Thermodynamic properties of calcium alkali phosphates Ca(Na,K)PO₄

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Received: 12 February 2020
Accepted: 26 March 2020
Published online: 12 April 2020
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ABSTRACT
Calcium alkali phosphates Ca(Na,K)PO₄ are main constituents of bioceramics and thermochemically produced phosphorus fertilizers because of their bioavailability. Sparse thermodynamic data are available for the endmembers CaNaPO₄ and CaKPO₄. In this work, the missing data were determined for the low-temperature phase modifications of the endmembers CaNaPO₄ and CaKPO₄ and three intermediate Ca(Na,K)PO₄ compositions. Standard enthalpy of formation ranges from $-2018.3 \pm 2.2$ kJ mol⁻¹ to $-2030.5 \pm 2.1$ kJ mol⁻¹ and standard entropy from $137.2 \pm 1.0$ J mol⁻¹ K⁻¹ to $148.6 \pm 1.0$ J mol⁻¹ K⁻¹ from sodium endmember $\beta$-CaNaPO₄ to potassium endmember $\beta$'-CaKPO₄. Thermodynamic functions are calculated up to 1400 K for endmembers and the sodium-rich intermediate phase $\beta$-Ca(Na0.93K0.07)PO₄. Functions above 640 K are extrapolated because of the phase transition from low- to high-temperature phase. Impurities in the synthesized intermediate phases $\gamma$-Ca(Na0.4K0.6)PO₄ and $\gamma$'-Ca(Na0.35K0.65)PO₄ and one additional phase transition around 500 K impeded the determination of high-temperature thermodynamic functions. In general, data for phase transition temperatures agree with the previously reported phase diagrams.

Introduction

Calcium alkali phosphates Ca(Na,K)PO₄ are of interest for fertilizer production and bioceramics used for bone tissue reconstructions. They possess higher bioavailability in comparison to the calcium phosphates such as whitlockite or apatite [1]. If used as bone substitution, they should be slowly decomposed and gradually replaced by a new fully functional bone [2, 3]. For the use as fertilizers, the nutrient elements should be available to plants. Therefore, calcium alkali phosphates are produced by thermochemical treatment of rock phosphate or sewage sludge ash at 800–1400 °C with alkali sulfates, carbonates or hydroxides [4–6].
The earliest description of CaNaPO₄ and CaKPO₄ dates back to the time of the development of the Rhenania process for thermochemical treatment of rock phosphate in the 1920s [6, 7] and the research continues until today [4, 8, 9]. Based on these procedures, a comparable thermochemical process was developed to treat phosphorus-rich sewage sludge ash for fertilizer production [5, 10, 11].

The phase diagram of the system CaNaPO₄–CaKPO₄ was investigated by Orlov et al. [12] and Znamierowska [13] (Fig. 1). The transformation temperatures from the low- to the high-temperature modification of calcium alkali phosphates are in the range of 823 K to 1033 K. The low-temperature modifications are divided by two miscibility gaps into three stability fields (β-, β'- and γ-phase) [13]. The sodium-rich β-phase includes the chemical composition ranging from CaNaPO₄ to Ca(Na₀.₈K₀.₂)PO₄ and the potassium-rich β'-phase that from CaKPO₄ to Ca(Na₀.₀₅K₀.₉₅)PO₄. The intermediate γ-phase, with a composition centered around Ca(Na₀.₅K₀.₅)PO₄ to Ca(Na₀.₄K₀.₆)PO₄, is a target phase for bioceramic applications [14, 15]. The endmember CaNaPO₄ was intensively characterized [12, 16–18], whereas CaKPO₄ was investigated less [12, 18, 19].

Incomplete thermodynamic data are available for the endmembers CaNaPO₄ and CaKPO₄ as well as for the intermediate phase Ca(Na₀.₄K₀.₆)PO₄. The transition enthalpy from the low- to the high-temperature modification (Δ_transH) of CaNaPO₄, Ca(Na₀.₄K₀.₆)PO₄ and CaKPO₄ is 8.2, 1.4 and 2.8 kJ mol⁻¹, respectively [12]. The database of FactSage, without citing data sources or specifying low- and high-temperature modifications, contains the standard entropy of 128.7 J mol⁻¹ K⁻¹ and enthalpy of formation of −2033 kJ mol⁻¹ for CaNaPO₄. The enthalpy of formation for CaKPO₄ is calculated as −2037.8 kJ mol⁻¹ [20]. To the best of our knowledge, there are no thermodynamic data for the potassium and sodium-containing intermediate calcium alkali phosphates. To close some of these gaps, this work presents heat capacity, standard entropy and standard enthalpy of formation for the end-members β-CaNaPO₄ and β'-CaKPO₄ as well as for three intermediate phases.

