

# Energetics of phosphate frameworks containing zinc and cobalt: $\text{NaZnPO}_4$ , $\text{NaH}(\text{ZnPO}_4)_2$ , $\text{NaZnPO}_4 \cdot \text{H}_2\text{O}$ , $\text{NaZnPO}_4 \cdot \frac{4}{3}\text{H}_2\text{O}$ , and $\text{NaCo}_x\text{Zn}_{1-x}\text{PO}_4 \cdot \frac{4}{3}\text{H}_2\text{O}$

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## Abstract

Differential scanning calorimetry and high temperature oxide melt solution calorimetry were used to study the enthalpy of the  $\alpha$ - $\beta$  phase transformation of  $\text{NaZnPO}_4$  and enthalpies of formation of  $\alpha$ - $\text{NaZnPO}_4$ ,  $\text{NaH}(\text{ZnPO}_4)_2$ ,  $\text{NaZnPO}_4 \cdot \text{H}_2\text{O}$ , and  $\text{NaCo}_x\text{Zn}_{1-x}\text{PO}_4 \cdot \frac{4}{3}\text{H}_2\text{O}$  ( $x = 0, 0.1, 0.2, 0.3$ ). The enthalpies of formation from the oxides of cobalt substituted in  $\text{NaZnPO}_4 \cdot \frac{4}{3}\text{H}_2\text{O}$  do not depend on cobalt content, confirming similar acid–base interactions for  $\text{Zn-PO}_4$  and  $\text{Co-PO}_4$ . While water molecules stabilize zinc phosphate frameworks through solvating a cation or forming extra hydrogen bonds, the partial substitution of water for sodium oxide to form  $\text{NaH}(\text{ZnPO}_4)_2$  represents the formation of an acidic compound with weaker acid–base interactions and less exothermic enthalpy of formation from oxides than  $\text{Na}_2(\text{ZnPO}_4)_2$ .

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## 1. Introduction

Aluminosilicate zeolites with porous structures have attracted great interest in science and technology for more than 50 years because of their potential applications in ion exchange, absorption, separation, and catalysis [1]. In attempts to modify the composition of aluminosilicate zeolites, a new class of transition metal phosphate porous materials was discovered in the last decade. Among transition metal phosphates,  $\text{MPO}_4$  (M:  $\text{Co}^{2+}$  and  $\text{Zn}^{2+}$ ) can produce anionic frameworks similar to aluminosilicate zeolite framework containing  $\text{AlSiO}_4$ . Examples are  $(\text{H}_3\text{NCH}_2\text{CH}_2\text{NH}_3)_{0.5}\text{CoPO}_4$  with DFT and GIS frameworks [2,3],  $\text{NaZnPO}_4$  with ABW [4],  $\text{Na}_6(\text{ZnPO}_4)_6 \cdot 8\text{H}_2\text{O}$  with SOD [5,6], or  $\text{Na}_{67}(\text{tma})_{12}\text{Zn}_8(\text{ZnPO}_4)_{96} \cdot 192\text{H}_2\text{O}$  (tma: tetramethyl ammonium cation) with FAU structure [7] (three-capital-letters above are framework-type codes of zeolite structures [8]). However, thermodynamic data for these materials, which provide insight into fundamental

structure–stability relations and which can guide synthesis, are unavailable. Therefore, this study addresses energetics of some inorganic zinc phosphate frameworks,  $\text{NaZnPO}_4$ ,  $\text{NaH}(\text{ZnPO}_4)_2$ , a chiral framework— $\text{NaZnPO}_4 \cdot \text{H}_2\text{O}$ , and a SOD framework— $\text{Na}_6(\text{ZnPO}_4)_6 \cdot 8\text{H}_2\text{O}$  (or  $\text{NaZnPO}_4 \cdot \frac{4}{3}\text{H}_2\text{O}$ ) and its cobalt-substituted analogous ( $\text{NaCo}_x\text{Zn}_{1-x}\text{PO}_4 \cdot \frac{4}{3}\text{H}_2\text{O}$ ,  $x = 0.1, 0.2, 0.3$ ).

All compounds in this study have frameworks constructed by  $\text{TO}_4$  tetrahedra sharing corners ( $T = \text{P}, \text{Zn}, \text{or Co}$ ).  $\alpha$ - $\text{NaZnPO}_4$ , the low-temperature phase of anhydrous sodium zinc phosphate, has the beryllonite structure and crystallizes in the space group  $P2_1/n$  [9–11].  $\alpha$ - $\text{NaZnPO}_4$  undergoes a reversible transformation to  $\beta$ - $\text{NaZnPO}_4$  at about 1160 K [11]. High temperature X-ray diffraction (XRD) reveals that  $\beta$ - $\text{NaZnPO}_4$  crystallizes in the space group  $P6_3$  with the kalsilite structure. Recently,  $\text{NaZnPO}_4$  with ABW zeolite framework (space group  $P2_1/n$ ) has been found from hydrothermal synthesis [4].

When half of the sodium in  $\text{NaZnPO}_4$  is replaced by hydrogen,  $\text{NaH}(\text{ZnPO}_4)_2$  is formed. It crystallizes in the triclinic space group  $P-1$  with a layer structure, in which zinc phosphate layers are held together by hydrogen bonds

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of  $\text{PO}_3\text{OH}$  groups and by interlayer bonding with  $\text{Na}^+$  ions located between layers [12–14].  $\text{NaH}(\text{ZnPO}_4)_2$  decomposes with loss of water at 548 K and becomes amorphous [14].

The chiral framework  $\text{NaZnPO}_4 \cdot \text{H}_2\text{O}$  crystallizes in the  $P6_122$  or the  $P6_522$  space group with  $\text{Na}^+$  ions and  $\text{H}_2\text{O}$  molecules disordered in pear-shaped cavities in the zinc phosphate framework [15].  $\text{NaZnPO}_4 \cdot \frac{4}{3}\text{H}_2\text{O}$  and its cobalt-substituted analogous,  $\text{NaCo}_x\text{Zn}_{1-x}\text{PO}_4 \cdot \frac{4}{3}\text{H}_2\text{O}$ , are isostructural with sodalite zeolite and crystallize in the  $P-43n$  space group,  $\text{Na}^+$  ions and  $\text{H}_2\text{O}$  molecules reside in the  $\beta$  cages [5,6,16]. However, unlike many aluminosilicate and aluminophosphate zeolites, these hydrated sodium zinc phosphate frameworks convert to denser structures on removing the non-framework water by heating at 423–573 K [6,15]. By differential scanning calorimetry (DSC) and high temperature oxide melt solution calorimetry, the enthalpy of the  $\alpha$ – $\beta$  transformation of  $\text{NaZnPO}_4$  and enthalpies of formation of above compounds are determined in this study. Energetic roles of water or hydroxyl groups, and of cobalt compared to zinc in tetrahedral sites are discussed based on the new enthalpy data.

## 2. Experimental methods

### 2.1. Sample preparation

Except for  $\alpha$ - $\text{NaZnPO}_4$ , other samples in this study were prepared by soft chemistry methods. Chemicals used in syntheses are listed in Table 1. The preparation of  $\text{NaZnPO}_4 \cdot \frac{4}{3}\text{H}_2\text{O}$  followed the method described by Gier and Stucky [5], and that of  $\text{NaH}(\text{ZnPO}_4)_2$  followed Gier et al. [13]. In order to produce  $\text{NaZnPO}_4 \cdot \text{H}_2\text{O}$ , a milky solution was prepared by stirring a mixture of 34 mL of 2 M NaOH (68 mmol) and 1.22 g ZnO (15 mmol) for several hours. Then 2.5 mL of 85%  $\text{H}_3\text{PO}_4$  (39 mmol) was added dropwise, the reaction mixture first turned to a thick gel and then became liquid with heat released. This was continuously stirred and heated at 343 K overnight. Crystalline product of  $\text{NaZnPO}_4 \cdot \text{H}_2\text{O}$  was recovered under vacuum filtration, then washed with deionized water and dried at 383 K.

