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# Syntheses, Crystal Structures, Vibrational Spectra and $^{31}\text{P}$ MAS NMR Spectra of the Thiophosphates $\text{Na}M(\text{PO}_3\text{S})\cdot 9\text{H}_2\text{O}$ ( $M = \text{Ca}, \text{Ba}$ )

Karolina Kazmierczak,<sup>[a]</sup> Joachim G. Heck,<sup>[a]</sup> and Henning A. Höppe\*<sup>[a]</sup>

*Dedicated to Professor Hans-Jörg Deiseroth on the Occasion of His 65th Birthday*

**Keywords:** Thiophosphates; Calcium; Barium; Sodium; Vibrational spectroscopy; Solid state NMR spectroscopy

**Abstract.**  $\text{NaBa}(\text{PO}_3\text{S})\cdot 9\text{H}_2\text{O}$  was obtained as single-phase crystalline powder starting from  $\text{NaOH}$ ,  $\text{PSCl}_3$  and  $\text{BaCl}_2$ . Single-crystals of  $\text{NaCa}(\text{PO}_3\text{S})\cdot 9\text{H}_2\text{O}$  were grown by a gel crystallisation technique. The crystal structures of  $\text{NaCa}(\text{PO}_3\text{S})\cdot 9\text{H}_2\text{O}$  ( $P2_13$ ,  $Z = 4$ ,  $a = 10.7845(12)$  Å,  $R1 = 0.034$ ,  $wR2 = 0.083$ , 711 reflections, 64 parameters) and  $\text{NaBa}(\text{PO}_3\text{S})\cdot 9\text{H}_2\text{O}$  ( $P2_13$ ,  $Z = 4$ ,  $a = 11.0216(2)$  Å, 754 reflections,  $2\theta_{\text{max}} = 70.0^\circ$ ,  $R_{\text{F}2} = 0.099$ ,  $R_{\text{p}} = 0.034$ ,  $wR_{\text{p}} = 0.047$ ,  $\chi^2 = 3.34$ ) are isotopic with that of  $\text{NaSr}(\text{PO}_3\text{S})\cdot 9\text{H}_2\text{O}$  and these three are homeotypic with  $\text{NaMPO}_4\cdot 9\text{H}_2\text{O}$  ( $M = \text{Sr}, \text{Ba}$ ). The crystal structures of

$\text{Na}M(\text{PO}_3\text{S})\cdot 9\text{H}_2\text{O}$  ( $M = \text{Ca}, \text{Ba}$ ) consist of isolated  $(\text{PO}_3\text{S})$  tetrahedra,  $[\text{NaO}_6]$  distorted octahedra and  $[\text{MO}_9]$  polyhedra with the latter forming a network according to  $^3_{\infty}[\{\text{Na}(\text{H}_2\text{O})_{6/2}\}\{\text{Ca}(\text{H}_2\text{O})_{6/2}(\text{H}_2\text{O})_3\}]^{3+}$ . Nine crystal water molecules are situated in the voids of the resulting structure. The vibrational spectra of the title compounds have been measured and the relevant bands were assigned. Solid-state  $^{31}\text{P}$  MAS NMR spectra gave chemical shifts of 49 ppm for  $\text{NaCa}(\text{PO}_3\text{S})\cdot 9\text{H}_2\text{O}$ , 34 ppm for  $\text{NaBa}(\text{PO}_3\text{S})\cdot 9\text{H}_2\text{O}$  and 38 ppm for  $\text{Na}_3(\text{PO}_3\text{S})$ .

## Introduction

Alkaline earth phosphates and respective homologues attract interest in materials science because of the possibility of doping them with divalent or trivalent rare earth ions to produce efficient fluorescent materials [1, 2]. The absorption and emission properties of divalent europium are very efficient due to the participation of parity allowed  $4f-5d$  transitions. Moreover, the emission wavelength depends strongly on the energetic position of the  $5d$  levels which are subject to crystal field splitting and the nephelauxetic effect of the coordinating atoms [2].