### Experimental methods

#### Synthesis

Low-temperature modifications of each calcium alkali phosphate Ca(Na,K)PO₄ were synthesized using protocols that avoid the use of excessive heat in order to remain well below the transformation temperature to the high-temperature modification. Other syntheses, e.g. β-CaNaPO₄ by Morris et al. [21] and Ben Amara et al. [16], Ca₂NaK(PO₄)₂ by Schneider et al. [14] and β-CaKPO₄ by Franck et al. [22], include steps above the transformation temperatures. The syntheses of β-CaNaPO₄ and the sodium-rich intermediate phase β-Ca(Na₀.₉₃K₀.₀₇)PO₄ completely below the transformation temperature are only possible if all chemicals can be initially dissolved in water and thoroughly mixed. Thus, stoichiometric mixtures of Ca(NO₃)₂·2H₂O, H₃PO₄, NaNO₃ and KNO₃ (all p.a. grade) were completely dissolved in double-distilled water. The solution was treated at first at 383 K to evaporate the water and subsequently the powder at 573 K for 3 h in a muffle furnace to remove NOₓ. The sintering process at 773 K was interrupted by grinding and re-grinding after 12, 24, 48, 96 and 192 h. However, β'-CaKPO₄ and the intermediate phases γ-Ca(Na₀.₄K₀.₆)PO₄ and γ'-Ca(Na₀.₃₅K₀.₆₅)PO₄ could not be synthesized in a pure form using this protocol. Therefore, the syntheses of intermediate phases and β'-CaKPO₄ were modified and combined with the protocol of Schneider et al. [14]. The chemicals CaHPO₄·2H₂O, Na₂CO₃ and K₂CO₃ (all p.a. grade) were thoroughly mixed and heated to 1173 K for 1 h. Afterwards they were...
ground, sintered at 773 K with interruption of re-grinding after 12, 24, 48, 96 and 192 h, as described for the \( \beta \)-phases. Additionally, \( \alpha \)-CaKPO\(_4\) was prepared with the same chemicals as \( \beta \)-CaKPO\(_4\) but heated to 1273 K for 6 h. Afterwards, this sample was quenched in water.

**Sample characterization**

**Chemical analysis**

The chemical composition was analysed by inductively coupled plasma mass spectrometry (ICP-MS; Thermo iCAP Q, Dreieich, Germany) after digestion with aqua regia (chemicals p.a. grade) of 0.05–0.1 g sample in a microwave. Blanks, KCl (p.a. grade), NaCl (p.a. grade) and a reference material D826-1 for Ca and P were used to evaluate the analytical accuracy and precision. All digestions and ICP-MS measurements were carried out in triplicates.

**Powder X-ray diffraction (PXRD)**

PXRD measurements of the samples were performed in transmission geometry over a 2\( \theta \) range from 5° to 70°, with a step size of 0.0009° (D8 Discover, Bruker AXS) and with Cu K\( \alpha_1 \) (\( \lambda = 1.54056 \) Å) radiation. The diffraction patterns were recorded with a Lynxeye detector. The PXRD were evaluated using the Match! Software (version 3.6). Full-profile refinements were done for the samples \( \beta \)-CaNaPO\(_4\) and \( \beta \)-Ca(Na\(_{0.93}\)K\(_{0.07}\))PO\(_4\) (TOPAS version 6). The content of impurities was estimated additionally by the area method. This method is more closely described in the supplementary information.

**Calorimetry**

**Acid-solution calorimetry**

For the solution calorimetric experiments at \( T = 298.15 \) K, we used a commercial IMC-4400 isothermal microcalorimeter (Calorimetry Sciences Corporation), modified for the purposes of acid-solution calorimetry [23]. The liquid bath of the calorimeter was held at a constant temperature of 298.15 K with fluctuations smaller than 0.0005 K. The calorimetric solvent was 25 g of 5 N HCl contained in a polyetheretherketone (PEEK) cup with a total volume of 60 mL. The cup was then closed with a PEEK screwable lid and inserted into the calorimeter well. The calorimeter stabilized after \( \approx 8 \) h. During the stabilization and the experiment, the solvent was stirred by a SiO\(_2\) glass stirrer by a motor positioned about 40 cm from the active zone of the instrument. The samples were pressed into a pellet and weighed on a micro-balance with a precision of 0.002 mg (as stated by the manufacturer). The pellets were then dropped through a SiO\(_2\) glass tube into the solvent and the heat produced or consumed during the dissolution was measured. The heat flow between the reaction cup and the constant temperature reservoir was then integrated to calculate the calorific effect. A typical experiment lasted 70–80 min and the end of the experiment was judged from the return of the baseline to the pre-experiment position. The calorimeter was calibrated by dissolving \( \approx 20 \) mg pellets of KCl in 25 g of deionized water. Prior to each calibration measurement, the potassium chloride was heated overnight in the furnace to 800 K to remove the adsorbed water. The expected heat effect for the calibration runs was calculated from Parker [24].

**Relaxation calorimetry (PPMS)**

Heat capacity (\( C_p \)) was measured by relaxation calorimetry using a commercial Physical Properties Measurement System (PPMS, from Quantum Design, San Diego, California). With due care, accuracy can be within 1% for 5 K to 300 K, and 5% for 0.7 K to 5 K [25]. Powdered samples were wrapped in a thin Al foil and compressed to produce a \( \approx 0.5 \) mm thick pellet which was then placed onto the sample platform of the calorimeter for measurement. Heat capacity was measured in the PPMS in the temperature interval 2 K to 300 K.

**Differential scanning calorimetry (DSC and STA)**

The heat capacities between 259 and 640 K for sample \( \beta \)-CaNaPO\(_4\) and 282 K and 464 K for other samples were measured by differential scanning calorimetry (DSC) using a Perkin Elmer Diamond DSC. Details of the method are described in Benisek et al. [26].

\( C_p \) measurements at 310–1370 K were done with a Netzsch STA 449 C Jupiter thermoanalytical system (STA). The sample was loaded into platinum crucibles covered by platinum lids. Accuracy was regularly tested by the determination of \( C_p \) of sapphire.
Accuracy of transformation enthalpy ($\Delta_{\text{trans}}H$) measurements was tested by measurements on quartz, SiO$_2$. The measured $\Delta_{\text{trans}}H$ of $0.543 \pm 0.007$ kJ mol$^{-1}$ (in duplicate) compares roughly to the 0.625 kJ mol$^{-1}$ from Hemingway [27], the deviation being 13%.