$\alpha$ - $\text{NaZnPO}_4$  was obtained by heating  $\text{NaZnPO}_4 \cdot \text{H}_2\text{O}$  at 573 K to remove water, then palletizing and annealing in a

muffle furnace at 1123 K for 1 day and cooling in the furnace to room temperature.

Cobalt substituted sodium zinc phosphates with sodalite structure were prepared by the same method used for producing the end member  $\text{NaZnPO}_4 \cdot \frac{4}{3}\text{H}_2\text{O}$  [5], but appropriate amounts of  $\text{Zn}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$  were replaced by  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  to produce samples with desired composition  $\text{NaCo}_x\text{Zn}_{1-x}\text{PO}_4 \cdot \frac{4}{3}\text{H}_2\text{O}$  ( $x = 0.1, 0.2, 0.3$ ). A small amount (about 1–2 mg) of  $\text{NaZnPO}_4 \cdot \frac{4}{3}\text{H}_2\text{O}$  was used as seed crystals for the preparation of  $\text{NaCo}_{0.1}\text{Zn}_{0.9}\text{PO}_4 \cdot \frac{4}{3}\text{H}_2\text{O}$ . Then,  $\text{NaCo}_{0.1}\text{Zn}_{0.9}\text{PO}_4 \cdot \frac{4}{3}\text{H}_2\text{O}$  was used as a seed for the synthesis of  $\text{NaCo}_{0.2}\text{Zn}_{0.8}\text{PO}_4 \cdot \frac{4}{3}\text{H}_2\text{O}$  and  $\text{NaCo}_{0.3}\text{Zn}_{0.7}\text{PO}_4 \cdot \frac{4}{3}\text{H}_2\text{O}$ . We found the presence of seeds in synthesis processes was helpful in competing for the formation of the sodalite phase against a hexagonal phase described elsewhere [16,17]. The content of cobalt in zinc phosphate sodalite was limited to  $x \leq 0.3$  in this study because samples with higher cobalt substitution could not be isolated as pure phases.

$\text{NaZnPO}_4 \cdot \text{H}_2\text{O}$  is somewhat hygroscopic, so it was kept in an argon glovebox after drying at 383 K. Other samples were kept in sealed vials in a desiccator containing  $\text{CaCl}_2$ .

### 2.2. Sample characterization

Powder XRD patterns were obtained on a Scintag PAD-V diffractometer operated at 45 kV and 40 mA with  $\text{CuK}\alpha$  radiation. Data were collected from  $10^\circ$  to  $60^\circ$  of  $2\theta$  with a step size of  $0.02^\circ$  and dwell time of 1 s for zinc phosphate samples and 1.5–2 s for cobalt substituted samples. Quartz was used as an external standard for diffractometer calibration. Powder simulation patterns from the ICSD database [18] were used as references for phase identification. Lattice parameters of zinc phosphate samples were calculated from the XRD patterns using JADE software [19]. The Rietveld method [20,21] was applied to the refined XRD data of samples with sodalite structure ( $\text{NaCo}_x\text{Zn}_{1-x}\text{PO}_4 \cdot \frac{4}{3}\text{H}_2\text{O}$ ,  $x = 0, 0.1, 0.2, 0.3$ ). Full Rietveld refinements were completed by using the EXP-GUI/GSAS software package [22,23]. Atomic coordinates of  $\text{Na}_6[\text{Co}_{0.1}\text{Zn}_{0.9}\text{PO}_4]_6 \cdot 8\text{H}_2\text{O}$  [16] were used as the initial model of these refinements. Ratios of Co/Zn were set as the nominal compositions for refinements. The lattice parameters, atomic displacement of oxygen and sodium, peak profile parameters, and scale factors were allowed to vary freely in all refinements.

Chemical compositions of samples were determined by combination of thermogravimetric analysis (TGA) for water content (see below) and electron microprobe or inductively coupled plasma-optical emissions spectroscopy (ICP-OES) analysis.

A Cameca SX-100 electron microprobe was used for quantitative determination of Co, Zn, and P in  $\alpha$ - $\text{NaZnPO}_4$ ,  $\text{NaZnPO}_4 \cdot n\text{H}_2\text{O}$ , and  $\text{NaCo}_x\text{Zn}_{1-x}\text{PO}_4 \cdot \frac{4}{3}\text{H}_2\text{O}$  samples. Samples of hydrate compounds were heated at 773 K to remove water before making pellets for microprobe analysis. These pellets were annealed at 1223 K

Table 1  
Source of chemicals used in syntheses

| Chemical   | Purity              | Supplier          |
|--|---------------------|-------------------|
| ZnO  | 99.99%              | Aldrich           |
| $\text{Zn}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ | 99% Metals basis    | Alfa Aesar        |
| $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ | >99% (Assay)        | Fluka             |
| NaOH   | $\geq 97\%$ (Assay) | EM Science        |
| NaBr   | 99% (Assay)         | EM Science        |
| $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$   | 100.2% (Assay)      | Fisher Scientific |
| $\text{H}_3\text{PO}_4$                              | $\geq 85\%$ (Assay) | Fisher Scientific |

overnight and then polished. Zinc metal, cobalt metal, and apatite were used as standards for Zn, Co, and P, respectively.

$\text{NaH}(\text{ZnPO}_4)_2$  decomposed on heating, liberating water at about 550 K [14]. The residue melted when heated to 973 K. Since a homogeneous sample for microprobe analysis could not be obtained when annealing this sample below its melting point, its chemical composition was determined by ICP-OES analysis at Galbraith Laboratory (Knoxville, TN).

### 2.3. Thermogravimetric analysis and differential scanning calorimetry

Water content in samples and appropriate temperature for drying them were determined from TGA and DSC carried on a Netzsch STA 449 instrument. About 50 mg of each sample was palletized and heated in platinum crucibles from 303 to 1327 K at 10 K/min under argon flow of  $40 \text{ cm}^3/\text{min}$ . DSC was also used to study enthalpy of the  $\alpha$ - $\beta$  phase transition of  $\text{NaZnPO}_4$ . About 50 mg of  $\text{NaZnPO}_4$  was heated and cooled between 873 and 1233 K under the same conditions on a Netzsch DSC 404 unit. Heat flow calibration was based on heat capacity of a transparent corundum disk run in the same platinum crucible.

### 2.4. High temperature oxide melt solution calorimetry

Enthalpies of formation of compounds in this study were determined by drop solution calorimetry of samples and their component oxides in sodium molybdate melt ( $3\text{Na}_2\text{O} \cdot 4\text{MoO}_3$ ) at 973 K. A custom built Tian–Calvet twin calorimeter described elsewhere [24,25] was used. Enthalpy of drop solution was measured when a pellet of about 5 or 15 mg sample was dropped from room temperature into the molten solvent in the hot calorimeter. The enthalpy of drop solution ( $\Delta H_{\text{ds}}$ ) includes the enthalpy of heating the sample from room temperature to calorimeter temperature (heat content), the enthalpy of any phase transition, decomposition, or evaporation of water that occurs on heating, and the enthalpy of dissolving the sample in the solvent at the calorimeter temperature. The difference in the enthalpy of drop solution of component oxides and compound gives the enthalpy of formation at 298 K.

