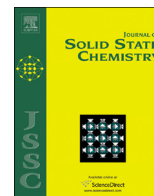




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Synthesis and characterization of novel barium iron phosphates: Insight into new structure types tailored by hydrogen atoms

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ABSTRACT

A significant gap in our knowledge of phosphate crystal chemistry is the lack of understanding of what controls the depolymerization of $[\text{PO}_4]$ tetrahedra. A new route using phosphoric acid without any added water at 240 °C has been developed to synthesize two new compounds $\text{Ba}_2\text{Fe}_2[\text{H}(\text{PO}_3\text{OH})_2][\text{H}(\text{P}_2\text{O}_7)_2]$ and $\text{Ba}_2\text{Fe}[\text{H}(\text{P}_2\text{O}_7)_2]$, as well as a new polymorph $\beta\text{-BaFe}_2(\text{P}_2\text{O}_7)_2$ from annealing the former at ≥ 500 °C. Structural characterizations show that $\text{Ba}_2\text{Fe}_2[\text{H}(\text{PO}_3\text{OH})_2][\text{H}(\text{P}_2\text{O}_7)_2]$ features a novel $2\text{D} \infty [[\text{Fe}_2[\text{H}(\text{PO}_3\text{OH})_2][\text{H}(\text{P}_2\text{O}_7)_2]]^{4-}]$ layer structure containing both hydrogen-diphosphate $[\text{H}(\text{P}_2\text{O}_7)_2]$ and hydrogen-monophosphate $[\text{H}(\text{PO}_3\text{OH})_2]$ groups, whereas $\text{Ba}_2\text{Fe}[\text{H}(\text{P}_2\text{O}_7)_2]$ and $\beta\text{-BaFe}_2(\text{P}_2\text{O}_7)_2$ possess an 1D chain structure and a 3D framework structure, respectively. These structures support a control of hydrogen on the depolymerization of $[\text{PO}_4]$ groups and our work opens a new way for the synthesis of other novel phosphates using controlled water activities.

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1. Introduction

Phosphates are some of the most intensively researched compounds for not only their rich crystal chemistry but also numerous agricultural and industrial applications (e.g., green fertilizers, biomaterials, etc.) [1–3]. Each coordinated oxygen atom in the phosphate $[\text{PO}_4]$ groups receives the formal valence of $5/4 = 1.25$ valence unit (vu). Therefore, an oxygen atom bridging two $[\text{PO}_4]$ tetrahedra receives, on average, $1.25 \times 2 = 2.5$ vu, which violates the valence rule [1]. For this reason, $[\text{PO}_4]$ tetrahedra, unlike their $[\text{BO}_4]$ and $[\text{SiO}_4]$ counterparts, do not extensively polymerize in crystal structures, resulting in relatively small numbers of pyrophosphate, polyphosphate and cyclophosphate compounds among thousands of natural and synthetic phosphates in the inorganic database [4]. In particular, compounds containing both orthophosphate and pyrophosphate groups (i.e. PO_4 and P_2O_7), are exceedingly rare, and only several dozen such phosphates are known to date [5–7]. The molar $\text{PO}_4/\text{P}_2\text{O}_7$ ratios in those phosphates vary from 4:1, 3:1, 2:1, 1:1 to 1:1.5, 1:3.5, 1:4 and 1:6, including $\text{A}_6(\text{VO})_2(\text{V}_2\text{O}_3)_2(\text{PO}_4)_4(\text{P}_2\text{O}_7)$ ($\text{A} = \text{K}, \text{Rb}$) [8], $\text{A}_3\text{Ti}_3\text{O}$

$(\text{PO}_4)_3(\text{P}_2\text{O}_7)$ ($\text{A} = \text{Rb}, \text{Ti}$) [9], $\text{Na}_4\text{M}_3(\text{PO}_4)_2(\text{P}_2\text{O}_7)$ ($\text{M} = \text{Mn}, \text{Co}, \text{Ni}$) [10], $\text{Pb}_2\text{Mo}(\text{PO}_4)(\text{P}_2\text{O}_7)$ [11], $\text{Li}_9\text{M}_3(\text{PO}_4)_2(\text{P}_2\text{O}_7)_3$ ($\text{M} = \text{Ga}, \text{Co}, \text{Ni}$) [12], $\text{PbTa}_3(\text{PO}_4)(\text{P}_2\text{O}_7)_{3.5}$ [13], $\text{Na}_7\text{M}_4(\text{PO}_4)(\text{P}_2\text{O}_7)_4$ ($\text{M} = \text{Al}, \text{Cr}, \text{Fe}$) [14], and $\text{Cs}_{11}\text{Eu}_4(\text{UO})_2(\text{PO}_4)(\text{P}_2\text{O}_7)_6$ [15].