**Results and discussion**

**Chemical and phase characterization**

The chemical compositions of the synthesis products were determined by ICP-MS and compared to the nominal elemental mass fractions calculated from the ratios of the starting chemicals (Table 1). The accuracies for calcium and phosphorus were between 97 and 103 wt% compared to the expected values and for sodium and potassium slightly below 100 wt% for all samples. Chemical analysis by ICP-MS was confirmed by X-ray fluorescence spectroscopy (data not shown).

All samples were crystalline, with sharp PXRD peaks. The models for the sample $\beta$-CaNaPO$_4$ (space group $Pn2_1$; $a = 20.3806(3)$ Å; $b = 5.40518(9)$ Å; $c = 9.1562(2)$ Å; $V = 1008.6(1)$ Å$^3$) and the sample $\beta$-Ca(Na$_{0.93}$K$_{0.07}$)PO$_4$ ($Pn2_1$; $a = 20.4633(9)$ Å; $b = 5.4124(2)$ Å; $c = 9.1771(4)$ Å; $v = 1016.4(1)$ Å$^3$) were refined by using ICSD entry 35629 (supplementary Fig. S1 and S2). The indexing of the diffraction pattern of $\beta$-Ca(Na$_{0.93}$K$_{0.07}$)PO$_4$ documents expansion of the unit cell in comparison to $\beta$-CaNaPO$_4$, because of incorporation of the larger K atoms in its structure. Furthermore, there are additional CaK$_2$P$_2$O$_7$ reflexes in the PXRD data for the sample $\beta$-Ca(Na$_{0.93}$K$_{0.07}$)PO$_4$ (Fig. S2). The amount of CaK$_2$P$_2$O$_7$ (COD entry 9007955) was quantified by Rietveld refinement as 3 wt%. Application of the semiquantitative area method yielded 4 wt% (see supplementary information). Combined with the results of chemical analysis, the assumed composition of this sample is 96 wt% $\beta$-Ca(Na$_{0.93}$K$_{0.07}$)PO$_4$ and 4 wt% CaK$_2$P$_2$O$_7$.

The PXRD peaks of the two samples of $\gamma$-Ca(Na$_{0.4}$K$_{0.6}$)PO$_4$ and $\gamma$-Ca(Na$_{0.35}$K$_{0.65}$)PO$_4$ are slightly shifted to lower 2θ angles compared to the data entry Ca$_2$NaK(PO$_4$)$_2$ (ICDD PDF entry 00-051-0579) (Fig. S3). Furthermore, similar refinement is achieved with lattice parameters for a monoclinic system postulated for Ca(Na$_{0.4}$K$_{0.6}$)PO$_4$ by Orlov et al. [12]. Both samples contain impurities but the quantification of these impurities by Rietveld refinement was not possible, because a structural model for Ca$_2$NaK(PO$_4$)$_2$ [14] or Ca(Na$_0.4$K$_{0.6}$)PO$_4$ [12] is not available. Therefore, the content of impurities was estimated by the area method. Accordingly, $\gamma$-Ca(Na$_{0.4}$K$_{0.6}$)PO$_4$ contains 5 wt% whitlockite (ICSD entry 91525), 1 wt% CaK$_2$P$_2$O$_7$, and 0.5 wt% hydroxyapatite (Ca$_5$(PO$_4$)$_3$OH) (COD entry 9011095). $\gamma$-Ca(Na$_{0.35}$K$_{0.65}$)PO$_4$ contains 2 wt% hydroxyapatite as an impurity.

There are very few structural data for the low-temperature phase $\beta_0$-CaKPO$_4$. Our data could be refined with lattice parameters $a = 5.492(4)$ Å; $b = 9.603(2)$ Å; $c = 16.245(5)$ Å; $\beta = 68.9(1)$; $V = 799.6(4)$ Å$^3$ from Orlov et al. [12]. Evdokimov et al. [3] described this phase as “a monoclinic distortion of the hexagonal structure of $\alpha$-CaKPO$_4$” and, therefore, the reflexes of $\beta'$-CaKPO$_4$ coincide largely with those of $\alpha$-CaKPO$_4$ (Fig. S4). The sample $\beta'$-CaKPO$_4$ contains 2 wt% CaK$_2$P$_2$O$_7$, 3 wt% **Table 1** Chemical composition of calcium alkali phosphates Ca(Na,K)PO$_4$, measured in triplicates. Chemical composition is normalized to the molar proportions to 1 P atom per formula unit in the row below the mass fraction

| Sample               | Mass fraction [wt%] |
|----------------------|---------------------|
|                      | Ca  | K   | Na  | P   |
| $\beta$-CaNaPO$_4$   | 24.59 ± 0.34        |
|                      | 1.00 | –   | 13.55 ± 0.01 |
|                      | 1.00 | 0.96| 19.03 ± 0.17 |
| $\beta$-Ca(Na$_{0.93}$K$_{0.07}$)PO$_4$ | 24.85 ± 1.61        |
|                      | 1.00 | 2.51± 0.37     |
|                      | 0.10 | 12.21 ± 0.16   |
|                      | 1.00 | 19.29 ± 1.03   |
| $\gamma$-Ca(Na$_0.4$K$_{0.6}$)PO$_4$ | 24.46 ± 0.27        |
|                      | 1.04 | 13.25 ± 0.02   |
|                      | 0.58 | 5.26 ± 0.01    |
|                      | 1.00 | 18.10 ± 0.13   |
| $\gamma$-Ca(Na$_{0.35}$K$_{0.65}$)PO$_4$ | 23.97 ± 0.28        |
|                      | 1.05 | 14.05 ± 0.16   |
|                      | 0.63 | 4.61 ± 0.02    |
|                      | 1.00 | 17.70 ± 0.08   |
| $\beta'$-CaKPO$_4$   | 23.63 ± 0.21        |
|                      | 1.05 | 20.06 ± 0.01   |
|                      | 0.92 | 17.35 ± 0.20   |
whitlockite and 3 wt% hydroxylapatite as impurities, estimated with the area method.