Drop solution experiments were conducted while argon gas was bubbled through the solvent continuously at a rate of  $5 \text{ cm}^3/\text{min}$  to facilitate the dissolution as well as to prevent any local . We note that Co exists as Co(II) in the solvent [25,26]. Argon at  $50 \text{ cm}^3/\text{min}$  was flushed steadily above the solvent to sweep water vapor out of the calorimeter. These procedures have been used for over a decade and have become standard in our laboratory [24–26]. All samples were easy to handle in air, except  $\text{NaZnPO}_4 \cdot \text{H}_2\text{O}$  which is hygroscopic. Therefore, pellets of  $\text{NaZnPO}_4 \cdot \text{H}_2\text{O}$ , after being dried at 383 K, were kept in an

argon glovebox. They were taken out of the glovebox, then weighted and dropped directly into the high temperature calorimeter. The maximum time each pellet was exposed to air was less than 2 min. Eight measurements were performed for each sample. Calibration was achieved by dropping 5 and 15 mg pellets of corundum (Aldrich, 99.99%  $\text{Al}_2\text{O}_3$ ; heated overnight at 1773 K) from room temperature into empty platinum crucibles in the calorimeter as described in previous work [25].

## 3. Results and discussion

### 3.1. Characterization of samples

XRD patterns of all sodium zinc phosphate samples showed they are pure phases (Fig. 1(A)). Their calculated lattice parameters are summarized in Table 2, they are very close to those from single crystals [6,10,14,15].

P/Zn ratios of  $\alpha$ - $\text{NaZnPO}_4$ ,  $\text{NaZnPO}_4 \cdot \text{H}_2\text{O}$ , and  $\text{NaZnPO}_4 \cdot \frac{4}{3}\text{H}_2\text{O}$  samples from microprobe analysis are close to theoretical values of  $1.01 \pm 0.01$ ,  $1.01 \pm 0.02$ , and  $1.00 \pm 0.02$ , respectively (averages and standard deviations from 8 to 12 analyzed points). TGA experiments showed no water in  $\alpha$ - $\text{NaZnPO}_4$  sample. The weight losses of  $\text{NaZnPO}_4 \cdot \text{H}_2\text{O}$  and  $\text{NaZnPO}_4 \cdot \frac{4}{3}\text{H}_2\text{O}$  from TGA were 9.0% and 11.5%, respectively, consistent with the theoretical 8.95% and 11.58%. Uncertainties of all TGA experiments in this study were estimated to be  $\pm 0.1\%$ . Therefore, chemical compositions of these samples are taken as their ideal stoichiometry.

As-synthesized  $\text{NaH}(\text{ZnPO}_4)_2$ , after initial drying at 383 K, showed 3.0% weight loss on TGA. That is somewhat higher than the theoretical 2.61%. The TGA trace revealed the sample started losing water around 523 K, but 90% of the weight loss occurred at 670–790 K (see Fig. 2). Drying at 623 K for 36 h produced a sample with the same XRD patterns as the initial, but water content was 2.6%, consistent with the theoretical values. XRD pattern and lattice parameters of this annealed sample are reported in Fig. 1 and Table 2, respectively. This sample was used for high temperature drop solution experiments. Atomic ratios of this sample determined from ICP-OES were close to its stoichiometric values of Na/Zn/P = 1/1.96/1.97. Based on those results, thermodynamic data for all sodium zinc phosphate samples are calculated and discussed in terms of their ideal stoichiometry.

XRD patterns of cobalt-substituted samples showed they are pure sodalite phases. Observed, calculated, and difference patterns of the Rietveld refinement of the  $\text{NaCo}_{0.3}\text{Zn}_{0.7}\text{PO}_4 \cdot \frac{4}{3}\text{H}_2\text{O}$  sample are presented in Fig. 1(B). Final refinement results of cobalt substituted sodalite samples are summarized in Table 3. The substitution of Co(II) into zinc tetrahedral sites increases the lattice parameters of sodalite structures slightly although the ionic radius of Co(II) in tetrahedral coordination is slightly smaller than that of Zn(II) (0.72 and 0.74 Å, respectively [27]). This is consistent with the smaller lattice

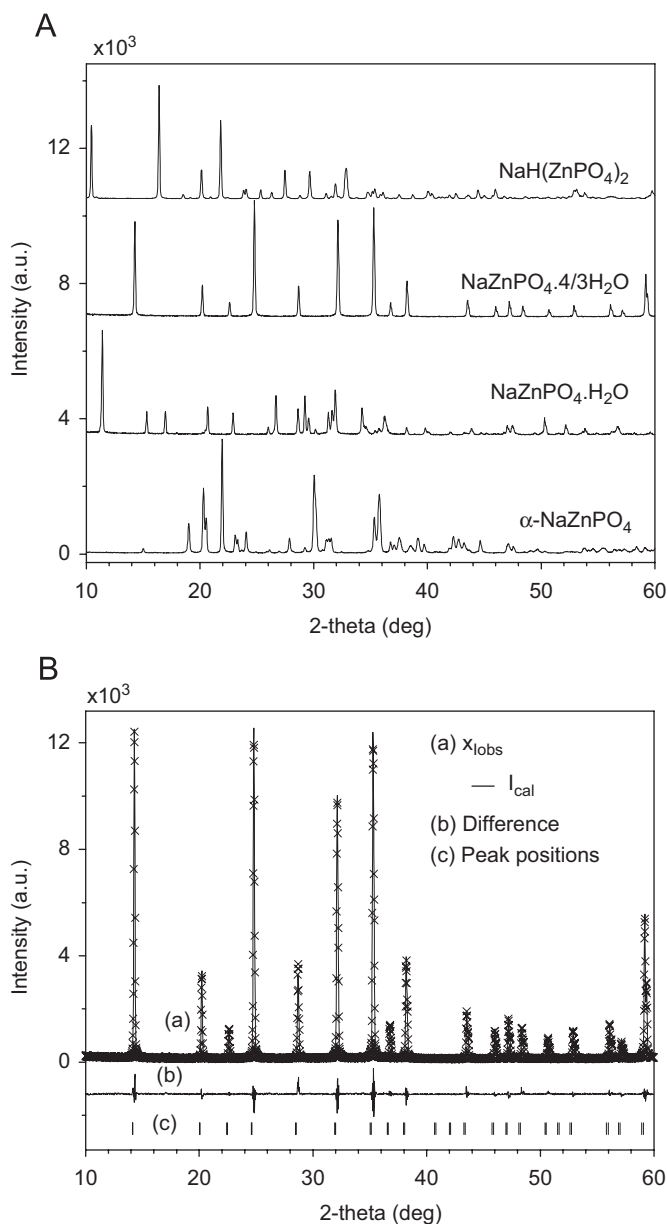


Fig. 1. (A) XRD patterns of sodium zinc phosphate samples. (B) Observed, calculated, difference patterns, and Bragg peak positions of the Rietveld refinement of  $\text{NaCo}_{0.3}\text{Zn}_{0.7}\text{PO}_4 \cdot 4/3\text{H}_2\text{O}$  sample.

Table 2

Summary of crystallographic data for sodium zinc phosphate samples in this study

|                | $\alpha\text{-NaZnPO}_4$ | $\text{NaH}(\text{ZnPO}_4)_2$ | $\text{NaZnPO}_4 \cdot \text{H}_2\text{O}$ | $\text{NaZnPO}_4 \cdot 4/3\text{H}_2\text{O}$ (*) |
|----------------|--------------------------|-------------------------------|--|---|
| Space group    | $P2_1/n$                 | $P-1$                         | $P6_122$                                   | $P-43n$   |
| $a$ (Å)        | 8.620(5)                 | 8.595(4)                      | 10.470(2)                                  | 8.8522(9)   |
| $b$ (Å)        | 8.106(5)                 | 8.777(2)                      | 10.470(2)                                  | 8.8522(9)   |
| $c$ (Å)        | 15.063(5)                | 5.100(3)                      | 15.048(3)                                  | 8.8522(9)   |
| $\alpha$ (deg) | 90                       | 100.4475(6)                   | 90   | 90  |
| $\beta$ (deg)  | 90.08(4)                 | 105.773(4)                    | 90   | 90  |
| $\gamma$ (deg) | 90                       | 96.931(3)                     | 120  | 90  |

Numbers in parentheses are estimated standard deviations from JADE calculation or GSAS (\*) refinement.

parameters of  $\text{Na}_6(\text{ZnPO}_4)_6 \cdot 8\text{H}_2\text{O}$  compared to that of  $\text{Na}_6(\text{Co}_{0.1}\text{Zn}_{0.9}\text{PO}_4)_6 \cdot 8\text{H}_2\text{O}$  observed elsewhere [6,16]. This anomalous behavior was also found in sodium gallosilicate and sodium aluminosilicate with sodalite structure [28,29], that is, the unit cell of gallosilicate is smaller than that of aluminosilicate, even though the ionic radius of  $\text{Ga}^{3+}$  is bigger than that of  $\text{Al}^{3+}$ . This behavior appears to be related to variations in the intertetrahedral angles of the framework [28,29].

