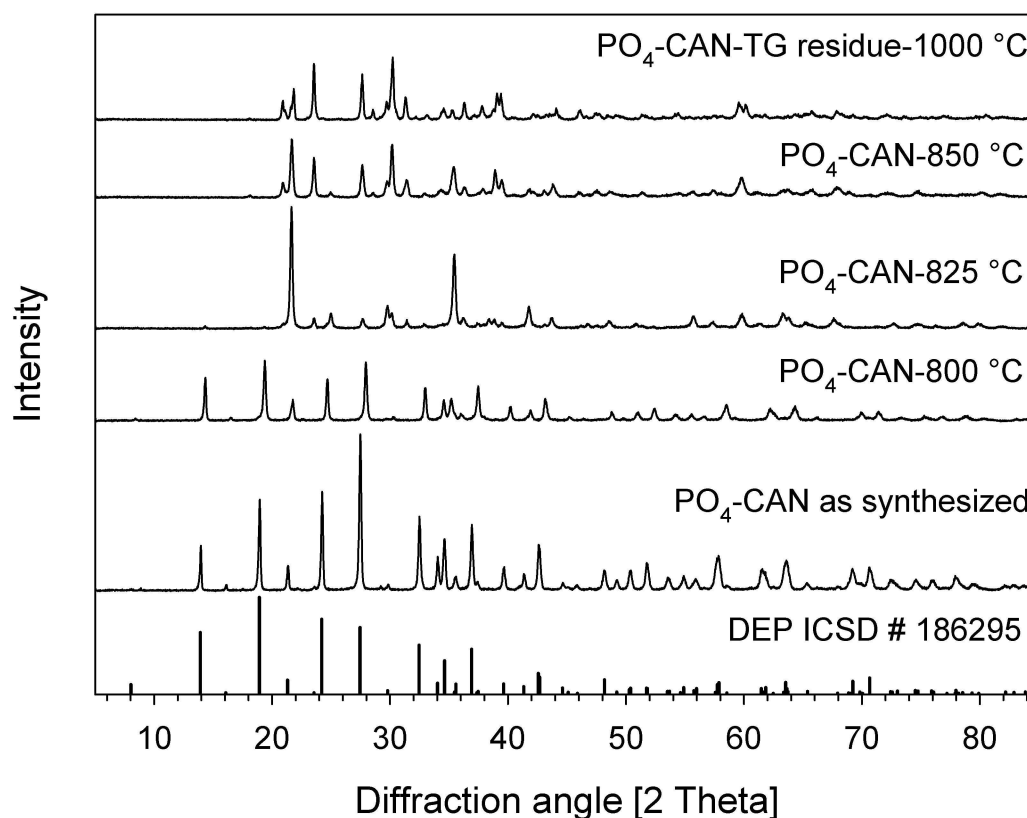


Figure 1. X-ray powder patterns, from bottom to top: PO_4 -CAN as synthesized, the products, obtained from heating at 800 °C, 825 °C and 850 °C in the muffle furnace and the TG residue after thermal analysis up to 1000 °C. A simulated pattern on the basis of the data of depmeierite,^[17] given in the database ICSD #186295^[30] is inserted at the bottom as stick-pattern for comparison.