**Acid-solution calorimetry**

The enthalpies of formation of calcium alkali phosphates Ca(Na,K)PO$_4$ were determined by acid-solution calorimetry. All samples and reference compounds dissolved rapidly, and the results were reproducible, with uncertainties typical for this type of measurement. The measured bulk enthalpies in 5 N HCl are weighed sums of the enthalpies of dissolution ($\Delta_{\text{diss}}H$) of the Ca(Na,K)PO$_4$ phase and the impurities. To evaluate and correct for the latter, we also measured $\Delta_{\text{diss}}H$ for K-whitlockite [Ca$_{10}$K(PO$_4$)$_7$] as $336.7 \pm 0.3 \text{ kJ mol}^{-1}$ and $\Delta_{\text{diss}}H$ for hydroxylapatite [Ca$_5$(PO$_4$)$_3$OH] as $-124.3 \text{ kJ mol}^{-1}$. The $\Delta_{\text{diss}}H$ for CaK$_2$P$_2$O$_7$ was not measured but calculated from enthalpy of formation of CaK$_2$P$_2$O$_7$ of $-3286.9 \text{ kJ mol}^{-1}$ from Zdukos et al. [20]. The calculated value is $-69.4 \text{ kJ mol}^{-1}$.

The corrected $\Delta_{\text{diss}}H$ in 5 N HCl decreases monotonically with increasing potassium content in the Ca(Na$_{1-n}$K$_n$)PO$_4$ solid solution from $-52.23 \pm 0.30 \text{ kJ mol}^{-1}$ for sample $\beta$-CaNaPO$_4$ to $-62.69 \pm 0.14 \text{ kJ mol}^{-1}$ for the sample $\beta'$-CaKPO$_4$ (Table 3). The corrected $\Delta_{\text{diss}}H$ are used to calculate deviations of the intermediate phases Ca(Na$_{1-n}$K$_n$)PO$_4$ from the enthalpy of theoretical mixtures of the endmembers (Fig. 2). This calculation is comparable to the determination of enthalpy of mixing [28].

The enthalpy of formation from elements in their standard state has to be calculated via a thermochemical cycle (Table 2) with respect to the known enthalpies of carefully chosen substances called the reference compounds. Special attention should be given to these reference compounds. Their formation enthalpies must be known with high accuracy and precision.

The thermochemical cycles were constructed with KH$_2$PO$_4$, NaH$_2$PO$_4$, 2H$_2$O, CaO, and H$_2$O as the reference compounds (Table 2). The $\Delta_{\text{diss}}H$ of CaO was reported by Majzlan [23]. The dissolution enthalpy of KH$_2$PO$_4$ in 5 N HCl at $T = 298$ K at low final molalities was measured as $24.61 \pm 0.46 \text{ kJ mol}^{-1}$ [29]. In our study, the $\Delta_{\text{diss}}H$ of $25.08 \pm 0.28 \text{ kJ mol}^{-1}$ was measured for higher final molalities. The dissolution enthalpy of NaH$_2$PO$_4$.2H$_2$O in 5 N HCl at $T = 298$ K was measured in our study as $29.83 \pm 0.32 \text{ kJ mol}^{-1}$; no data are available in the literature for comparison.

There are only few data for the formation enthalpies of the phosphates KH$_2$PO$_4$ and NaH$_2$PO$_4$.2H$_2$O. The formation enthalpy of KH$_2$PO$_4$ can be found in Rud’ko et al. ([30]; $-1561.9 \text{ kJ mol}^{-1}$), Wagman et al. ([31]; $-1586.3 \text{ kJ mol}^{-1}$), and Luff and Reed ([32]; $-1573.6 \text{ kJ mol}^{-1}$). Majzlan [23] re-determined the formation enthalpy of KH$_2$PO$_4$ as $-1573.6 \text{ kJ mol}^{-1}$ and adopted the value from Luff and Reed [32], as done in this paper. For NaH$_2$PO$_4$.2H$_2$O, only the data in Wagman [31] are available and are adopted in this work.

The calculated enthalpies of formation from elements in their standard state ($\Delta H^\circ$) decrease with increasing potassium content from $-2018.3 \pm 2.2 \text{ kJ mol}^{-1}$ ($\beta$-CaNaPO$_4$) to $-2030.5 \pm 2.1 \text{ kJ mol}^{-1}$ ($\beta'$-CaKPO$_4$) (Table 3).

**Standard entropy and Gibbs free energy of formation**

Standard entropies were calculated by heat capacity data of PPMS. These data of the Ca(Na$_3$K$_{10}$)PO$_4$ samples in the temperature range 2 to 303 K were fitted with polynomials:

$$\sum_{N=0}^{11} A_N T^N$$
Experimental data in the temperature range 2–15 K could not be fitted with a simple \((N=3)\) or extended Debye \((N=3, 5, 7)\) model. Therefore, the low-temperature data were fitted and extrapolated to 0 K with polynomials with \(N=1–7\). The physical meaning of all these terms is not clear but the achieved fits are satisfactory. The temperature range 15–300 K was subdivided in three sections (15–60 K, 60–160 K and 160–300 K) and fitted with orthogonal polynomials. All coefficients \((A_N)\) are listed in the supplementary information. The relative deviation between experimental data and fits \([28]\) are shown in Fig. 3 for \(\beta\)-CaNaPO\(_4\) and in the supplementary information for the other phases. The integration according to these orthogonal polynomials for heat capacity was used to calculate standard entropies \(S^\circ\):

