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Dimensionality Changes in Solid Phase at Room Temperature: 2D→1D→3D Evolution Induced by Ammonia Sorption/desorption on Zinc Phosphates

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Supporting Information

1. Reagents

All chemicals used were of reagent grade (Merck) and were employed without further purification.

2. Synthesis

Hydrothermal crystallization of $NH_4Zn_2(PO_4)(HPO_4)$ (**1**) was carried out in a Teflon-lined stainless steel vessel (100 mL) under autogenous pressure. Details about its preparation are reported in a previous paper (Ramajo, B.; Espina, A.; Khainakov, S. A.; García, J. R. *J. Incl. Phenom. Macro.* **2004**, *49*, 241). The crystals obtained were ground to a particle size of less than 0.045 mm. A fraction of the sample was ground gently in an agate mortar for analytical procedures.

$NH_4Zn(NH_3)PO_4$ (**2**) was obtained by storing compound **1** (powder sample) over a saturated ammonia aqueous solution at room temperature. The time contact solid-vapor needed to reach saturation is of *ca.* 9 hours.

NH_4ZnPO_4 (**3**) was obtained by outgassing procedure (rotary pump) of compound **2** at room temperature.

3. Structural data for $NH_4Zn(NH_3)PO_4$ (2)

The synchrotron radiation X-ray powder diffraction pattern was recorded at SpLine beamline BM25A at the European Synchrotron Radiation Facility (ESRF), Grenoble (France). The sample was finely powdered and loaded in a 1.0 mm diameter borosilicate glass capillary, which was mounted on a spinning goniometer. Room-temperature data was collected in a step 2θ-scan mode from 4° to 50°, with an interval step of 0.02° and counting time of 5 seconds per step, using an incident wavelength of 0.82401(11) Å (calibrated with NIST SRM 640c silicon powder; *a* = 5.4311946(92) Å). The structure Zn-1D was solved *ab initio* by using EXPO2009 program (A. Altomare, M. Camalli, C. Cuocci, C. Giacovazzo, A. Moliterni, R. Rizzi. *J. Appl. Cryst*. 2009, **42**, 1197-1202) and refined using Rietveld method with FULLPROF program (Rodriguez-Carvajal J. Commission on Powder Diffraction (IUCr) Newsletter 2001, **26**, 12-19). Hydrogen atoms were placed geometrically and structural modeling with DFT based methods was used for position optimization of protons. After that, next refinement cycles were carried out with FULLPROF using constraints for N-H bonds and H-N-H angles. In order to obtain a good refinement result, a diffraction contribution from compound NH_4ZnPO_4 (**3**) was introduced in the fit. Results showed that there was a ~3% in weight fraction of that compound. The final Rietveld plot is given in Figure S1. Crystallographic parameters are summarized in Table S1. Final atomic positions are shown in Table S2. Selected bond distances and angles are shown in Table S3.

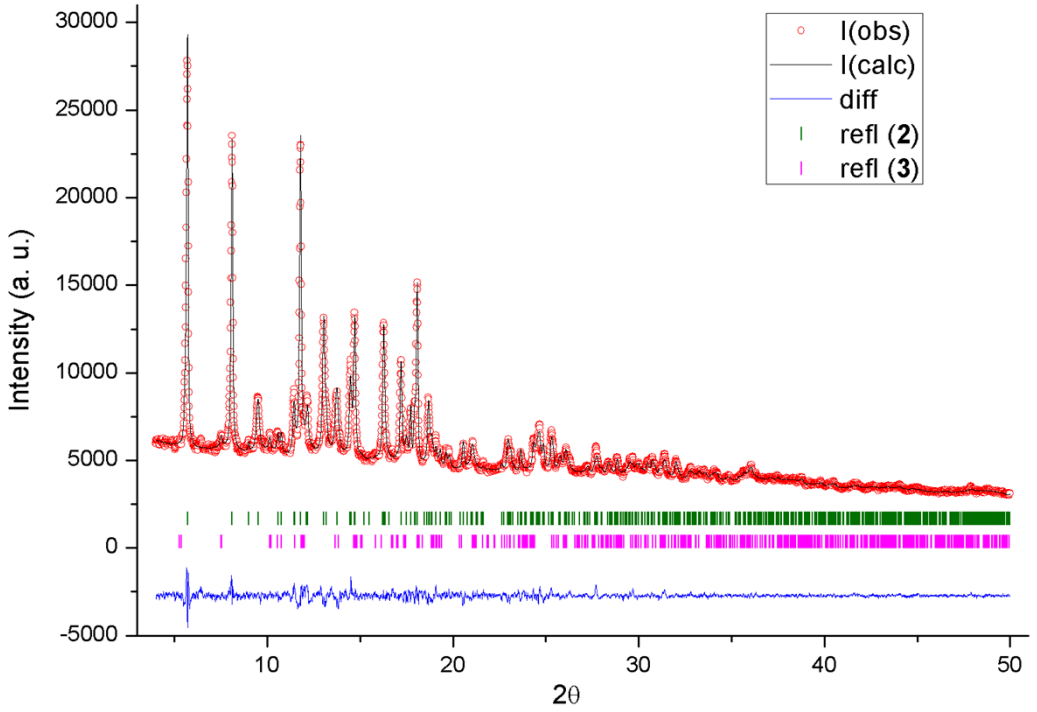

Figure S1. Final Rietveld refinement plots for $NH_4Zn(NH_3)PO_4$ (**2**), showing the experimental (red circles), calculated (black line) and difference profiles (blue line); green and pink tick marks indicate reflection positions.