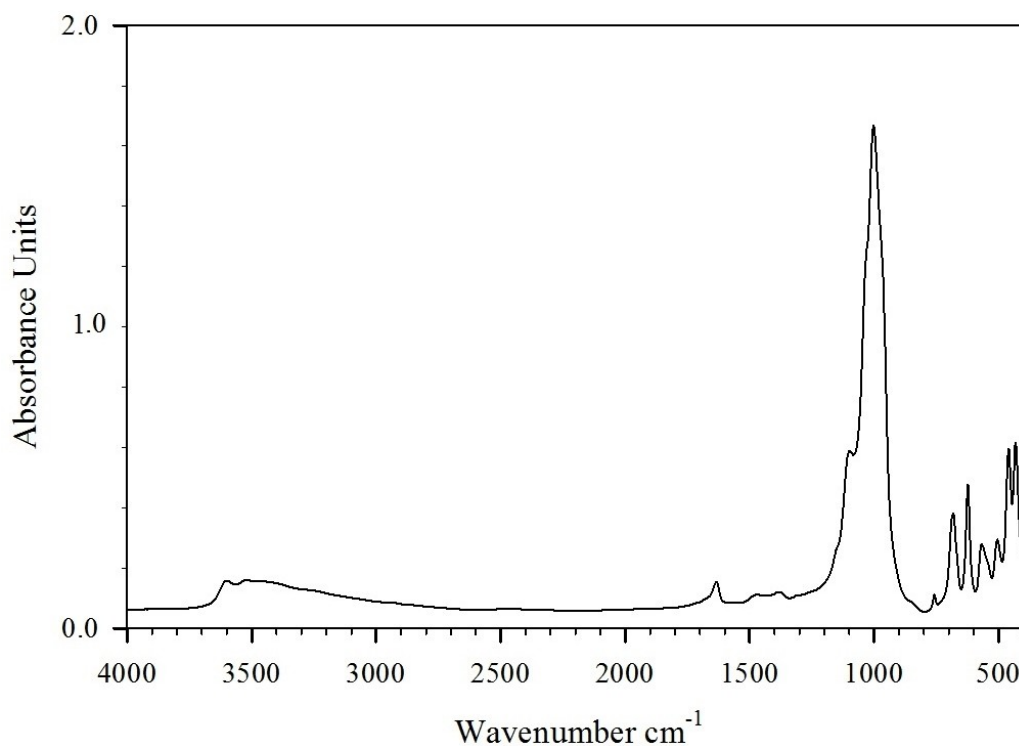


Figure 2. FTIR spectrum of $\text{PO}_4\text{-CAN}$.

belong to the asymmetric Si–O–Al stretching modes of the cancrinite framework. The weaker band at 754 cm^{-1} is assigned by Chukanov et al. as liberation vibration of H-bonded water molecules.^[17] In the range of symmetric Si–O–Al framework vibrations the three narrow bands at 679 cm^{-1} (ν_3), 621 cm^{-1} (ν_2) and 564 cm^{-1} (ν_1) are well resolved. In the direction to lower wave number the Si–O–Al bending vibrations are well resolved signals at 503 cm^{-1} , 456 cm^{-1} , 427 cm^{-1} and 387 cm^{-1} .

In the region of the asymmetric Si–O–Al stretching modes and in the region of the Si–O–Al bending vibrations of the CAN-framework in each case a band of the PO_4^{3-} anions is located. The PO_4^{3-} group is a tetrahedral anion with four internal modes $\nu_1\text{--}\nu_4$, where only the ν_3 mode (1002 cm^{-1} for the free group) and the ν_4 mode (546 cm^{-1} for the free anion) are IR active.^[31] Beside the values for the free anion the bands may shift in crystalline environment and a range of $980\text{ cm}^{-1}\text{--}1100\text{ cm}^{-1}$ is found for the strongest band ν_3 (the asymmetric stretch) in crystalline phosphates^[32] but nevertheless both stretching vibrations are superimposed by the very strong framework vibrations around these wavenumbers, described above.

SEM and EDXS

The results of SEM analysis of $\text{PO}_4\text{-CAN}$ are shown in Figure 3.

Nanoparticles of mostly very short prismatic habit can be seen beside larger micro-crystals. The particle dimensions ranged from about 200 nm up to lengths of 2 μm for the larger column shaped crystals.