\[
\Delta H_1 = \Delta_{\text{diss}}H(Ca_{1-n}K_nPO_4) = \text{CaNa}_{1-n}K_nPO_4 \rightarrow \text{Ca}^{2+} \text{(aq)} + (1-n) \text{Na}^+ \text{(aq)} + n \text{K}^+ \text{(aq)} + \text{PO}_4^{3-} \text{(aq)}
\]

\[
\Delta H_2 = \Delta_{\text{diss}}H(NaH_2PO_42H_2O) = \text{NaH}_2PO_42H_2O \rightarrow \text{Na}^+ \text{(aq)} + 2H^+ \text{(aq)} + \text{PO}_4^{3-} \text{(aq)} + 2H_2O \text{(aq)}
\]

\[
\Delta H_3 = \Delta_{\text{diss}}H(KH_2PO_4) = \text{KH}_2PO_4 \rightarrow \text{K}^+ \text{(aq)} + 2H^+ \text{(aq)} + \text{PO}_4^{3-} \text{(aq)}
\]

\[
\Delta H_4 = \Delta_{\text{diss}}H(CaO) = \text{CaO} \rightarrow \text{Ca}^{2+} \text{(aq)} + H_2O \text{(aq)}
\]

\[
\Delta H_5 = \Delta_{\text{diss}}H(H_2O) = H_2O \rightarrow H_2O \text{(aq)}
\]

\[
\Delta H_6 = \Delta H^f(NaH_2PO_42H_2O) = \text{Na} \text{(cr)} + 3H_2 \text{(g)} + P \text{(cr)} + 3O_2 \text{(g)} \rightarrow \text{NaH}_2PO_42H_2O \text{(cr)}
\]

\[
\Delta H_7 = \Delta H^f(KH_2PO_4) = \text{K} \text{(cr)} + H_2 \text{(g)} + P \text{(cr)} + 2O_2 \text{(g)} \rightarrow \text{KH}_2PO_4 \text{(cr)}
\]

\[
\Delta H_8 = \Delta H^f(CaO) = \text{Ca} \text{(cr)} + 1/2O_2 \text{(g)} \rightarrow \text{CaO} \text{(cr)}
\]

\[
\Delta H_9 = \Delta H^f(H_2O) = H_2 \text{(g)} + 1/2O_2 \text{(g)} \rightarrow H_2O \text{(l)}
\]

\[
\Delta H_{10} = \Delta H^f(CaNa_{1-n}K_nPO_4) = \text{CaNa}_{1-n}K_nPO_4 \rightarrow (1-n)\text{Na} \text{(cr)} + n\text{K} \text{(cr)} + P \text{(cr)} + 2O_2 \text{(g)} \rightarrow \text{NaH}_2PO_4 \text{(cr)}
\]

\[
\Delta H_{10} = \Delta H^f(CaNa_{1-n}K_nPO_4) = -\Delta H_1 + (1-n)\Delta H_2 + n\Delta H_3 + \Delta H_4 - (3-2n)\Delta H_5 + (1-n)\Delta H_6 + n\Delta H_7 + \Delta H_8 - (3-2n)\Delta H_9
\]

\[\text{Table 2 Thermodynamic cycle for calcium-alkali-phosphates used for acid solution calorimetry}
\]

- Mean
- Two standard deviations of the mean
- Number of measurements
- Majzlan [23]
- Calculated from Parker [24]
- Wagman et al. [31]
- No uncertainty available; estimated as 1.0 kJ mol\(^{-1}\)
- Luff and Reed [32]
- Robie and Hemingway [33]

Figure 3 Deviation of experimental \(C_P\) and fitted \(C_P\) of PPMS (empty circles) against temperature for \(\beta\)-CaNaPO\(_4\). The inset shows the temperature range 2–10 K. Experimental \(C_P\) of DSC (filled circles) plotted against fitted \(C_P\) of PPMS.
The calculated standard entropies are, just as the enthalpies, weighed averages of the entropy of the Ca(Na$_{1-n}$K$_n$)PO$_4$ phases and the impurities. The $S^0$ value for hydroxyapatite of 390.4 J mol$^{-1}$ K$^{-1}$ was taken from Robie and Hemingway [33]. The $S^0$ values for the other impurities were estimated with the Neumann-Kopp rule, stating that the entropy of a phase is the sum of entropies of its suitably chosen components. In this case, the components are simple oxides and their entropies were taken from Robie and Hemingway [33]. The estimated entropies of K-whitlockite and CaK$_2$P$_2$O$_7$ are 828.5 J mol$^{-1}$ K$^{-1}$ and 246.6 J mol$^{-1}$ K$^{-1}$, respectively. The $S^0$ values for the Ca(Na$_{1-n}$K$_n$)PO$_4$ phases, corrected for the impurities, increase from 137.2 ± 1.0 J mol$^{-1}$ K$^{-1}$ for $\beta$-CaNaPO$_4$ to 148.6 ± 1.0 J mol$^{-1}$ K$^{-1}$ for $\beta'$-CaKPO$_4$ (Table 3). Their deviations from entropies of theoretical mixtures of the endmembers are displayed in Fig. 4.

The calculated Gibbs free energies of formation decrease with increasing potassium content from $-1896.5 \pm 2.4$ kJ mol$^{-1}$ for $\beta$-CaNaPO$_4$ to $-1908.1 \pm 2.4$ kJ mol$^{-1}$ for $\beta'$-CaKPO$_4$. The $\Delta G^0$ for $\beta$-CaNaPO$_4$ is 12 kJ mol$^{-1}$ higher than that in the database of the software FactSage (Table 3).