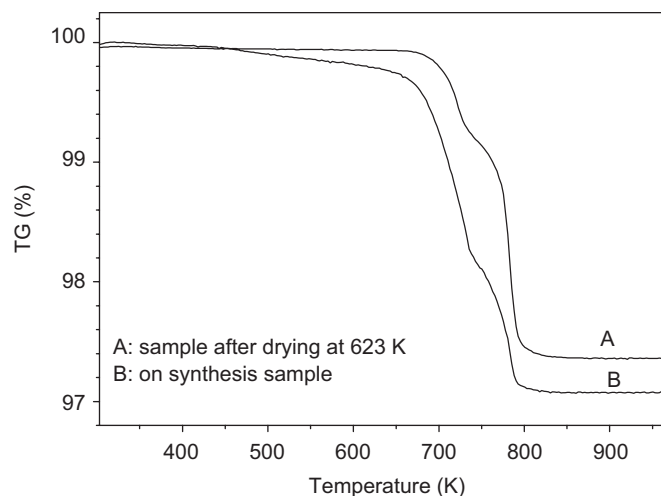


Fig. 2. TGA traces of  $\text{NaH}(\text{ZnPO}_4)_2$  samples.

Table 3

Summary of Rietveld refinement of  $\text{NaCo}_x\text{Zn}_{1-x}\text{PO}_4 \cdot 4/3\text{H}_2\text{O}$  samples

| $X$         | 0.0       | 0.1       | 0.2       | 0.3       |
|-------------|-----------|-----------|-----------|-----------|
| Space group | $P-43n$   | $P-43n$   | $P-43n$   | $P-43n$   |
| $a$ (Å)     | 8.8522(9) | 8.8567(7) | 8.8587(9) | 8.8614(7) |
| $\chi^2$    | 2.500     | 2.659     | 2.815     | 2.304     |
| $R_p$ (%)   | 8.13      | 8.69      | 8.35      | 7.87      |
| $wR_p$ (%)  | 6.37      | 6.57      | 6.38      | 6.11      |

Numbers in parentheses are estimated standard deviations from GSAS refinement. There are 2499 observations and 17 variables in each refinement.

Table 4

Chemical composition from microprobe analysis and water content from TGA of  $\text{NaCo}_x\text{Zn}_{1-x}\text{PO}_4 \cdot \frac{4}{3}\text{H}_2\text{O}$  samples

| Samples (nominal composition)   | Atomic ratios |              | Water content (wt%) |             |
|---|---------------|--------------|---------------------|-------------|
|   | P/(Co + Zn)   | Co/(Co + Zn) | Experimental        | Theoretical |
| $\text{NaCo}_{0.1}\text{Zn}_{0.9}\text{PO}_4 \cdot \frac{4}{3}\text{H}_2\text{O}$ | 1.00(1)       | 0.102(2)     | $11.7 \pm 0.1$      | 11.62       |
| $\text{NaCo}_{0.2}\text{Zn}_{0.8}\text{PO}_4 \cdot \frac{4}{3}\text{H}_2\text{O}$ | 1.011(7)      | 0.202(3)     | $11.7 \pm 0.1$      | 11.66       |
| $\text{NaCo}_{0.3}\text{Zn}_{0.7}\text{PO}_4 \cdot \frac{4}{3}\text{H}_2\text{O}$ | 1.004(6)      | 0.303(5)     | $11.7 \pm 0.1$      | 11.69       |

Numbers in parentheses are standard deviations from 10–12 analyzed points.

Table 5

Summary of thermodynamic data used in this study

| Compound   | $\Delta H_{\text{ds}}$ (kJ/mol) | $\Delta H_{\text{f-ox, 298 K}}$ (kJ/mol) | $\Delta H_{\text{f, 298 K}}^{\circ}$ (kJ/mol) |
|--|---------------------------------|--|---|
| $\text{Na}_2\text{O}$ (cr)   | $-217.56 \pm 4.25$ [30]         | –  | $-414.8 \pm 0.3$ [33]                         |
| $\text{CoO}$ (cr)  | $15.35 \pm 0.46$ [26]           | –  | $-237.9 \pm 1.3$ [33]                         |
| $\text{ZnO}$ (cr)  | $17.2 \pm 0.3$ [31]             | –  | $-350.5 \pm 0.3$ [33]                         |
| $\text{P}_2\text{O}_5$ (cr)  | $-164.60 \pm 0.85$ [32]         | –  | $-1504.9 \pm 0.5$ [33]                        |
| $\text{H}_2\text{O}$ (l)   | 68.95*                          | –  | $-285.83 \pm 0.04$ [33]                       |
| $\alpha\text{-NaZnPO}_4$ (cr)  | $165.74 \pm 1.30$               | $-339.6 \pm 2.6$                         | $-1649.9 \pm 2.6$                             |
| $\text{NaH}(\text{ZnPO}_4)_2$ (cr)   | $310.96 \pm 1.20$               | $-515.5 \pm 2.7$                         | $-3071.7 \pm 2.8$                             |
| $\text{NaZnPO}_4 \cdot \text{H}_2\text{O}$ (cr)  | $241.98 \pm 0.85$               | $-346.9 \pm 2.4$                         | $-1943.1 \pm 2.4$                             |
| $\text{NaZnPO}_4 \cdot \frac{4}{3}\text{H}_2\text{O}$ (cr)                             | $262.74 \pm 1.06$               | $-344.7 \pm 2.4$                         | $-2036.1 \pm 2.5$                             |
| $\text{NaCo}_{0.1}\text{Zn}_{0.9}\text{PO}_4 \cdot \frac{4}{3}\text{H}_2\text{O}$ (cr) | $262.68 \pm 1.33$               | $-344.8 \pm 2.6$                         | $-2025.0 \pm 2.6$                             |
| $\text{NaCo}_{0.2}\text{Zn}_{0.8}\text{PO}_4 \cdot \frac{4}{3}\text{H}_2\text{O}$ (cr) | $261.40 \pm 1.38$               | $-343.7 \pm 2.6$                         | $-2012.6 \pm 2.6$                             |
| $\text{NaCo}_{0.3}\text{Zn}_{0.7}\text{PO}_4 \cdot \frac{4}{3}\text{H}_2\text{O}$ (cr) | $261.59 \pm 0.89$               | $-344.1 \pm 2.4$                         | $-2001.8 \pm 2.4$                             |

$\Delta H_{\text{ds}}$ , enthalpy of drop solution in sodium molybdate at 973 K;  $\Delta H_{\text{f-ox, 298 K}}$ , enthalpy of formation from oxides; and  $\Delta H_{\text{f, 298 K}}^{\circ}$ , standard enthalpy of formation (enthalpy of formation from elements). Values without cited reference are from this work.