A typical EDX-spectrum of $\text{PO}_4\text{-CAN}$ is shown in Figure 4. Quantitative evaluation of 12 analyses (average of 6 area- and 6 point-analyses) and consideration of the water content analysed by TG (see below), yield to a composition of 23.99 wt% Na_2O , 29.38 wt% Al_2O_3 , 34.69 wt% SiO_2 , 3.85 wt% P_2O_5 and 8.0 wt% H_2O . With respect to the ideal composition $\text{Na}_8[\text{SiAlO}_4]_6(\text{PO}_4)_{0.66}(\text{H}_2\text{O})_3$, given by Pekov et al. the P_2O_5 content of $\text{PO}_4\text{-CAN}$ is somewhat lower and the water content is higher (ideal values are 4.61 wt% P_2O_5 and 5.33 wt% H_2O).^[17] The empirical formula $\text{Na}_8[\text{SiAlO}_4]_6(\text{PO}_4)_{0.58}(\text{CO}_3)_{0.13}(\text{H}_2\text{O})_{4.6}$ can be calculated for $\text{PO}_4\text{-CAN}$ from EDXS analyses and TG data as model case under consideration of the minor carbonate content, detected by FTIR spectroscopy. The broad channel of the cancrinite structure is thus filled by 88% with PO_4 anions. It cannot be excluded, that the further extra-framework anions are carbonate anions exclusively. According to the high concentration of NaOH in our synthesis even hydroxyl-groups can enter the channel but their detection in low concentration via FTIR spectroscopy is difficult as there are several strong O–H stretching vibrations, caused by the water molecules (see Figure 2).

^{31}P MAS NMR spectroscopy

The ^{31}P MAS NMR spectrum of $\text{PO}_4\text{-CAN}$ is shown in Figure 5, above and in an expanded plot below.

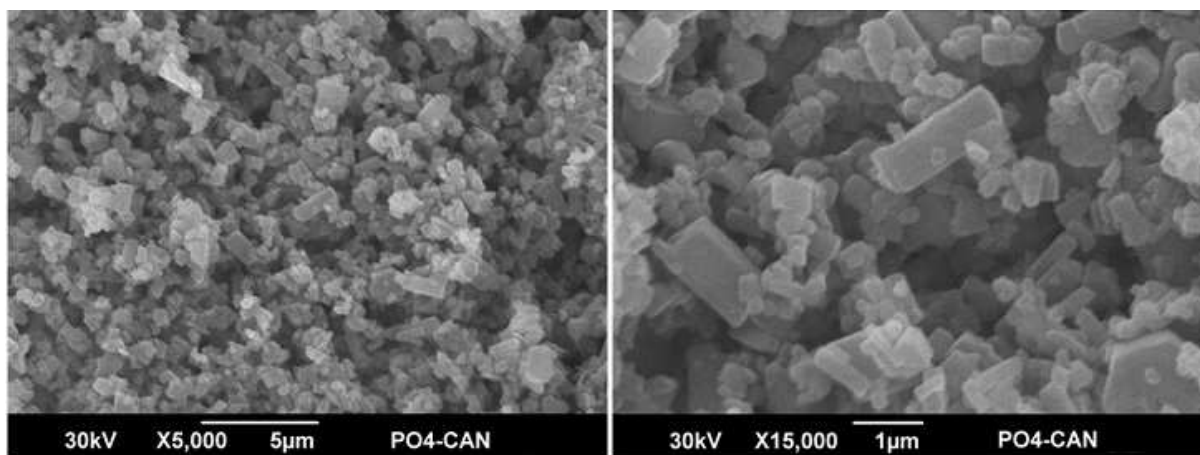


Figure 3. SEM images of PO₄-CAN.