Strontium oxophosphates doped with  $\text{Eu}^{2+}$  give blue emissions around 410 nm [3], to shift the emission wavelength to longer wavelengths one can either reduce the average void size by using calcium phosphates as host material [4] or by substituting oxygen with a more polarisable element like sulphur and use thiophosphates instead of oxophosphates. In the course of our systematic search for novel thiophosphates we obtained the title compounds which are expected to be precursors for efficient host materials.

Whereas monothiophosphates of alkali metals like  $\text{Na}_3(\text{PO}_3\text{S})$  [5, 6] or of tetravalent metals like  $\text{H}_2M(\text{PO}_3\text{S})_2$

( $M = \text{Zr}, \text{Hf}$  [7]) are well known, there is only a single monothiophosphate containing an alkaline earth metal, i.e.  $\text{NaSr}(\text{PO}_3\text{S})\cdot 9\text{H}_2\text{O}$  [8]. Besides the crystal structure no spectroscopic data of this thiophosphate are known so far as well as the knowledge about the existence of the calcium and barium homologues. These will be important for the formation of solid solutions which will be used for tuning the void size for doped rare earth ions before the novel phosphors can be obtained by a subsequent dehydration.

In this contribution we report on the synthesis, crystal structures, vibrational and solid state NMR spectra of the thiophosphates  $\text{Na}M(\text{PO}_3\text{S})\cdot 9\text{H}_2\text{O}$  with  $M = \text{Ca}$  (**1**),  $\text{Ba}$  (**2**) and compare their structures with previously published  $\text{NaSr}(\text{PO}_3\text{S})\cdot 9\text{H}_2\text{O}$  [8]. Initial syntheses showed that the targeted thiophosphates are difficult to crystallise. Therefore we optimised the synthesis method to obtain phase-pure microcrystalline powders and furthermore single-crystals by gel-crystallisation.

## Results and Discussion

### 1. Crystal Structures of $\text{Na}M(\text{PO}_3\text{S})\cdot 9\text{H}_2\text{O}$ ( $M = \text{Ca}, \text{Ba}$ )

The crystal structures of  $\text{NaCa}(\text{PO}_3\text{S})\cdot 9\text{H}_2\text{O}$  (**1**) and  $\text{NaBa}(\text{PO}_3\text{S})\cdot 9\text{H}_2\text{O}$  (**2**) are isotopic with that of  $\text{NaSr}(\text{PO}_3\text{S})\cdot 9\text{H}_2\text{O}$  and these three are homeotypic with  $\text{NaMPO}_4\cdot 9\text{H}_2\text{O}$  ( $M = \text{Sr}, \text{Ba}$ ) [9, 10].

The crystal structures of **1** and **2** consist of isolated  $(\text{PO}_3\text{S})$  tetrahedra, distorted  $[\text{NaO}_6]$  octahedra and  $[\text{MO}_9]$  polyhedra ( $M = \text{Ca}, \text{Ba}$ ), described best as tricapped trigonal prisms. Nine crystal water molecules are situated in the voids of the resulting structure (Figure 1). Each of the ions  $\text{Na}^+$ ,  $\text{Ca}^{2+}$  and

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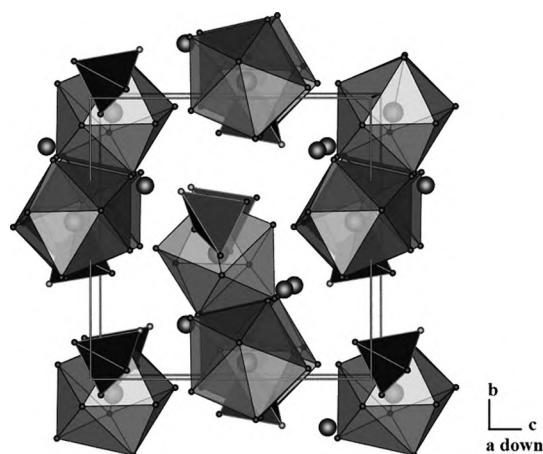
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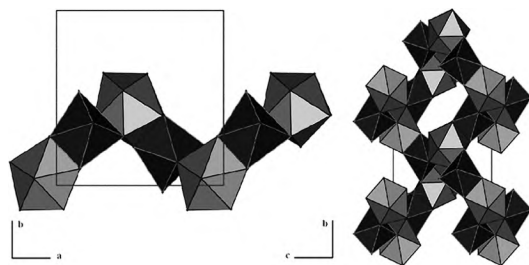
under <http://dx.doi.org/10.1002/zaac.200900437> or from the

author.