Polymerization of these phosphate groups is commonly achieved via other polyhedral units. For example, polymerization of the phosphate groups in $\text{KV}_4(\text{PO}_4)(\text{P}_2\text{O}_7)(\text{P}_4\text{O}_{13})$, which contains monophosphate $[\text{PO}_4]$, diphosphate $[\text{P}_2\text{O}_7]$ and tetraphosphate $[\text{P}_4\text{O}_{13}]$, exhibits a complicated fashion involving the vanadyl groups [16]. However, phosphate groups rarely polymerize to form infinite chains or ribbons except for ultraphosphates (as $\text{SmP}_5\text{O}_{14}$) [17], the layer or framework structures of phosphates without involving other tetrahedrally coordinated elements (e.g., Be, B, Al and Zn, etc.) have never been reported yet (with the exception of a few special cases, e.g. polymorphs of P_2O_5) [1,18,19].

It is also well known that phosphates containing both orthophosphate and pyrophosphate groups generally do not contain hydrogen atoms in the structural backbone. Wiench and Jansen first reported a hydrated sodium phosphate $\text{Na}_{10}[\text{H}(\text{HPO}_4)_2][\text{H}(\text{P}_2\text{O}_7)_2]$ with the $\text{H}(\text{HPO}_4)_2$ and $\text{H}(\text{P}_2\text{O}_7)_2$ units [20]. Dvoncova, Murashova, Pralong, Weng and their coworkers have since reported a few more cases: i.e. $\text{Ba}_2\text{M}_3[\text{H}(\text{PO}_4)_2](\text{P}_2\text{O}_7)_2$ ($\text{M} = \text{Fe}, \text{V}$) with $\text{H}(\text{PO}_4)_2$ and P_2O_7 units [21], $\text{Rb}_2\text{Mn}(\text{H}_2\text{PO}_4)_2(\text{HP}_2\text{O}_7)$ [22] and $\text{K}_2\text{Fe}(\text{H}_2\text{PO}_4)_2(\text{HP}_2\text{O}_7)$ [23] with H_2PO_4 and HP_2O_7 , and $\text{Na}_{10}\text{Sn}_3(\text{HPO}_4)_6(\text{PO}_4)_{12}(\text{P}_2\text{O}_7)_6$ with PO_4 , HPO_4 and P_2O_7 [24]. Rare examples may also be found in metal organic compounds such as $[\text{NH}_3(\text{CH}_2)_2\text{NH}_3][\text{M}(\text{P}_2\text{O}_7)(\text{H}_2\text{PO}_4)]$

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($M = \text{Ga}, \text{V}$) [25] and $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3][\text{Ga}(\text{P}_2\text{O}_7)(\text{H}_2\text{PO}_4)]$ [26]. The presence of any H atoms was commonly thought to attack the bridging anion, resulting in the depolymerization of phosphates [1]. However, the mechanism of how the H atoms affect the depolymerization of phosphates remains unclear. Huminicki and Hawthorne [1] proclaimed that “Our lack of understanding concerning this issue is obviously an important gap in our knowledge of phosphate crystal chemistry”.