### Table 3: Thermodynamic properties of five calcium alkali phosphates derived from calorimetric measurements based on corrected values of $\Delta_\text{diss} H$ and $S^0$. Data in italics in the first row are from the modelling software FactSage [35]. All enthalpy and Gibbs free energy values in kJ mol$^{-1}$, all entropies in J mol$^{-1}$ K$^{-1}$

| Phase          | $\Delta_\text{diss} H$ HCl | $\Delta_\text{diss} P$ | $S^0$ | $\Delta_\text{sol}$ | $\Delta_\text{G}$ |
|----------------|----------------------------|-------------------------|-------|----------------------|-------------------|
| Na-phase       | $-52.22 \pm 0.30$          | $-2018.3 \pm 2.2$       | $128.7 \pm 1$ | $-408.6 \pm 1.1$    | $-1988.5 \pm 2.4$ |
| $\beta$-CaNaPO$_4$ | $-52.22 \pm 0.30$          | $-2018.3 \pm 2.2$       | $128.7 \pm 1$ | $-408.6 \pm 1.1$    | $-1988.5 \pm 2.4$ |
| $\gamma$-CaNa$_{0.45}K_{0.6}PO_4$ | $-52.22 \pm 0.30$          | $-2018.3 \pm 2.2$       | $128.7 \pm 1$ | $-408.6 \pm 1.1$    | $-1988.5 \pm 2.4$ |
| $\beta'$-CaKPO$_4$ | $-52.22 \pm 0.30$          | $-2018.3 \pm 2.2$       | $128.7 \pm 1$ | $-408.6 \pm 1.1$    | $-1988.5 \pm 2.4$ |

*a* Mean
*b* Two standard deviations of the mean
*c* Number of measurement
*d* Calculated with standard entropies of elements from Robie and Hemingway [33]
Figure 5 Phase transition region for (a) β-CaNaPO₄, (b) β-Ca(Naₐ₉₃K₀.₀₇)PO₄, (c) γ-Ca(Na₀₄K₀.₆)PO₄, (d) γ-Ca(Na₀.₃₅K₀.₆₅)PO₄ and (e) β’-CaKPO₄. The dotted line is for first heating, the solid curve for second heating and dashed line for cooling. The shaded area is the area used for calculation of the transition enthalpy [kJ mol⁻¹] which value is displayed. T onset [K] stands below graphs and T peak [K] above graphs.

Superambient heat capacity measurements

Heat capacity (Cₚ) measurements using the DSC method were done between 259 and 640 K for sample β-CaNaPO₄ and between 282 and 464 K for the other samples. The agreement between PPMS (2–303 K) and DSC data is very good. The differences at 295 K were 0.3% for all samples. Additionally, semiquantitative Cₚ measurements (named as STA) between 310 and 1370 K were done with a Netzsch STA thermoanalytical system. The latter data were used for the characterization of the phase transitions (between 850 and 1000 K for the studied phases) and only used up to 640 K for fitting Cₚ’s for β-Ca(Na₀.₉₃K₀.₀₇)PO₄ and β’-CaKPO₄. Phase transition temperatures depend on chemical composition and show a hysteresis during heating and cooling cycles (Fig. 5).

Phase transition

The phase transitions for β-CaNaPO₄ and β-Ca(Na₀.₉₃K₀.₀₇)PO₄ take place in two steps [13]. She reported that the low-temperature phase β-CaNaPO₄ and high-temperature α-CaNaPO₄ coexist between 883 K and 933 K. In contrast, Orlov et al. [12] postulated only one transition at T around 950 K.

Experimental Cₚ data for β-CaNaPO₄ show anomalies at 894 K and 945 K (Fig. 5a). The temperature difference between the two anomalies (50 K) and T onset of 926 K for the second peak correlates well with the data of Znamierowska [13] (Fig. 1). The temperature onset of 894 K for β-Ca(Na₀.₉₃K₀.₀₇)PO₄ is 20 K below that for the second peak (Fig. 5e). Comparable data are reported by Znamierowska [13] (Fig. 1). Additionally, a broad Cₚ anomaly is observed in the temperature interval 950–1010 K.

Enthalpy and entropy of phase transition

Data for enthalpy and entropy of phase transition are listed in Table 4. The enthalpy of phase transition of the intermediate phases γ-Ca(Na₀₄K₀.₆)PO₄ and γ-Ca(Na₀.₃₅K₀.₆₅)PO₄ is smaller compared to other phases, because both low- and high-temperature phases of the intermediate samples are structurally related [14]. The more complex change from orthorhombic (β-CaNaPO₄, β-Ca(Na₀.₉₃K₀.₀₇)PO₄) to hexagonal symmetry results in higher enthalpy values. The transition enthalpies of the intermediate phases are comparable to the transition enthalpy of Ca(Na₀.₄K₀.₆)PO₄ reported by Orlov et al. [12] but lower enthalpies are reported for β-CaNaPO₄ and β’-CaKPO₄. Calculated transition enthalpies (ΔₜₛₐₜₕₜH) and entropies (ΔₜₛₐₜₕS) in Table 4 are considered in the thermodynamic functions for β-CaNaPO₄ at the onset temperature (Table 6).

Determination of superambient heat capacity

For the high-temperature regions, the DSC data were combined with STA data and estimate for the highest temperature (1400 K). In the region of 640–1400 K, phase transitions of the studied phosphates preclude accurate and precise Cₚ determination. The function used by Berman and Brown [34] was selected to allow for extrapolation to T = 1400 K.