$(\text{PO}_3\text{S})^{3-}$  are completely surrounded by crystal water molecules. The sodium ion is sixfold coordinated by crystal water oxygen atoms ( $\text{Na}-\text{O}_\text{W}$  2.441(3)–2.505(3) Å in **1**), whereas the alkaline earth cation is ninefold coordinated with distances  $\text{Ca}-\text{O}_\text{W}$  of 2.442(3)–2.797(3) Å. Both coordination environments are illustrated in Figure S1 (Supporting Information). Each  $[\text{NaO}_6]$  polyhedron shares three edges with three different alkaline earth polyhedra and each  $[\text{MO}_9]$  polyhedron also shares three edges with two different sodium polyhedra. Thus, chains of alternating condensed sodium and alkaline earth polyhedra along  $[100]$  are formed (Figure 2 left). Perpendicular to  $[100]$ , the sodium polyhedra in these chains are condensed to further alkaline earth polyhedra forming a three dimensional network structure according the notation  ${}^3[\{\text{Na}(\text{H}_2\text{O})_{6/2}\}\{\text{Ca}(\text{H}_2\text{O})_{6/2}(\text{H}_2\text{O})_3\}]^{3+}$  (Figure 2 right). In the  $(\text{PO}_3\text{S})^{3-}$  tetrahedra, the P–O distances are 1.527(2) Å, the P–S distance amounts to 2.043(2) Å (**1**). Accordingly, the anion exhibits an ideal  $C_{3v}$  symmetry.



**Figure 1.** Representation of the unit cell of  $\text{NaCa}(\text{PO}_3\text{S})\cdot 9\text{H}_2\text{O}$  viewed approx. along  $[100]$ . The medium grey spheres represent the sodium atoms, the  $[\text{CaO}_9]$  polyhedra are drawn as semitransparent polyhedra and the  $(\text{PO}_3\text{S})^{3-}$  tetrahedra are drawn as closed black polyhedra (sulfur light grey, oxygen black); the hydrogen atoms have been omitted for clarity.



**Figure 2.** Curled chains of condensed alternating  $\text{Na}(\text{H}_2\text{O})_6$  (dark grey) and  $\text{Ca}(\text{H}_2\text{O})_9$  polyhedra (light grey) along  $[100]$  (left) and visualisation of the condensed cationic network  ${}^3[\{\text{Na}(\text{H}_2\text{O})_{6/2}\}\{\text{Ca}(\text{H}_2\text{O})_{4/2}(\text{H}_2\text{O})_5\}]^{3+}$  viewed along  $[100]$  (right).

The hydrogen bonds determined in  $\text{NaCa}(\text{PO}_3\text{S})\cdot 9\text{H}_2\text{O}$  are presented in Table 1 and shown in Figure S2 (Supporting Information). All hydrogen atoms were located by difference

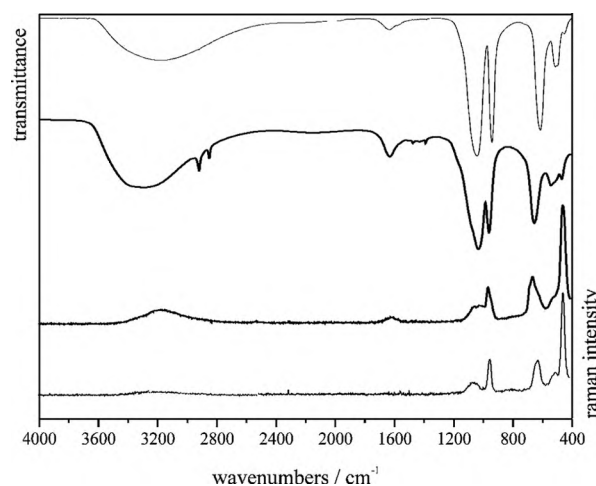
fourier syntheses and refined isotropically with fixed  $U_{\text{iso}} = 0.05 \text{ \AA}^2$ . The O–H distances were commonly refined to a value of 0.83(2) Å, the hydrogen bond angles vary from 154 to 173°. The strength of these hydrogen bonds can therefore be classified as moderate [11].