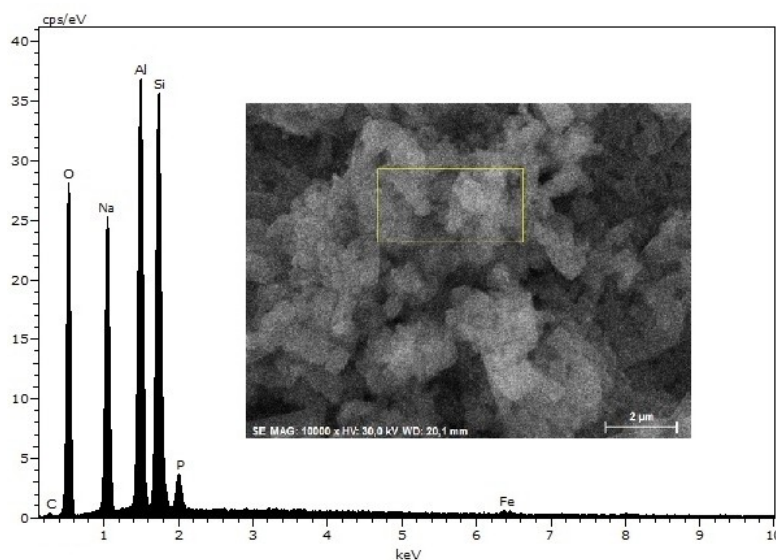


Figure 4. Typical EDX spectrum of PO₄-CAN from area analysis.

³¹P MAS NMR spectroscopy

The ³¹P MAS NMR spectrum of PO₄-CAN is shown in Figure 5 on top and with an expanded plot of the chemical shift axis at the bottom. The spectrum consists of sharp line with a chemical shift of 2.84 ppm. The expanded plot of the spectrum reveals two weak shoulders on the left flank of the strong main line, i.e. in the lowfield direction and at chemical shifts at around 5 ppm as well as 8 ppm.

Depending on the number of bridging oxygen atoms around a PO₄ tetrahedra, the ³¹P nucleus possesses a broad range of chemical shift. The Q_n nomenclature is used to distinguish isolated or linked units, where n denotes the number of bridging oxygen atoms between the P atoms in phosphates or other atoms like Al in many Al-phosphate minerals.^[33–34] Thus the spectra of minerals with higher n-values

exhibit chemical shifts in highfield direction, like $\delta_{\text{iso}} = -25,3$ ppm for berlinite or $\delta_{\text{iso}} = -19,2$ ppm for Variscite.^[34] In contrast structures with isolated PO₄ groups (n=0) show values in lowfield direction, like Na₃PO₄ ($\delta_{\text{iso}} = 14$ ppm).^[35]

Even the strong signal in the spectrum of PO₄-CAN is typical for isolated PO₄³⁻ anions (Q₀ groups). Compared with the chemical shift of sodium orthophosphate Na₃PO₄ mentioned above, several reasons must be discussed causing the upfield shift to 2.84 ppm in the ³¹P MAS NMR spectrum of PO₄-CAN. Beside a typical matrix effect of the cancrinite framework the influence of the interaction of the PO₄ groups with water molecules in the broad cancrinite channel must be carefully attended. The role of water molecules can be clearly seen in this context for instance in the case of hydrated sodium orthophosphate Na₃PO₄·10H₂O, where a remarkable upfield shift is observed ($\delta_{\text{iso}} = 7.7$ ppm^[35]). Dipole-Dipole interactions