\* This is enthalpy of the reaction:  $\text{H}_2\text{O}$  (l, 298 K)  $\rightarrow$   $\text{H}_2\text{O}$  (g, 973 K)  $\Delta H_{\text{ds}}(\text{H}_2\text{O})$

It is calculated from the following equation:

$$\Delta H_{\text{ds}}(\text{H}_2\text{O}) = (\Delta H_{\text{f, H}_2\text{O, g, 298 K}}^{\circ} - \Delta H_{\text{f, H}_2\text{O, l, 298 K}}^{\circ}) + \int_{298}^{973} C_{\text{p}(\text{H}_2\text{O, g})} dT.$$

Data for this calculation were taken from Robie and Hemingway [33], its uncertainty is discarded for convenience.

Water content determined from TGA and chemical composition from microprobe analysis of the cobalt-substituted samples are presented in Table 4. Atomic ratios of P/(Co + Zn) are close to 1, of Co/(Co + Zn) are close to the nominal compositions, and water contents are consistent with the theoretical values. Thermodynamic data of these samples are calculated based on their nominal compositions.

### 3.2. Enthalpies of formation of sodium zinc phosphate and cobalt substituted frameworks

All samples dissolved quickly in sodium molybdate solvent at 973 K with return to baseline in about 30–40 min and produced consistent results. Values of enthalpies of drop solution ( $\Delta H_{\text{ds}}$ ) of all compounds are in Table 5 (uncertainties of these experimental values are two standard deviations of the mean).

Thermodynamic cycle A in Table 6 with appropriated  $x$  and  $n$  values for  $\text{NaCo}_x\text{Zn}_{1-x}\text{PO}_4 \cdot n\text{H}_2\text{O}$  was used to calculate enthalpies of formation from oxides ( $\Delta H_{\text{f-ox, 298 K}}$ ) of all compounds in this study, except  $\text{NaH}(\text{ZnPO}_4)_2$ . Enthalpy of formation from oxides of  $\text{NaH}(\text{ZnPO}_4)_2$  was calculated following cycle B in Table 6. Similarly, their standard enthalpies of formation ( $\Delta H_{\text{f, 298 K}}^{\circ}$ ) was calculated using Eqs. (1) and (2). All auxiliary thermodynamic data needed for those calculations are in Tables 5. Results are summarized in Table 5. Propagation of errors from Miller and Miller [34] was used to estimate uncertainties of computed thermodynamic data.

$$\begin{aligned} \Delta H_{\text{f, 298 K}}^{\circ}(\text{NaCo}_x\text{Zn}_{1-x}\text{PO}_4 \cdot n\text{H}_2\text{O}) &= \Delta H_{\text{f-ox, 298 K}}(\text{NaCo}_x\text{Zn}_{1-x}\text{PO}_4 \cdot n\text{H}_2\text{O}) \\ &+ \frac{1}{2}\Delta H_{\text{f, 298 K}}^{\circ}(\text{Na}_2\text{O}) + x\Delta H_{\text{f, 298 K}}^{\circ}(\text{CoO}) \\ &+ (1-x)\Delta H_{\text{f, 298 K}}^{\circ}(\text{ZnO}) + \frac{1}{2}\Delta H_{\text{f, 298 K}}^{\circ}(\text{P}_2\text{O}_5) \\ &+ n\Delta H_{\text{f, 298 K}}^{\circ}(\text{H}_2\text{O}), \end{aligned} \quad (1)$$

Table 6  
Thermodynamic cycles used for the calculation of enthalpies of formation from oxides

|   |  |
|---|--|
| Cycle A: Thermodynamic cycle for the enthalpies of formation from oxides of $\text{NaCo}_x\text{Zn}_{1-x}\text{PO}_4 \cdot n\text{H}_2\text{O}$   |  |
| $\text{Na}_2\text{O}$ (cr, 298 K) $\rightarrow$ $\text{Na}_2\text{O}$ (sol, 973 K)  | $\Delta H_{\text{ds}}(\text{Na}_2\text{O})$  |
| $\text{CoO}$ (cr, 298 K) $\rightarrow$ $\text{CoO}$ (sol, 973 K)  | $\Delta H_{\text{ds}}(\text{CoO})$   |
| $\text{ZnO}$ (cr, 298 K) $\rightarrow$ $\text{ZnO}$ (sol, 973 K)  | $\Delta H_{\text{ds}}(\text{ZnO})$   |
| $\text{P}_2\text{O}_5$ (cr, 298 K) $\rightarrow$ $\text{P}_2\text{O}_5$ (sol, 973 K)  | $\Delta H_{\text{ds}}(\text{P}_2\text{O}_5)$   |
| $\text{H}_2\text{O}$ (l, 298 K) $\rightarrow$ $\text{H}_2\text{O}$ (g, 973 K)   | $\Delta H_{\text{ds}}(\text{H}_2\text{O})$   |
| $\text{NaCo}_x\text{Zn}_{1-x}\text{PO}_4 \cdot n\text{H}_2\text{O}$ (cr, 298 K) $\rightarrow$ $\frac{1}{2}\text{Na}_2\text{O}$ (sol, 973 K) + $x\text{CoO}$ (sol, 973 K) + $(1-x)\text{ZnO}$ (sol, 973 K) + $\frac{1}{2}\text{P}_2\text{O}_5$ (sol, 973 K) + $n\text{H}_2\text{O}$ (g, 973 K)*  | $\Delta H_{\text{ds}}(\text{NaCo}_x\text{Zn}_{1-x}\text{PO}_4 \cdot n\text{H}_2\text{O})$          |
| $\frac{1}{2}\text{Na}_2\text{O}$ (cr, 298 K) + $x\text{CoO}$ (cr, 298 K) + $(1-x)\text{ZnO}$ (cr, 298 K) + $\frac{1}{2}\text{P}_2\text{O}_5$ (cr, 298 K) + $n\text{H}_2\text{O}$ (l, 298 K) $\rightarrow$   | $\Delta H_{\text{f-ox, 298 K}}(\text{NaCo}_x\text{Zn}_{1-x}\text{PO}_4 \cdot n\text{H}_2\text{O})$ |
| $\Delta H_{\text{f-ox, 298 K}}(\text{NaCo}_x\text{Zn}_{1-x}\text{PO}_4 \cdot n\text{H}_2\text{O}) = \frac{1}{2}\Delta H_{\text{ds}}(\text{Na}_2\text{O}) + x\Delta H_{\text{ds}}(\text{CoO}) + (1-x)\Delta H_{\text{ds}}(\text{ZnO}) + \frac{1}{2}\Delta H_{\text{ds}}(\text{P}_2\text{O}_5) + n\Delta H(\text{H}_2\text{O}) - \Delta H_{\text{ds}}(\text{NaCo}_x\text{Zn}_{1-x}\text{PO}_4 \cdot n\text{H}_2\text{O})$ |  |
| Cycle B: Thermodynamic cycle for the enthalpy of formation from oxides of $\text{NaH}(\text{ZnPO}_4)_2$   |  |
| $\text{Na}_2\text{O}$ (cr, 298 K) $\rightarrow$ $\text{Na}_2\text{O}$ (sol, 973 K)  | $\Delta H_{\text{ds}}(\text{Na}_2\text{O})$  |
| $\text{ZnO}$ (cr, 298 K) $\rightarrow$ $\text{ZnO}$ (sol, 973 K)  | $\Delta H_{\text{ds}}(\text{ZnO})$   |
| $\text{P}_2\text{O}_5$ (cr, 298 K) $\rightarrow$ $\text{P}_2\text{O}_5$ (sol, 973 K)  | $\Delta H_{\text{ds}}(\text{P}_2\text{O}_5)$   |
| $\text{H}_2\text{O}$ (l, 298 K) $\rightarrow$ $\text{H}_2\text{O}$ (g, 973 K)   | $\Delta H_{\text{ds}}(\text{H}_2\text{O})$   |
| $\text{NaH}(\text{ZnPO}_4)_2$ (cr, 298 K) $\rightarrow$ $\frac{1}{2}\text{Na}_2\text{O}$ (sol, 973 K) + $2\text{ZnO}$ (sol, 973 K) + $\text{P}_2\text{O}_5$ (sol, 973 K) + $\frac{1}{2}\text{H}_2\text{O}$ (g, 973 K)*  | $\Delta H_{\text{ds}}(\text{NaH}(\text{ZnPO}_4)_2)$  |
| $\frac{1}{2}\text{Na}_2\text{O}$ (cr, 298 K) + $2\text{ZnO}$ (cr, 298 K) + $\text{P}_2\text{O}_5$ (cr, 298 K) + $\frac{1}{2}\text{H}_2\text{O}$ (l, 298 K) $\rightarrow$ $\text{NaH}(\text{ZnPO}_4)_2$ (cr, 298 K)  | $\Delta H_{\text{f-ox, 298 K}}(\text{NaH}(\text{ZnPO}_4)_2)$                                       |
| $\Delta H_{\text{f-ox, 298 K}}(\text{NaH}(\text{ZnPO}_4)_2) = \frac{1}{2}\Delta H_{\text{ds}}(\text{Na}_2\text{O}) + 2\Delta H_{\text{ds}}(\text{ZnO}) + \Delta H_{\text{ds}}(\text{P}_2\text{O}_5) + \frac{1}{2}\Delta H(\text{H}_2\text{O}) - \Delta H_{\text{ds}}(\text{NaH}(\text{ZnPO}_4)_2)$  |  |