**Table 1.** Hydrogen bonds in  $\text{NaCa}(\text{PO}_3\text{S})\cdot 9\text{H}_2\text{O}$ ; D = donor, A = acceptor, all distances are given in Å.

D–H	A	$d_{\text{D–H}}$	$d_{\text{H–A}}$	angle(DHA)	$d_{\text{D–A}}$
OW1–H11	O	0.83	1.87	168	2.69
OW1–H12	OW3	0.83	2.20	160	2.99
OW2–H21	O	0.83	1.93	155	2.70
OW2–H22	S	0.83	2.77	159	3.56
OW3–H31	O	0.83	1.85	172	2.67
OW3–H32	S	0.83	2.38	166	3.20

## 2. Vibrational Spectroscopy

The IR and Raman spectra of  $\text{NaM}(\text{PO}_3\text{S})\cdot 9\text{H}_2\text{O}$  ( $M = \text{Ca}, \text{Ba}$ ) are shown in Figure 3. The absorption at  $3200 \text{ cm}^{-1}$  is assigned to stretching vibrations  $[\nu(\text{OH})]$  of the crystal water molecules, the bending modes  $[\sigma(\text{OH})]$  of different water molecules are observed between  $1627$  and  $1636 \text{ cm}^{-1}$ . Characteristic bands of the monothiophosphate tetrahedra are expected in the region from  $1070$  to  $340 \text{ cm}^{-1}$  [12]. The spectra of  $\text{NaM}(\text{PO}_3\text{S})\cdot 9\text{H}_2\text{O}$  ( $M = \text{Ca}, \text{Ba}$ ) exhibit strong signals with a maximum at  $1027$   $[\nu_{\text{as}}(\text{PO}_3)]$  and  $955 \text{ cm}^{-1}$   $[\nu_{\text{s}}(\text{PO}_3)]$  for **1** ( $\text{NaCa}(\text{PO}_3\text{S})\cdot 9\text{H}_2\text{O}$ ) and  $1041$  and  $941 \text{ cm}^{-1}$  for **2** ( $\text{NaBa}(\text{PO}_3\text{S})\cdot 9\text{H}_2\text{O}$ ). The  $\delta_{\text{as}}(\text{PO}_3)$  vibrations of  $(\text{PO}_3\text{S})^{3-}$  are detected at  $649$  (**1**) and  $671 \text{ cm}^{-1}$  (**2**). At  $462 \text{ cm}^{-1}$  (**1**) and  $455 \text{ cm}^{-1}$  (**2**), respectively, the weak  $\nu(\text{PS})$  vibration is detected. Two weak sharp signals in the IR spectrum of **1** around  $2900$  and  $1400 \text{ cm}^{-1}$  are attributed to the use of gloves of the respective technician.



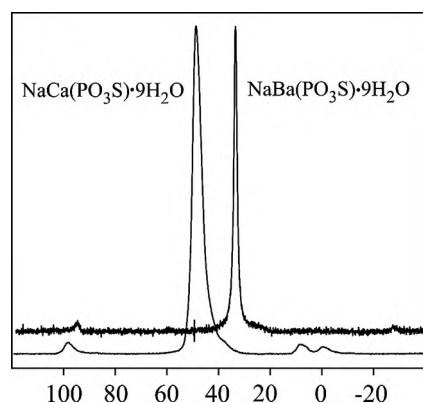
**Figure 3.** Infrared und Raman vibrational spectra of  $\text{NaBa}(\text{PO}_3\text{S})\cdot 9\text{H}_2\text{O}$  (grey line) and  $\text{NaCa}(\text{PO}_3\text{S})\cdot 9\text{H}_2\text{O}$  (black line).