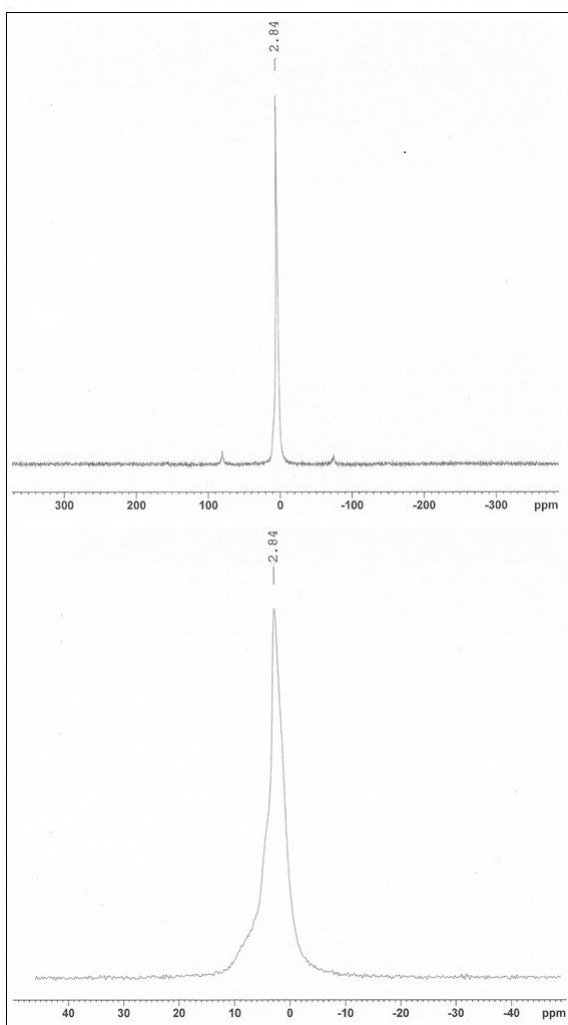


Figure 5. ^{31}P MAS NMR spectrum of $\text{PO}_4\text{-CAN}$ (top) and with an expanded plot of the chemical shift axis (bottom).

with the proton spins of the water molecules are responsible for this behaviour.^[35] In the case of $\text{PO}_4\text{-CAN}$ this interaction is effective and a further interaction between the sodium cations in the broad channel and the PO_4 groups via the surrounding water molecules is quite likely.

In addition the existence and distribution of the few amounts of other extra-framework anions like the divalent CO_3^{2-} beside PO_4^{3-} in the broad channel are influencing the local symmetry of the adjacent phosphate and surrounding water molecules, interacting via cations and anions. All those effects are probably even responsible for the two shoulders observed in lowfield direction of the spectrum.

TG, DTG and heating experiments under open conditions

The result of thermogravimetric analysis (TG+DTG) of the sample is given in Figure 6.

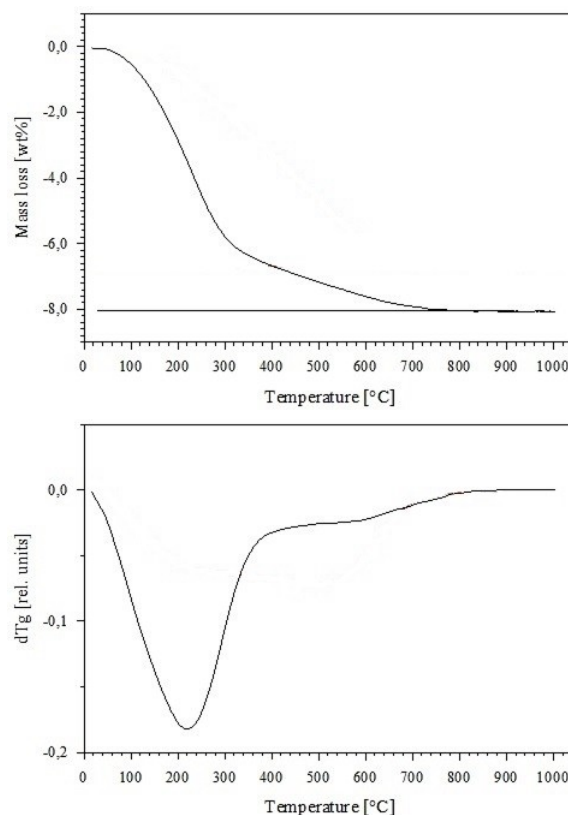


Figure 6. TG (top) and DTG (bottom) curves of $\text{PO}_4\text{-CAN}$.

A loss in weight of 8 wt% can be observed, consistent with a total water content of 4.6 H_2O of $\text{PO}_4\text{-CAN}$. The course of the TG and DTG indicate that the main water release occurred already at about 220 °C.