Table S1. Crystallographic data and Rietveld refinement summary for compound $NH_4Zn(NH_3)PO_4$ (**2**).

CCDC nos.	977982
Formula	$NH_4Zn(NH_3)PO_4$
Formula weight (g/mol)	195.43
Crystal system	monoclinic
Space group	$P2_1/a$
a (Å)	16.5227(2)
b (Å)	6.21780(8)
c (Å)	5.24317(6)
β (°)	90.9998(20)
V (Å³)	538.576(12)
Z	4
Radiation type	Synchrotron
Diffractometer	SpLine (BM25A) at the ESRF, Grenoble
Data collection mode	Transmission
Wavelength (Å)	0.82401(11)
Rp	0.0197
Rwp	0.0265
R_F^2	0.0451
R_B	0.0348
χ^2	3.62

Table S2. Fractional atomic coordinates of non-H atoms for compound $NH_4Zn(NH_3)PO_4$ (**2**).

Atom	x	y	z
Zn1	0.55746(20)	0.2144(4)	0.7990(6)
P1	0.6150(3)	-0.0325(2)	0.2974(10)
O1	0.6132(8)	0.0098(19)	0.5870(16)
O2	0.4402(4)	0.2146(11)	0.802(2)
O3	0.5828(8)	0.1676(10)	0.1561(15)
O4	0.7034(5)	-0.059(2)	0.259(3)
N1	0.7736(12)	-0.024(2)	0.779(4)
N2	0.5826(9)	0.5259(12)	0.726(3)

Table S3. Selected Bond Distances (Å) and Angles (°) of $NH_4Zn(NH_3)PO_4$ (**2**).

Atoms	Bond, Å	Atoms	Angle, °
Zn1-O1	1.933(12)	O1-Zn1-O2	119.4(8)
Zn1-O2	1.938(7)	O1-Zn1-O4	111.1(7)
Zn1-O4	1.933(9)	O1-Zn1-N2	114.9(8)
Zn1-N2	2.019(9)	O1-P1-O2	115.9(10)
P1-O1	1.542(10)	O1-P1-O4	108.9(9)
P1-O2	1.539(8)	O1-P1-O5	100.8(11)
P1-O4	1.538(8)		
P1-O5	1.487(10)		

4. Powder thermodiffraction studies.

Thermal evolution of $NH_4Zn(NH_3)PO_4$ (**2**) to NH_4ZnPO_4 (**3**) was monitored by synchrotron radiation powder diffraction. The sample was placed in a sealed capillary as the previously described conditions. Each powder pattern was recorded in the 10-17° range (2θ) at intervals of *ca.* 10 °C up to 210 °C. The temperature ramp between two consecutive temperatures was 10 °C/min.

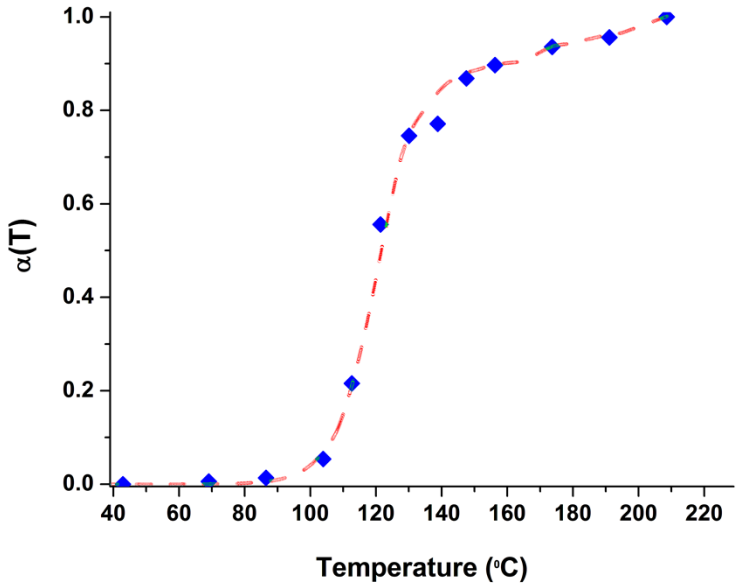

Figure S2. Extents of conversion from **2** to **3** as a function of temperature (see paper text).