The Raman spectra show intense bands between  $1200$  and  $400 \text{ cm}^{-1}$ . The strongest emission at  $465 \text{ cm}^{-1}$  originates from  $\nu(\text{PS})$ , and the emissions at  $671$  and  $975 \text{ cm}^{-1}$  can be assigned

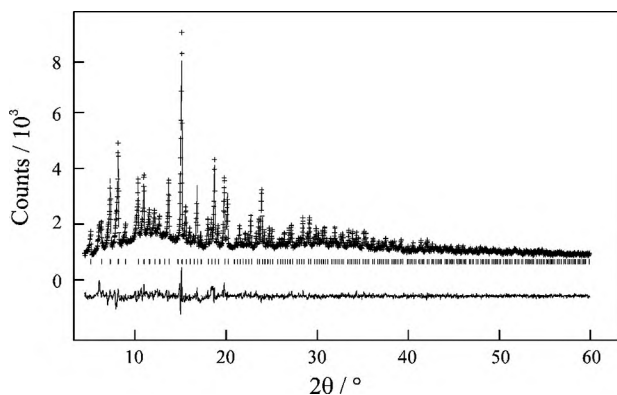
to the  $\delta_{\text{as}}(\text{PO}_3)$  and  $\nu_{\text{s}}(\text{PO}_3)$  vibrations, respectively. The observed frequencies in the spectra correspond very well with the expected values.

### 3. Solid State NMR Spectroscopy

On single-phase powders of  $\text{NaCa}(\text{PO}_3\text{S})\cdot 9\text{H}_2\text{O}$ ,  $\text{NaBa}(\text{PO}_3\text{S})\cdot 9\text{H}_2\text{O}$  and  $\text{Na}_3(\text{PO}_3\text{S})$  solid state  $^{31}\text{P}$  MAS NMR spectra were recorded. The chemical shifts of the phosphorus atoms were determined relatively to phosphoric acid (85 %). As shown in Figure 4, the title compounds yielded single signals at 49 ppm ( $\text{NaCa}(\text{PO}_3\text{S})\cdot 9\text{H}_2\text{O}$ ) and 34 ppm ( $\text{NaBa}(\text{PO}_3\text{S})\cdot 9\text{H}_2\text{O}$ ). For  $\text{Na}_3(\text{PO}_3\text{S})$  (not shown) a chemical shift of 38 ppm could be determined which is in good agreement with an earlier measurement on  $\text{Na}_3(\text{PO}_3\text{S})$  where a chemical shift of 33 ppm had been recorded [13]. Normally, a substitution of oxygen atoms bound to phosphorus by sulfur leads to a downfield shift of the signal of 40 to 44 ppm and with Oxophosphates having shifts around  $-20$  to 10 ppm (relatively to phosphoric acid); for monothiophosphates shifts between 30 to 50 ppm are expected [14]. Thus, all observed chemical shifts are in the range of typical chemical shifts for



**Figure 4.** Solid state  $^{31}\text{P}$  MAS NMR spectra of **2** (top) and **1** (bottom); the chemical shifts are referenced against phosphoric acid (85 %).



**Figure 5.** Observed (crosses) and calculated (line) X-ray powder diffraction pattern (Mo- $K_{\alpha}$  radiation) as well as the difference profile of the Rietveld refinement of  $\text{NaBa}(\text{PO}_3\text{S})\cdot 9\text{H}_2\text{O}$ . The row of vertical lines indicates possible peak positions of  $\text{NaBa}(\text{PO}_3\text{S})\cdot 9\text{H}_2\text{O}$ .

monothiophosphates. The NMR spectrum of **1** shows one additional signal around 10 ppm, probably due to partial decomposition. According to powder X-ray diffraction (Figure 5 and S3), the only crystalline components are the title compounds with minor amorphous contributions. Our results also confirm that the phosphorus atoms are located on a single crystallographic site in both crystal structures and additionally the phase purity of the investigated samples.