Further heating in the 750 °C–875 °C interval was performed in a muffle furnace to investigate the stability of $\text{PO}_4\text{-CAN}$ after thermal dehydration. After cooling down at RT the samples were analyzed by XRD. The powder patterns are included in Figure 1. $\text{PO}_4\text{-CAN}$ is stable up to 800 °C. Further heating up to 825 °C and 30 minutes holding time results in a complete thermal destruction into a high carnegieite like phase (PDF–No. 11–220).^[36] An expected transition into low carnegieite during cooling surprisingly fails. Maybe the heterogeneous character of the high temperature decomposition product consisting of aluminosilicate, Na_3PO_4 or P_2O_5 and Na_2O will impede a transition into low carnegieite, but a clarification of this finding needs future research. Heating at higher temperature yield to formation of a nepheline analogous phase (PDF–No. 19-1176^[36]) beside carnegieite as can be seen in the 850 °C pattern in Figure 1. At 1000 °C only the nepheline phase remains as the final crystalline product (see the pattern of the TG residue Figure 1, top).

To clarify the disposition of the PO_4 -content, SEM-EDX-analyses of the TG residue of $\text{PO}_4\text{-CAN}$ was performed and shown in Figure 7.

The former crystals now appear in form of small fused particle agglomerations. The EDX analyses (average of 5 area-

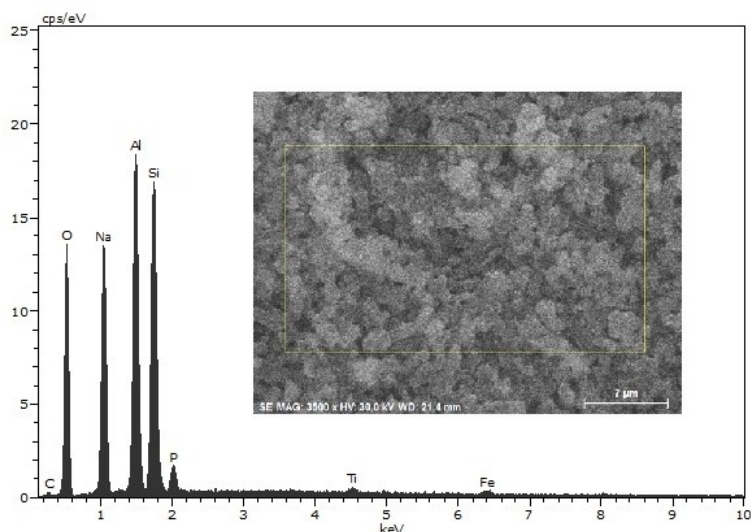


Figure 7. Typical EDX spectrum of the TG residue of PO₄-CAN (area analysis).

and 5 point-analyses yield 4.0 wt% P₂O₅) reveal that the whole P₂O₅ content still exists within the TG residue. Formation of Na₃PO₄ or P₂O₅ is suggested but if one of these possible compounds is present in crystalline form the lines in the XRD pattern (see Figure 1, top) would be very weak according to the low concentration and would be in coincidence with strong nepheline reflections. Thus the question of formation of a crystalline or an amorphous phosphate phase and its real composition in the TG-product still remains open.

Conclusions

Our experiments show, that:

- (1) Phosphate cancrinite can be synthesized under mild hydrothermal strong alkaline conditions at 473 K under addition of an excess of sodium orthophosphate-dodecahydrate.
- (2) Crystals of composition Na₈[SiAlO₄]₆(PO₄)_{0.58}(CO₃)_{0.13}(H₂O)_{4.6} of rod-like habit and maximum lengths up to 2 μm were observed and the PO₄ anions were characterized by ³¹P MAS NMR.
- (3) Kaolin is a cheap but very suitable Si–Al-source for cancrinite synthesis even in the presence of phosphate anions.
- (4) After dehydration PO₄-CAN is stable up to 800 °C. A nepheline-like phase is the final crystalline decomposition product together with the phosphate part, enlarged during synthesis.
- (5) The X-ray powder pattern and the FTIR spectrum of the synthesized PO₄-CAN well agree with literature data of the rare mineral depmeierite.^[17] Compared with the synthesis product of^[19] the cell volume of the present sample is slightly enlarged as a result of a higher amount of water inside the broad cancrinite channel.

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Keywords: microporous solids · hydrothermal synthesis · framework type CAN · phosphate enclathrated zeolites · ³¹P MAS NMR

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