Cₚ(T) = A₀ + A₁ × T⁻₀.₅ + A₂ × T⁻² + A₃ × T⁻₃

The procedure chosen here agrees with the way the data in the FactSage database were derived, where the data were adjusted to reproduce the main features of the known phase diagrams. We acknowledge that there should be separate Cₚ functions for the low- and high-temperature phases but the data
available do not allow for fitting in such a detail. Instead, just as practiced in FactSage, a single function is proposed. Given that these structures are closely related, and the transitions are only displacive in their nature, such treatment may be deemed acceptable. For calculating one single function, we force the extrapolation to a fixed point at $T = 1400 \text{ K}$ and $C_p = 182.5 \text{ J mol}^{-1} \text{ K}^{-1}$, a value higher than the Dulong–Petit limit of $174.6 \text{ J mol}^{-1} \text{ K}^{-1}$, in agreement with the FactSage approach, and STA data for $\beta$-CaNaPO$_4$ and $\beta_0$-CaKPO$_4$. Coefficients of all fits are summarized in Table 5.

Heat capacities were fitted well in the temperature ranges from 260 to 640 K for sample $\beta$-CaNaPO$_4$ and from 280 to 640 K for $\beta$-Ca(Na$_{0.93}$K$_{0.07}$)PO$_4$ and $\beta_0$-CaKPO$_4$. These were extrapolated to 1400 K for these three samples (Fig. 6a, b, d, Table 5). In the measured range for $\beta$-CaNaPO$_4$, our data are consistently lower than those listed in FactSage (Fig. 6a). An explanation of the difference is difficult because it is not clear if the FactSage data are based on measurements or estimates. Furthermore, the values for the thermodynamic functions, calculated from the fit polynomials, are reported for $\beta$-CaNaPO$_4$ in Table 6.

Measurements for the intermediate compositions $\gamma$-Ca(Na$_{0.4}$K$_{0.6}$)PO$_4$ and $\gamma$-Ca(Na$_{0.35}$K$_{0.65}$)PO$_4$ compositions show a similar $C_p$ increase between 380 and 460 K. Fitting was impeded due to the $\beta'$ to $\gamma$-phase transition between 480 to 580 K (Fig. 6c), also displayed in phase diagram (Fig. 1).

The heat capacity for $\beta'$-CaKPO$_4$ was fitted between 280 and 640 K. The extrapolated $C_p$ values also fixed at 182.5 J mol$^{-1}$ K$^{-1}$, differ strongly from the semiquantitative $C_p$ measurements between 1000 and 1400 K (Fig. 6d).

### Table 4 Thermodynamic properties of the phase transformations. $T_{trs}$ is onset temperature of phase transition

| Phase                  | $\beta$-CaNaPO$_4$ | $\beta$-Ca(Na$_{0.93}$K$_{0.07}$)PO$_4$ | $\beta_0$-CaKPO$_4$ |
|------------------------|---------------------|----------------------------------------|---------------------|
| $T_{trs}$ [K]          | 926 K               | 894 K                                  | 942 K               |
| $\Delta_{trs}H$ [kJ mol$^{-1}$] | 12.0               | 11.5                                   | 2.0                 |
| $\Delta_{trs}S$ [J mol$^{-1}$]  | 13.0               | 12.9                                   | 2.1                 |

### Table 5 Heat capacities for the studied phases, fitted to polynomials $C_p (T) = A_0 + A_1 \cdot T^{-0.5} + A_2 \cdot T^{-2} + A_3 \cdot T^{-3}$ [34]. These polynomial-coefficients were determined between 260 and 640 K (DSC data) for sample $\beta$-CaNaPO$_4$; between 280 and 640 K (DSC/STA data) for samples $\beta$-Ca(Na$_{0.93}$K$_{0.07}$)PO$_4$ and $\beta_0$-CaKPO$_4$; and a fixed $C_p = 182.5 \text{ J mol}^{-1} \text{ K}^{-1}$ at $T = 1400 \text{ K}$

| Phase                  | $\beta$-CaNaPO$_4$ | $\beta$-Ca(Na$_{0.93}$K$_{0.07}$)PO$_4$ | $\beta_0$-CaKPO$_4$ |
|------------------------|---------------------|----------------------------------------|---------------------|
| $A_0$                  | 199.92              | 189.60                                  | 211.36              |
| $A_1$                  | -496.08             | -32.064                                 | -1047.5             |
| $A_2$                  | -8.0376$\times 10^6$ | -1.1879$\times 10^7$               | -3.0740$\times 10^6$ |
| $A_3$                  | 1.2116$\times 10^9$ | 1.9318$\times 10^9$                    | 3.1578$\times 10^8$ |

### Conclusion

Thermodynamic properties of technically important calcium alkali phosphates Ca(Na,K)PO$_4$ have been determined by different calorimetric measurements. Based on these data, standard enthalpies of formation and standard entropies were calculated for the low-temperature phases $\beta$-CaNaPO$_4$, $\beta$-Ca(Na$_{0.93}$K$_{0.07}$)PO$_4$, $\gamma$-Ca(Na$_{0.4}$K$_{0.6}$)PO$_4$, $\gamma$-Ca(Na$_{0.35}$K$_{0.65}$)PO$_4$ and $\beta'$-CaKPO$_4$. Besides, the sodium endmember all samples contain apatite, whitlockite, or pyrophosphate as impurities. All thermodynamic data were corrected for these impurities. The deviation is $\leq 1\%$ for standard entropy and $< 0.1\%$ for standard enthalpy of formation in case experimental values are compared with corrected ones.

The phase transformations from low- to high-temperature phases took place in the temperature range 890 K to 950 K which agrees with the phase diagram reported by Znamierowska [13]. Additionally observed heat capacity anomalies could not be
matched to phase transition reactions of calcium alkali phosphates or any impurities. Further investigations are required to interpret these anomalies.