### Conclusions

We were able to obtain single-phase powders of  $\text{NaCa}(\text{PO}_3\text{S})\cdot 9\text{H}_2\text{O}$  and  $\text{NaBa}(\text{PO}_3\text{S})\cdot 9\text{H}_2\text{O}$ , respectively. Additionally, our strategy to obtain single-crystals of  $\text{NaCa}(\text{PO}_3\text{S})\cdot 9\text{H}_2\text{O}$  suitable for X-ray structure determination were successful by gel crystallisation. Since all three homologous thiophosphates crystallise isotypically mixed crystal formation will be possible.

The single-phase powders could be used to record the vibrational spectra, which are in accordance with the structure model and to confirm the presence of sulphur by solid state NMR spectra.

Further work is under way to get rid of the crystal water resulting in suitable host lattices for doping with divalent europium atoms on the alkaline earth site and, moreover, to dope trivalent europium atoms on the sodium sites.

### Experimental Section

#### Syntheses

**$\text{Na}_3(\text{PO}_3\text{S})$ :** Trisodium monothiophosphate,  $\text{Na}_3(\text{PO}_3\text{S})$ , was synthesized according to Lambert [5].  $\text{PSCl}_3$  (1.75 mL, 0.017 mol; Aldrich, 98 %) was added to a solution of  $\text{NaOH}$  (4 g, 0.1 mol; Acros, 97 %) in distilled  $\text{H}_2\text{O}$  (30 mL) and subsequently dehydrated by suspending in anhydrous methanol. The yield was 42 %. The phase purity of sodium thiophosphate was checked by powder X-ray diffraction, which gave a diagram in excellent accordance with Jansen's data [6].

**$\text{NaM}(\text{PO}_3\text{S})\cdot 9\text{H}_2\text{O}$  ( $M = \text{Ba}, \text{Ca}$ ):** The syntheses had to be carried out below 50 °C because of decomposition of the products above this value. Sodium barium monothiophosphate nonahydrate ( $\text{NaBa}(\text{PO}_3\text{S})\cdot 9\text{H}_2\text{O}$ ) was prepared by aqueous precipitation.  $\text{BaCl}_2\cdot 2\text{H}_2\text{O}$  (137.6 mg, 0.5633 mmol; Acros, 99 %) was added to a solution of  $\text{Na}_3(\text{PO}_3\text{S})$  (101.2 mg, 0.5667 mmol) in distilled water (4 mL), maintained at a temperature of 42 °C. The solution was slowly cooled to room temperature and afterwards filtered. After drying in air 215.1 mg (yield: 88 %)  $\text{NaBa}(\text{PO}_3\text{S})\cdot 9\text{H}_2\text{O}$  were obtained as a crystalline, colourless and non-hygroscopic powder.

The calcium compound was synthesised analogously to the barium compound (yield: 59 %). The growth of single-crystals was successful by gel crystallisation. The powder diffraction pattern of **1** contains only **1** as crystalline component with some amorphous contributions.

#### Growth of Single Crystals of $\text{NaCa}(\text{PO}_3\text{S})\cdot 9\text{H}_2\text{O}$

Direct mixing of aqueous solution of trisodium monothiophosphate and calcium chloride in near-stoichiometric proportion resulted in an

amorphous product of NaCa(PO<sub>3</sub>S)·9H<sub>2</sub>O in contrast to the barium compound.

Thus, the growth of single-crystals of NaCa(PO<sub>3</sub>S)·9H<sub>2</sub>O was successfully achieved by a gel diffusion method in a glass tube by means of three different gelatine layers, which were stacked on top of each other. The top layer was prepared by dissolving gelatine powder in distilled water at boiling temperature. After cooling to 40 °C, Na<sub>3</sub>(PO<sub>3</sub>S) (101.0 mg, 0.5611 mmol) was dissolved in the gelatine solution. The second layer consisted of gelatine only. The third layer was prepared like the top layer except the fact that CaCl<sub>2</sub> (62.9 mg, 0.567 mmol; Merck, p. a.) were dissolved in the gel solution. Before the layers were stacked, each was cooled to 2 °C to obtain a stable gel layer. The growth was conducted in a fridge for about two weeks. Afterwards, the colourless crystals were separated from the gel medium.