\*Previous studies showed that water evaporates out of the solvent in high temperature drop solution experiments [25].

$$\begin{aligned} \Delta H_{\text{f, 298 K}}^{\circ}(\text{NaH}(\text{ZnPO}_4)_2) &= \Delta H_{\text{f-ox, 298 K}}(\text{NaH}(\text{ZnPO}_4)_2) + \frac{1}{2}\Delta H_{\text{f, 298 K}}^{\circ}(\text{Na}_2\text{O}) \\ &+ 2\Delta H_{\text{f, 298 K}}^{\circ}(\text{ZnO}) \\ &+ \Delta H_{\text{f, 298 K}}^{\circ}(\text{P}_2\text{O}_5) + \frac{1}{2}\Delta H_{\text{f, 298 K}}^{\circ}(\text{H}_2\text{O}). \end{aligned} \quad (2)$$

### 3.3. $\alpha$ - $\beta$ phase transition in $\text{NaZnPO}_4$

The DSC trace on heating  $\alpha$ - $\text{NaZnPO}_4$  showed two endothermic peaks at about 1160 and 1303 K (peak temperature, instrumental uncertainty is about  $\pm 1$  K). The first peak is associated with the reversible  $\alpha$ - $\beta$  phase transition discussed elsewhere [11]. The second peak accompanies the melting of  $\text{NaZnPO}_4$ , which was easy to detect after the DSC experiment.

Examining the reversible phase transition of  $\text{NaZnPO}_4$ , the heating showed endothermic peaks at  $1159.7 \pm 0.3$  K (average and standard deviation of three experiments), but cooling displayed exothermic peaks at  $1089.5 \pm 3.7$  K (see Fig. 3). Peaks on heating and cooling were sharp; the difference between onset and end temperatures was about 10 K for both heating and cooling. With the heating and cooling rate applied, these heat effects finished within a minute. Enthalpies of phase transition calculated from the DSC on heating and cooling are very consistent,  $-6.89 \pm 0.09$  kJ/mol and  $6.79 \pm 0.09$  kJ/mol, respectively. Thus the phase transition has some hysteresis, but is complete. The temperature window of the existence of  $\beta$ - $\text{NaZnPO}_4$  is relatively narrow ( $1160 \text{ K} < T < 1303 \text{ K}$ ), and the high-temperature phase reverts completely when cooling. This is consistent with the observation that  $\beta$ - $\text{NaZnPO}_4$  could not be retained when quenching  $\text{NaZnPO}_4$  from 1223 K to room temperature [11].

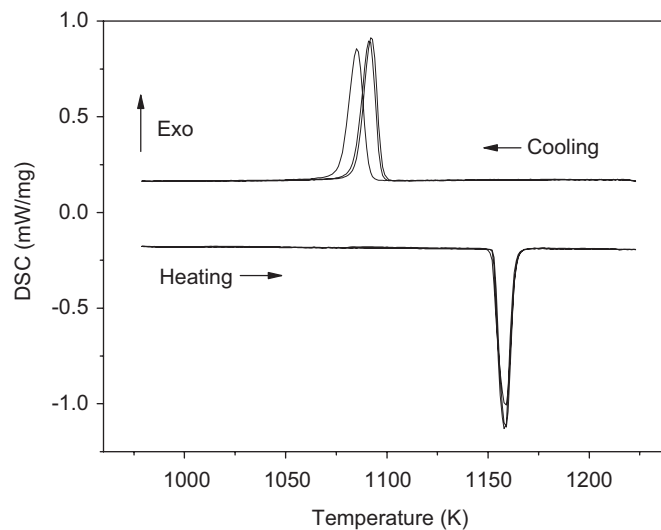


Fig. 3. DSC traces of heating and cooling  $\text{NaZnPO}_4$  through  $\alpha$ - $\beta$  phase transition (three runs).

$\alpha$ - $\text{NaZnPO}_4$  is the stable phase at room temperature. At 1160 K, this phase is about  $6.8 \pm 0.1$  kJ/mol (average from above values) lower in enthalpy than  $\beta$ - $\text{NaZnPO}_4$ . The enthalpy of the  $\alpha$ - $\beta$  phase transition of  $\text{NaZnPO}_4$  is smaller than that of  $\text{NaCoPO}_4$ , possibly because coordinations of Zn and P are retained in this phase transition, but that of Co changes from octahedral to tetrahedral. The entropy change of the reversible phase transition is estimated to be  $\Delta H/T = 5.9 \pm 0.1$  J/mol K at 1160 K.  $\alpha$ - $\text{NaZnPO}_4$ , the low temperature phase, is denser and has lower symmetry than  $\beta$ - $\text{NaZnPO}_4$ , the high-temperature phase. Such relationships are often seen, although not thermodynamically required.

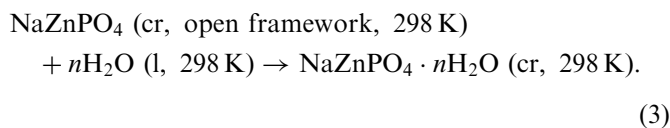
### 3.4. Contribution of water to energetics of sodium zinc phosphates

Of the four sodium zinc phosphate compounds in this study, only  $\alpha$ -NaZnPO<sub>4</sub> does not contain structural water. Water contributes to the structure and energetics of the other three phosphate compounds, NaH(ZnPO<sub>4</sub>)<sub>2</sub>, NaZnPO<sub>4</sub>·H<sub>2</sub>O, and NaZnPO<sub>4</sub>· $\frac{4}{3}$ H<sub>2</sub>O, in different ways. Therefore, they are considered separately.