Following our previous studies on synthetic iron phosphates [27–29], we have attempted to develop new experimental routes for the synthesis of novel iron phosphates, such as the compound (1), $\text{Ba}_2\text{Fe}_2[\text{H}(\text{PO}_3\text{OH})_2][\text{H}(\text{P}_2\text{O}_7)_2]$, containing both $[\text{H}(\text{PO}_3\text{OH})_2]$ and $[\text{H}(\text{P}_2\text{O}_7)_2]$ units. In the simple barium iron phosphate system, six orthophosphates (i.e. $\text{Ba}_3\text{Fe}_2(\text{HPO}_4)_6$ [30], $\text{BaFe}^{\text{II}}(\text{PO}_4)(\text{OH})$ [31], $\text{Ba}_3\text{Fe}_4(\text{PO}_4)_6$ [32], $\text{BaFe}_2^{\text{II}}(\text{PO}_4)_2$ [33], $\text{Ba}(\text{H}_2\text{O})\text{Fe}_2[\text{PO}_3(\text{OH})_4]$ [34] and johntomaite ($\text{BaFe}_2^{\text{II}}\text{Fe}_2^{\text{III}}(\text{PO}_4)_3(\text{OH})_3$) [35]) and two pyrophosphates (i.e. $\alpha\text{-BaFe}_2(\text{P}_2\text{O}_7)_2$ [36] and $\text{Ba}_2\text{Fe}_3[\text{H}(\text{PO}_4)_2](\text{P}_2\text{O}_7)_2$ [21]) are known. Moreover, systematic investigation on synthesis conditions led us to obtain another new barium iron pyrophosphate compound $\text{Ba}_2\text{Fe}[\text{H}(\text{P}_2\text{O}_7)_2]$ (2), as well as a new polymorph $\beta\text{-BaFe}_2(\text{P}_2\text{O}_7)_2$ (3). The compound (2) $\text{Ba}_2\text{Fe}[\text{H}(\text{P}_2\text{O}_7)_2]$ has the highest Ba/Fe ratio and only the second one with Ba/Fe > 1 in all known barium iron phosphates. Herein, we report on the crystal structures for these three new barium iron phosphates from single crystal or powder X-ray diffraction data. In particular, the crystal structure of the compound (1), determined from single crystal X-ray diffraction study and confirmed by Fourier transform infrared spectroscopy and thermogravimetric analysis, is a new type for phosphates. These results are then used to discuss the control of hydrogen atoms on the depolymerization of phosphate groups, which points to a new way for the synthesis of novel phosphates under controlled water activities.

2. Experimental

2.1. Syntheses of barium iron phosphates

Single crystals of $\text{Ba}_2\text{Fe}_2[\text{H}(\text{PO}_3\text{OH})_2][\text{H}(\text{P}_2\text{O}_7)_2]$ (1) were prepared by a facile route at 240 °C. First, a mixture of $\text{Ba}(\text{NO}_3)_2$ (0.523 g), $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (0.398 g) and H_3PO_4 (2 mL, 85%), in the molar ratio of Ba:Fe=1:1 was prepared without adding any water. This mixture was then transferred to a 20 mL Teflon-lined autoclave with the filling degree of circa 15%, which was heated to and held at 240 °C in an oven for 3 days. After this heat treatment, the autoclave was directly taken out of the oven, and cooled down to room temperature in air. After cooling, colorless-light pink, transparent crystals of the compound (1) were filtered, washed thoroughly with distilled water, and dried in air at 90 °C.

Systematic experiments demonstrate that the synthesis conditions of the compound (1) are very tricky. This compound as a single phase has been synthesized only from runs at conditions described above (i.e., Ba:Fe=1:1, 240 °C and no added water; Fig. S1a). Runs at the same conditions but different Ba:Fe ratios in the starting materials yielded either a pure hydrogen orthophosphate $\text{Ba}_3\text{Fe}_2(\text{HPO}_4)_6$ [37] (Fig. S1b) or mixed $\text{Ba}_3\text{Fe}_2(\text{HPO}_4)_6$ and $\text{Ba}_2\text{Fe}_2[\text{H}(\text{PO}_3\text{OH})_2][\text{H}(\text{P}_2\text{O}_7)_2]$ (Fig. S1c). Also, an experiment with Ba:Fe=1:1 and no added water at 190 °C produced mainly $\text{Ba}_3\text{Fe}_2(\text{HPO}_4)_6$, suggesting a temperature control on the compound (1) as well. Moreover, runs using the same conditions and same reagents of $\text{Ba}(\text{NO}_3)_2$, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and H_3PO_4 , except for adding small amounts of water, yielded a hydrated orthophosphate $\text{Ba}(\text{H}_2\text{O})\text{Fe}_2[\text{PO}_3(\text{OH})_4]$ [34] at various molar Ba/Fe ratios in the temperature range from 190 to 240 °C (Fig. S1d). Interestingly, experiments with the same starting materials (Ba:Fe=1:1) at 240 °C and no added water, except that the starting materials

were preheated at 190 °C for 24 h, yielded multi-phase products, including another new barium iron hydrogen diphosphate, $\text{Ba}_2\text{Fe}[\text{H}(\text{P}_2\text{O}_7)_2]$ (2), identifying from single crystal X-ray diffraction analysis. Unfortunately, attempts to produce a single phase of this new diphosphate were not successful, thus no further characterization were conducted except for single crystal X-ray diffraction analysis.