### Crystal Structure Analysis of NaCa(PO<sub>3</sub>S)·9H<sub>2</sub>O

X-ray diffraction data were collected with a Rigaku Spider Image-Plate diffractometer using Mo-K<sub>α</sub> radiation and corrected for Lorentz and polarisation effects (multi-scan absorption) [15]. The crystal structure of NaCa(PO<sub>3</sub>S)·9H<sub>2</sub>O was solved by direct methods and refined by using SHELXTL [16]. The experimental details of the single-crystal structure determination are given in Table 2. Tables S1 and S2 (given as Supporting Information) present the atomic coordinates and displacement parameters. Table S3 (given as Supporting Information) lists selected geometric parameters, Table 1 delivers hydrogen bonding geometry data.

**Table 2.** Crystallographic data of NaCa(PO<sub>3</sub>S)·9H<sub>2</sub>O.

Crystal Data	
NaCa(PO <sub>3</sub> S)·9H <sub>2</sub> O	$F(000) = 704$
$M = 336.24 \text{ g}\cdot\text{mol}^{-1}$	$\rho_{X\text{-ray}} = 1.781 \text{ g}\cdot\text{cm}^{-3}$
cubic	Mo-K <sub>α</sub> radiation
space group $P2_13$ (no.198)	$\lambda = 71.073$
$a = 10.7845(12) \text{ \AA}$	$\mu = 0.877 \text{ mm}^{-1}$
$V = 1254.3(2)\cdot 10^6 \text{ pm}^3$	$T = 293(2) \text{ K}$
$Z = 4$	crystal shape and colour: block, colourless
Data Collection	
Rigaku Spider Image-Plate	
absorption corr.: multi-scan	$h, k, l = -12 \rightarrow 12$ ( $2\theta_{\text{max}} = 50.0^\circ$ )
$T_{\text{min}} = 0.1598$ $T_{\text{max}} = 0.7254$ $R_{\text{int}} = 0.0942$	
16183 measured reflections	744 independent refl.
	711 observed refl. ( $F_o^2 \geq 2\sigma(F_o^2)$ )
Refinement	
refinement on $F^2$	
$R1 = 0.034$ , $wR2 = 0.083$	Flack parameter: $\chi = 0.04(9)$
$w^{-1} = \sigma^2 F_o^2 + (0.0419P)^2 + 0.8802P$ with $P = (F_o^2 + 2F_c^2)/3$	
GooF = 1.097	64 parameters
maximal/minimal residual electron density: 0.39 / -0.15 e·Å <sup>-3</sup>	

### Rietveld Refinement of NaBa(PO<sub>3</sub>S)·9H<sub>2</sub>O

X-ray powder diffraction data of NaBa(PO<sub>3</sub>S)·9H<sub>2</sub>O were collected in Debye-Scherrer geometry with a STOE Stadi P diffractometer using Mo-K<sub>α</sub> radiation (linear PSD detector, with steps of 0.5, acquisition time: 200 s per step) at room temperature. The structural parameters of NaBa(PO<sub>3</sub>S)·9H<sub>2</sub>O were refined applying the Rietveld method [17] using the computer program GSAS [18]. All reflections were indexed and their observed intensities were in very good agreement with the

calculated diffraction pattern based on the single crystal data of NaCa(PO<sub>3</sub>S)·9H<sub>2</sub>O. The Rietveld refinement (25 structural parameters, 8 profile parameters, 3299 data points, 754 reflections,  $2\theta_{\text{max}} = 70.0^\circ$ ) converged to  $R_F^2 = 0.099$ ,  $R_p = 0.034$ ,  $wR_p = 0.047$ ,  $\chi^2 = 3.34$ . The atomic parameters were refined but remained almost unchanged and therefore the detailed structural parameters are not reproduced herein; these are listed in the Supporting Information.

Further details of the crystal structure investigations presented in this work may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (E-Mail: crysdata@fiz-karlsruhe.de) on quoting the depository numbers CSD-420480 (NaCa(PO<sub>3</sub>S)·9H<sub>2</sub>O) and CSD-420481 (NaBa(PO<sub>3</sub>S)·9H<sub>2</sub>O), the names of the authors, and citation of this publication.