Although H<sub>2</sub>O is involved in the formation from oxides of NaH(ZnPO<sub>4</sub>)<sub>2</sub> (see reactions in cycle B, Table 6), there are no H<sub>2</sub>O molecules in its structure. H<sub>2</sub>O attaches to PO<sub>4</sub> groups [14] and its formula can be rewritten as Na(Zn<sub>2</sub>(PO<sub>4</sub>)(PO<sub>3</sub>OH)). As already noted [35], PO<sub>3</sub>OH<sup>2-</sup> is a weaker base than PO<sub>4</sub><sup>3-</sup>. Therefore, the presence of PO<sub>3</sub>OH<sup>2-</sup> groups decreases acid–base interaction in NaH(ZnPO<sub>4</sub>)<sub>2</sub> compared to 2NaZnPO<sub>4</sub> (rewritten as Na<sub>2</sub>(ZnPO<sub>4</sub>)<sub>2</sub>). This is reflected in the less-exothermic enthalpy of formation from oxides of NaH(ZnPO<sub>4</sub>)<sub>2</sub> ( $\Delta H_{f-ox, 298 K} = -515.5 \pm 2.7$  kJ/mol, Table 5) compared to that of Na<sub>2</sub>(ZnPO<sub>4</sub>)<sub>2</sub> ( $\Delta H_{f-ox, 298 K} = -679.2 \pm 3.7$  kJ/mol, calculated from Table 5). This result is consistent with the general findings discussed in our previous work [35], the acidic salt is less exothermic in enthalpy of formation from oxides, reflecting weaker acid–base interactions in an acidic compound than in a more basic one.

In NaZnPO<sub>4</sub>·H<sub>2</sub>O and NaZnPO<sub>4</sub>· $\frac{4}{3}$ H<sub>2</sub>O, water exists as molecules located in channels or cages of the zinc phosphate framework [6,15]. The incorporation of water molecules into NaZnPO<sub>4</sub> frameworks decreases their framework densities (FD, number of T atoms in 1000 cm<sup>3</sup>) from 22.8 in  $\alpha$ -NaZnPO<sub>4</sub> and 21.1 in  $\beta$ -NaZnPO<sub>4</sub> [11] to 16.7 and 17.4 in NaZnPO<sub>4</sub>·H<sub>2</sub>O and NaZnPO<sub>4</sub>· $\frac{4}{3}$ H<sub>2</sub>O, respectively, making their FD comparable to those of moderate-density zeolites such as SOD, HEU, AIPO-5, or AIPO-8 [8]. In terms of energetics, enthalpies of formation from oxides of these hydrated compounds are more exothermic than of the most stable phase of sodium zinc phosphate,  $\alpha$ -NaZnPO<sub>4</sub> (see Table 5), reflecting an exothermic interaction between H<sub>2</sub>O molecules and Na<sup>+</sup> ions in the cages and channels.

In order to elucidate the nature of interactions of water and frameworks in these hydrate compounds, enthalpies of interactions between water and zinc phosphate frameworks represented by reaction (3) are considered:



Since hydrated zinc phosphate frameworks collapse when removing water by heating, and such open dehydrated frameworks could not be isolated, neither DSC nor high temperature oxide melt calorimetry could be used to determine enthalpy of reaction (3) directly. Based on general results of energetic studies of zeolitic materials [36–38], relative stabilities of NaZnPO<sub>4</sub> open frameworks

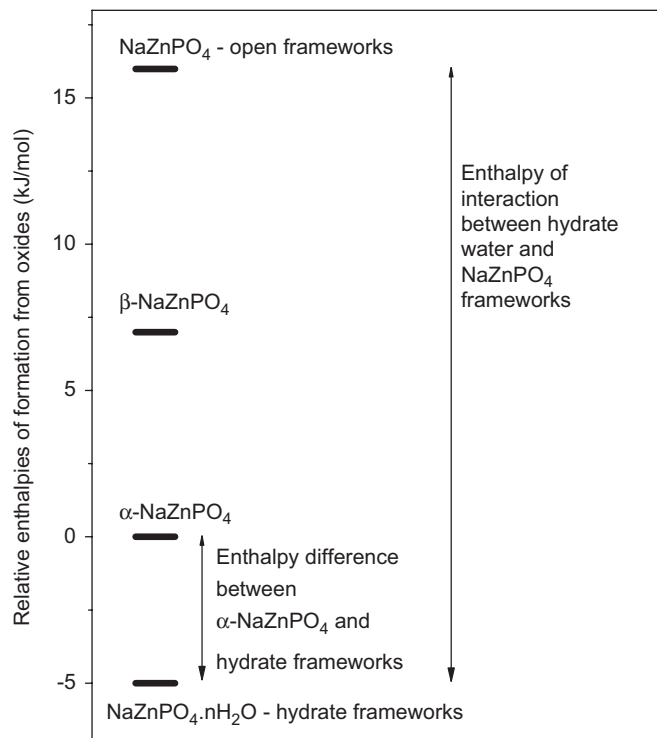


Fig. 4. Schematic diagram of relative stability of NaZnPO<sub>4</sub> dense phases, open frameworks, and hydrated frameworks.

and hydrated frameworks compared to dense phases of NaZnPO<sub>4</sub> are illustrated through the energy scheme in Fig. 4. Enthalpies of interactions between water and frameworks are the sum of the enthalpy difference of  $\alpha$ -NaZnPO<sub>4</sub> and NaZnPO<sub>4</sub>·nH<sub>2</sub>O and the enthalpy difference between  $\alpha$ -NaZnPO<sub>4</sub> and NaZnPO<sub>4</sub> open frameworks (after removing water).

The enthalpy difference between  $\alpha$ -NaZnPO<sub>4</sub> and hydrated frameworks ( $\Delta H_{\text{diff}}$ ) can be derived from their enthalpies of formation as follows:

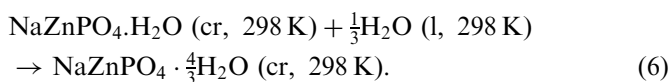
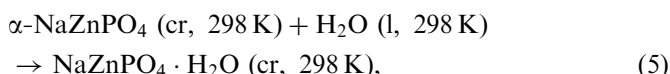
$$\begin{aligned} \Delta H_{\text{diff}} = &\Delta H_{f-ox, 298 K}(\alpha\text{-NaZnPO}_4) \\ &- \Delta H_{f-ox, 298 K}(\text{NaZnPO}_4 \cdot n\text{H}_2\text{O}). \end{aligned} \quad (4)$$

Using the data in Table 5,  $\Delta H_{\text{diff}}$  were calculated to be  $7.3 \pm 2.4$  kJ/mol and  $5.1 \pm 2.4$  kJ/mol for NaZnPO<sub>4</sub>·H<sub>2</sub>O and NaZnPO<sub>4</sub>· $\frac{4}{3}$ H<sub>2</sub>O, respectively. However, it is difficult to find a good way to estimate enthalpy difference between  $\alpha$ -NaZnPO<sub>4</sub> and the hypothetical open framework NaZnPO<sub>4</sub>. Assuming a linear relationship between FD and relative stability of NaZnPO<sub>4</sub> polymorphs, the enthalpy difference between  $\alpha$ -NaZnPO<sub>4</sub> and the hypothetical open frameworks of NaZnPO<sub>4</sub>·H<sub>2</sub>O and NaZnPO<sub>4</sub>· $\frac{4}{3}$ H<sub>2</sub>O can be extrapolated to be 24.4 kJ/mol and 21.6 kJ/mol, respectively. Therefore, enthalpies of interactions between water and NaZnPO<sub>4</sub> frameworks can be estimated to be -31.7 kJ/mol and -26.7 kJ/mol, or -31.7 kJ/mol and -20.0 kJ/mol water for NaZnPO<sub>4</sub>·H<sub>2</sub>O and NaZnPO<sub>4</sub>· $\frac{4}{3}$ H<sub>2</sub>O, respectively. These energies are in the range of those in hydrogen bonds and similar to enthalpies

of hydration in zeolite Y [39], hydrosodalite (6:0:8) [40], and many aluminophosphate zeolite [41].