Another interesting result is that both the compound (1) and $\text{Ba}(\text{H}_2\text{O})\text{Fe}_2[\text{PO}_3(\text{OH})_4]$ [34] are decomposed to form a new polymorph $\beta\text{-BaFe}_2(\text{P}_2\text{O}_7)_2$ (3) after annealing at ≥ 500 °C. The samples of $\beta\text{-BaFe}_2(\text{P}_2\text{O}_7)_2$ used in this study were obtained from annealing $\text{Ba}(\text{H}_2\text{O})\text{Fe}_2[\text{PO}_3(\text{OH})_4]$ at 650 °C for 2 h (Fig. S2). The powder sample of the compound (3) is dark black in color, which is different from the white to light pink color of its precursor. An attempt to grow single crystals was not successful due to its incongruent melting behavior. Further annealing of the compound (3) at 800 °C decomposes to two or more unidentified compounds (Fig. S2).

2.2. Characterization methods

Systematic characterizations have been performed for the compound (1), whereas only X-ray diffraction analyses have been made for the compounds (2) and (3) due to the lack of pure powder samples. The identity and purity of the compound (1) were first verified by means of powder X-ray diffraction (XRD) patterns, measured on a PANalytical X'Pert-PRO diffractometer with $\text{CuK}\alpha$ radiation ($\lambda = 1.54056$ Å, graphite monochromator). The morphology of the synthesized compound was observed by using a field emission scanning electron microscope (FE-SEM, LEO-1530) (Fig. S3). Chemical analyses were performed by using both an Oxford Instruments energy dispersive spectrometer and wavelength dispersive spectrometers on a JEOL JXA-8600 electron microprobe.

FTIR spectra were measured with both transmittance and reflectance modes. The FTIR transmittance spectrum was recorded on a powder sample mixed with KBr in a pressed pellet on a Nicolet 330 FTIR spectrometer over the range of 400–4000 cm^{-1} with the resolution of 2 cm^{-1} . The FTIR reflectance spectrum was measured on a Thermo Scientific Nicolet iS10 FT-IR Spectrometer with a smart endurance single-bounce diamond ATR (Attenuated Total Reflectance) cell. Thermal investigations were performed on a TG-209F1 thermo-gravimetric/differential thermal analyzer (TG-DTG/DTA) both in N_2 atmosphere and air with a heating rate of 10 K min^{-1} . Magnetic susceptibility was measured in the temperature range from 2 to 300 K, using a Quantum Design MPMS XL-7 SQUID magnetometer, with a resolution of 5×10^{-8} emu.

2.3. X-ray crystal structure determination

Single crystals of the compounds (1) and (2) were carefully selected on the basis of their extinction patterns under a petrographic microscope and were glued on a thin glass capillary for single-crystal X-ray diffraction data collection at 173(2) K, using a Bruker Apex CCD diffractometer equipped with a graphite-monochromatic $\text{MoK}\alpha$ radiation ($\lambda = 0.71073$ Å). 3510 observed reflections were collected from $2.53^\circ < \theta < 28.20^\circ$, yielding 1862 unique reflections ($R_{\text{int}} = 0.024$) with $1846 I > 2\sigma(I)$ for the compound (1). 2274 observed reflections were collected from $2.55^\circ < \theta < 28.13^\circ$, yielding 1222 unique reflections ($R_{\text{int}} = 0.027$) with $1200 I > 2\sigma(I)$ for the compound (2). The crystal structures of both compounds (1) and (2) were solved by direct methods and refined by the full-matrix least-squares method using the SHELXS-2013 and SHELXL-2013 software package [38].

Compound (1) crystallizes in the triclinic space group $P\bar{1}$, with a cell of $a = 7.6547(13)$ Å, $b = 8.6601(15)$ Å, $c = 6.8717(12)$ Å, $\alpha = 101.237(4)^\circ$,

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