### Vibrational Spectroscopy

An FTIR spectrum was measured at room temperature by using a Bruker IFS 66v/S spectrometer. The samples were thoroughly mixed with dried KBr (ca. 1 mg sample, 300 mg KBr). Raman spectra were recorded with a Bruker FRA 106/S module with a Nd-YAG laser ( $\lambda = 1064 \text{ nm}$ ) scanning a range from 400 to 4000 cm<sup>-1</sup>.

### Solid-state NMR Spectra

Solid-state <sup>31</sup>P NMR spectra of Na<sub>3</sub>(PO<sub>3</sub>S), **1** and **2** were recorded with a Bruker Avance II 400 in MAS technique using a 4 mm sample container at room temperature, the rotation frequency was 8 kHz (Na<sub>3</sub>(PO<sub>3</sub>S) and **1**) or 10 kHz (**2**). Chemical isotropic shifts are given with respect to phosphoric acid (85 %) as reference.

**Supporting Information** (see footnote on the first page of this article): Tables S1, S2, S3 and S4 and Figures S1, S2 and S3 with structural details of the crystal structure determinations of **1** and **2**.

### Acknowledgement

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### References

- [1] T. Jüstel, H. Nikol, C. Ronda, *Angew. Chem. Int. Ed.* **1998**, *37*, 3084.
- [2] H. A. Höpfe, *Angew. Chem. Int. Ed.* **2009**, *48*, 3572.
- [3] H. A. Höpfe, M. Daub, M. C. Bröhmer, *Chem. Mater.* **2007**, *19*, 6358.
- [4] H. A. Höpfe, J. M. U. Panzer, *Eur. J. Inorg. Chem.* **2009**, 3127.
- [5] S. K. Yasuda, J. L. Lambert, *Inorg. Synth.* **1957**, *5*, 102.
- [6] M. Pompetzki, M. Jansen, *Z. Anorg. Allg. Chem.* **2002**, *628*, 641.
- [7] A. E. Gash, P. K. Dorhout, S. H. Strauss, *Inorg. Chem.* **2000**, *39*, 5538.
- [8] M. Gjikaj, *Z. Kristallogr. NCS* **2008**, *223*, 1.
- [9] S. V. Baturin, Y. A. Malinovskii, N. V. Belov, *Dokl. Akad. Nauk SSSR* **1982**, *226*, 624.
- [10] S. Takagi, M. Mathew, W. E. Brown, *Acta Crystallogr., Sect. B* **1982**, *38*, 1408.
- [11] a) T. Steiner, *Angew. Chem. Int. Ed.* **2002**, *41*, 48; b) G. A. Jeffrey, *An Introduction to Hydrogen Bonding*, Oxford University Press, Oxford, **1997**.

- [12] a) D. B. Powell, J. G. V. Scott, *Spectrochim. Acta A* **1972**, 281067; b) W. Brockner, B. Jendrzok, F. Menzel, V. R. Jensen, M. Ystenes, *J. Mol. Struct.* **1994**, 31985.
- [13] M. Pompetzki, L. van Wüllen, M. Jansen, *Z. Anorg. Allg. Chem.* **2004**, 630, 384.
- [14] A. V. Lebedev, A. I. Rezvukhin, *Nucleic Acids Res.* **1984**, 12, 5547.
- [15] T. Higashi, *ABSCOR*. Rigaku Corporation, Tokyo, Japan, **1995**.
- [16] G. M. Sheldrick, *SHELXTL V 5.10*, Crystallographic System, Bruker AXS Analytical X-ray Instruments Inc., Madison, **1997**.
- [17] H. M. Rietveld, *J. Appl. Crystallogr.* **1969**, 2, 65.
- [18] a) R. B. von Dreele, A. C. Larson, *General Structure Analysis System (GSAS)*, Los Alamos National Laboratory Report LAUR 86-748, **2000**; b) B. H. Toby, *J. Appl. Crystallogr.* **2001**, 34, 210.