Heat capacity measurements at superambient temperatures were challenging because of phase transitions and low accuracy of the used high-temperature calorimetric method. Thus, heat capacities between 640 and 1400 K were estimated by extrapolation for samples $\beta$-CaNaPO$_4$, $\beta$-Ca(Na$_{0.93}$K$_{0.07}$)PO$_4$, and $\beta'$-CaKPO$_4$. The curve “FactSageData” in (a) was calculated from entries in the database of the software FactSage. $C_p$ anomaly between 480 and 580 K in (c) is the $\beta'$-to-$\gamma$ phase transition (Fig. 1). Light grey circles of STA represent values with low accuracy above 1100 K.

In summary, the determined thermodynamic properties of Ca(Na,K)PO$_4$ are valuable data for thermodynamic calculations that can improve manufacturing bioceramics and the production of phosphorus fertilizers containing these calcium alkali phosphates.
Table 6 Thermodynamic functions for $\beta$-CaNaPO$_4$ ($M_r = 158.04$ g mol$^{-1}$). Data for phase transition at 926 K are listed in Table 5.

| $T$ K | $C_p$ J mol$^{-1}$ K$^{-1}$ | $S^\circ$ J mol$^{-1}$ K$^{-1}$ | $[H(T) - H(0)]/T$ J mol$^{-1}$ K$^{-1}$ | $-[G(T) - H(0)]/T$ J mol$^{-1}$ K$^{-1}$ |
|------|-----------------|-----------------|-----------------|-----------------|
| 0    | 0               | 0               | 0               | 0               |
| 10   | 0.15            | 0.05            | 0.03            | 0.01            |
| 20   | 1.75            | 0.50            | 0.39            | 0.11            |
| 30   | 5.90            | 1.89            | 1.45            | 0.44            |
| 40   | 12.66           | 4.46            | 3.36            | 1.10            |
| 50   | 20.77           | 8.13            | 6.02            | 2.12            |
| 60   | 29.38           | 12.68           | 9.19            | 3.48            |
| 70   | 37.74           | 17.84           | 12.68           | 5.16            |
| 80   | 45.42           | 23.39           | 16.30           | 7.09            |
| 90   | 52.46           | 29.14           | 19.92           | 9.22            |
| 100  | 59.27           | 35.03           | 23.52           | 11.50           |
| 120  | 70.75           | 46.90           | 30.48           | 16.41           |
| 140  | 80.48           | 58.56           | 36.95           | 21.61           |
| 160  | 88.74           | 69.85           | 42.91           | 26.94           |
| 180  | 96.29           | 80.75           | 48.44           | 32.31           |
| 200  | 102.61          | 91.23           | 53.54           | 37.69           |
| 220  | 108.47          | 101.3           | 58.27           | 43.02           |
| 240  | 113.68          | 110.0           | 62.68           | 48.28           |
| 260  | 118.46          | 120.3           | 66.79           | 53.46           |
| 273.15 | 121.68      | 126.2           | 69.35           | 56.82           |
| 280  | 123.28          | 129.2           | 70.65           | 58.55           |
| 298.15 | 126.75      | 137.1           | 73.96           | 63.09           |
| 300  | 126.84          | 138.0           | 74.31           | 63.71           |
| 350  | 136.05          | 161.5           | 84.45           | 77.01           |
| 400  | 143.81          | 182.7           | 93.00           | 89.72           |
| 450  | 150.14          | 202.2           | 100.35          | 101.82          |
| 500  | 155.27          | 220.1           | 106.73          | 113.33          |
| 550  | 159.48          | 236.6           | 112.33          | 124.29          |
| 600  | 162.95          | 252.0           | 117.27          | 134.73          |
| 650  | 165.85          | 266.3           | 121.66          | 144.69          |
| 700  | 168.30          | 279.8           | 125.59          | 154.20          |
| 750  | 170.38          | 292.4           | 129.12          | 163.31          |
| 800  | 172.18          | 304.3           | 132.31          | 172.03          |
| 850  | 173.75          | 315.6           | 135.21          | 180.40          |
| 900  | 175.12          | 326.3           | 137.86          | 188.45          |
| 926  | 175.77          | 331.7           | 139.14          | 192.51          |

Phase transition $\beta \rightarrow \alpha$

| $T$ K | $C_p$ J mol$^{-1}$ K$^{-1}$ | $S^\circ$ J mol$^{-1}$ K$^{-1}$ | $[H(T) - H(0)]/T$ J mol$^{-1}$ K$^{-1}$ | $-[G(T) - H(0)]/T$ J mol$^{-1}$ K$^{-1}$ |
|------|-----------------|-----------------|-----------------|-----------------|
| 926  | 175.77          | 344.6           | 152.10          | 192.51          |
| 950  | 176.33          | 349.4           | 152.91          | 196.52          |
| 1000 | 177.40          | 359.1           | 154.51          | 204.60          |
| 1100 | 179.23          | 377.2           | 157.37          | 219.83          |
| 1200 | 180.71          | 393.8           | 159.87          | 233.95          |
| 1300 | 181.95          | 409.2           | 162.06          | 247.12          |
| 1400 | 183.00          | 423.5           | 164.00          | 259.45          |
Acknowledgements

Open Access funding provided by Projekt DEAL. The research was done in the framework of the Project ASHES financed by the German Federal Ministry of Education and Research (BMBF, Grant No. 031A288).

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

Electronic supplementary material: The online version of this article (https://doi.org/10.1007/s10853-020-04615-5) contains supplementary material, which is available to authorized users.

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