Generally, when water is a structural component, it affects thermodynamic properties of compounds in different ways depending on their structures. If water exists as molecules in the structure, it stabilizes the compound through solvating a cation or forming extra hydrogen bonds in the structure, leading to a more exothermic enthalpy of formation from oxides. If water appears as a part of component of anion in compounds (acidic salts), acid–base interactions among oxides of compounds are decreased, resulting in a less-exothermic enthalpy of formation from oxides.

Considering relative stability of the two hydrated zinc phosphate structures in this study, enthalpies of following reactions were calculated:



Enthalpies of reactions (5) and (6) are  $-7.3 \pm 1.6$  kJ and  $2.2 \pm 1.4$  kJ, respectively (calculated via enthalpies of drop solution). The data suggest that  $\text{NaZnPO}_4 \cdot \frac{4}{3}\text{H}_2\text{O}$  is metastable compared to  $\text{NaZnPO}_4 \cdot \text{H}_2\text{O}$ , and it is enthalpically unfavorable to incorporate a larger amount of hydrate water into a denser framework of  $\text{NaZnPO}_4 \cdot \frac{4}{3}\text{H}_2\text{O}$  compared to the framework of  $\text{NaZnPO}_4 \cdot \text{H}_2\text{O}$ .

### 3.5. Basicities of ZnO and CoO and energetics of the formation of their phosphates

In a previous study [42], we found acid–base interactions in  $\beta\text{-NaCoPO}_4$  are much stronger than those in nepheline  $\text{NaAlSi}_3\text{O}_8$  (these have frameworks built up from alternating connections of  $\text{CoO}_4$  and  $\text{PO}_4$  tetrahedra or of  $\text{AlO}_4$  and  $\text{SiO}_4$  tetrahedra). The enthalpy of formation from oxides of  $\beta\text{-NaCoPO}_4$  ( $-332.1 \pm 2.5$  kJ/mol [42]) is much more exothermic than that of nepheline  $\text{NaAlSi}_3\text{O}_8$  ( $-134.4$  kJ/mol [36]). Based on the acidity scale of Smith [43], ZnO and CoO are very close together in their basicity ( $-3.2$  and  $-3.8$ , respectively, compared to the whole scale ranging from  $-15.2$  for the strongest base,  $\text{Cs}_2\text{O}$ , to  $11.5$  for the strongest acid,  $\text{Cl}_2\text{O}_7$ ). Therefore, it is not surprising that, the enthalpy of formation from oxides of  $\alpha\text{-NaZnPO}_4$  ( $-339.6 \pm 2.6$  kJ/mol, Table 5) is very close to that of  $\beta\text{-NaCoPO}_4$ , and much more exothermic than enthalpy of formation from oxides of nepheline  $\text{NaAlSi}_3\text{O}_8$ .

The enthalpy of formation from oxides of the most stable phase of  $\text{NaCoPO}_4$ ,  $\alpha\text{-NaCoPO}_4$  with Co in octahedral environment,  $\Delta H_{\text{f-ox}, 298 \text{ K}} = -349.7 \pm 2.3$  kJ/mol [42], is slightly more exothermic than that of the most stable phase of  $\text{NaZnPO}_4$ ,  $\alpha\text{-NaZnPO}_4$ ,  $\Delta H_{\text{f-ox}, 298 \text{ K}} = -339.6 \pm 2.6$  kJ/mol (Table 5). This behavior is consistent with the slightly stronger basicity of CoO (Co in octahedral

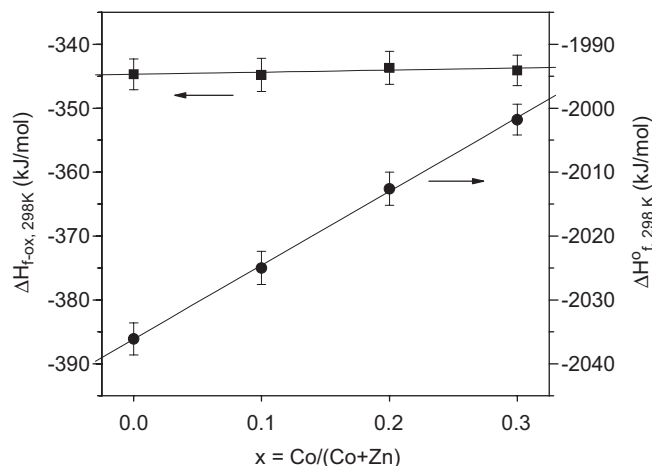


Fig. 5. Enthalpies of formation from oxides ( $\Delta H_{\text{f-ox}, 298 \text{ K}}$ ) and standard enthalpies of formation ( $\Delta H_{\text{f}^\circ, 298 \text{ K}}$ ) of  $\text{NaCo}_x\text{Zn}_{1-x}\text{PO}_4 \cdot \frac{4}{3}\text{H}_2\text{O}$  ( $x \leq 0.3$ ) as functions of cobalt content.

coordination) than of ZnO (Zn in tetrahedral coordination). This confirms that acidities of transition metal ions are affected by both their geometries and electron configurations.

Enthalpies of formation from oxides and standard enthalpies of formation of sodium zinc phosphate sodalite and its cobalt substitution ( $\text{NaCo}_x\text{Zn}_{1-x}\text{PO}_4 \cdot \frac{4}{3}\text{H}_2\text{O}$ ,  $0 < x \leq 0.3$ ) are plotted against the cobalt content in Fig. 5. Standard enthalpies of formation of  $\text{NaCo}_x\text{Zn}_{1-x}\text{PO}_4 \cdot \frac{4}{3}\text{H}_2\text{O}$  increase with cobalt content since standard enthalpy of formation of ZnO is more exothermic than of CoO (see Table 5). Because of the similarity of the acidity of CoO and ZnO [43], the substitution of less than 30% cobalt into zinc tetrahedral sites does not alter significantly the interactions of oxides in these compounds, expressed by the constancy of the enthalpies of formation from oxides of  $\text{NaCo}_x\text{Zn}_{1-x}\text{PO}_4 \cdot \frac{4}{3}\text{H}_2\text{O}$ . Although CoO and ZnO are stable in different structures (rock salt and wurtzite, respectively), the small enthalpy difference between octahedral and tetrahedral configuration of Co(II) [42] and the similarity of the acidity and ionic radii of Co(II) and Zn(II) would suggest a higher content of cobalt may substitute in zinc tetrahedra. For instance, 45% and 65% of cobalt can substitute in tetrahedral zinc sites of willemite  $\text{Zn}_2\text{SiO}_4$  [44] and of ZnO wurtzite [45], respectively. However, we did not succeed in preparing sodalite with comparably high cobalt contents.

## 4. Conclusions

Enthalpy of the  $\alpha$ - $\beta$  phase transition of  $\text{NaZnPO}_4$ , enthalpies of formation of  $\alpha\text{-NaZnPO}_4$ ,  $\text{NaH}(\text{ZnPO}_4)_2$ ,  $\text{NaZnPO}_4 \cdot \text{H}_2\text{O}$ , and a SOD framework,  $\text{NaZnPO}_4 \cdot \frac{4}{3}\text{H}_2\text{O}$  and its cobalt substitutions were determined. Acid–base interactions among oxides in  $\text{NaCoPO}_4$  and  $\text{NaZnPO}_4$  are similar because of the similarity of basicity of CoO and ZnO. These interactions are much stronger than in sodium



aluminosilicate. Because of the similarity of Co(II) and Zn(II) in ionic radius and in acid–base properties, at least 30% of Co can substitute in tetrahedral Zn sites in sodium zinc phosphate sodalite without significant change of their thermochemistry. When water is a constituent oxide in the formation of compounds, it affects their energetics in different ways. Molecular water stabilizes the frameworks through extra hydrogen bonds and cation hydration, resulting in more exothermic enthalpies of formation from oxides. Water that substitutes for a basic oxide decreases acid–base interactions in compounds and leads to less-exothermic enthalpies of formation from oxides.

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