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Synthesis and characterization of ZnAPO-34 molecular sieve with CHA structure type

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Abstract

Zinc substituted chabazite-like aluminophosphate ZnAPO-34 was synthesized hydrothermally. Rietveld refinement has been carried out over the X-ray spectrum. Atomic coordinates of the framework were refined assuming the space group $\bar{R}3m$. Results show that Zn^{2+}, P^{5+} and Al^{3+} occupy similar tetrahedral sites in the structure. The cell is rhombohedral; in hexagonal coordinates the lattice parameters are: $a = 13.827_1$ Å and $c = 15.401_3$ Å. Different crystal shapes have been revealed by scanning electron microscopy, and the elemental compositions of these crystals show variations, especially in their Ca and Zn content, but all of them belong to the same solid solution. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Aluminophosphate; CHA structure type; Molecular sieve; Zeolites; ZnAPO-34

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1. Introduction

Molecular sieves such as $AlPO_4$-*n* are expected to be materials with bio-compatibility properties due to their structure and chemical composition [1,2]. The synthesis of the aluminophosphate family of molecular sieves $AlPO_4$-*n*, where *n* denotes the structure type, was first reported in 1982 [3]. Their structure consists of alternating tetrahedra of aluminum and phosphorus linked by oxygen. Later on, Lok et al. [4] reported the synthesis of silicoaluminophosphate (SAPO-*n*) which contains Si^{4+} in the framework. Wilson, Flanigen and coworkers [5–7] reported the incorporation of metal cations Me^{2+} (Me = Zn, Mn, Co, Mg) into the framework; all these metal cations can substitute Al^{3+} and P^{5+} in aluminophosphate domains depending on the synthesis conditions and the molar ratio in the starting gel. In 1995, Novak et al. [8] reported a zinc-rich aluminophosphate similar to the compound described here, but with a different synthesis route.

In this work, another possible synthesis of ZnAPO-34 and a more accurate structural analysis of this MAPO are described.

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2. Experimental

2.1. Synthesis

The reaction mixture was as follows: 37.11 g of Al_2O_3 (Merck) (0.3630 mol), and 144 ml of deionized water were mixed together and stirred. In a separate vessel 5.86 g of $ZnSO_4H_2O$ (Merck) (0.1706 mol) was added to a solution of 57.20 ml of orthophosphoric acid (85 wt%) in 144 ml of deionized water (2.52 M) and mixed until dissolved; then 1.2 g of CaOH (0.0210 mol) was added to this solution. The presence of Ca is very important for obtaining the material, without Ca we get a gel. The Al_2O_3 suspension and the acid solution were combined by adding the solution to the suspension and then adding triethanolamine as an organic base to modify the gel chemistry, adjusting the pH in the range 2.5–3.5. In our case, 93.2 ml of triethanolamine (0.6975 mol) was needed to reach pH 3. The final mixture was stirred at room temperature to a homogeneous mixture and then charged into a 450 ml stainless steel autoclave for hydrothermal treatment at 383 K for 36 h.

Products were washed with distilled water several times and dried at 353 ± 5 K for 12 hours. The final product was a white powder.

2.2. Characterization

The chemical analysis of the product was determined by atomic absorption spectrometry (AAS). The density was measured with a pyknometer equipped with a temperature gauge.

The structural characterization was carried out by X-ray diffraction (XRD), which was performed on a Siemens D5000 X-ray diffractometer, operated at 40 kV and 30 mA with monochromatic Cu Kα radiation. The diffraction pattern was scanned over the angular range 5° to 80° (2θ) with a step of 0.02° (2θ).

The structural refinement was carried out using Rietveld analysis with PC compatible DBW9006 software.

Morphological studies were done by scanning electron microscopy (SEM, Leica, Cambridge 440). Elemental analysis was performed by energy dispersive spectrometry (EDS).

3. Results and discussion

The elemental composition of Al, Ca and Zn of the samples was measured by atomic absorption spectrometry, yielding 188.8 mg/g, 14.7 mg/g and 43.8 mg/g, respectively, and the P content was determined by colorimetry, giving 57.7 mg/g.

The measured density was 2.09 ± 0.01 g/cm^3.

The compound was characterized by XRD. The spectrum revealed a high crystallinity, shown by the sharp peak profile in Fig. 1. Observed intensities are listed in Table 1.

The spectrum was refined by the Rietveld method with a chabazite structure model. We assumed a rhombohedral cell $R\bar{3}m$ space group. The calculated data fit the experimental spectrum. No peak was discarded, indicating a single phase product. The peaks appearing in the difference spectrum of Fig. 1, which correspond to the (101), (211) and (214) planes, suggest a slight preferential orientation into the sample. The cell is rhombohedral; in hexagonal coordinates the parameters are:

Table 1
X-ray powder diffraction data for ZnAPO

h	k	l	2θ	I_{obs}	h	k	l	2θ	I_{obs}
1	0	1	9.35	100	2	3	2	35.31	12
1	1	0	12.80	13	4	0	4	38.13	10
0	1	2	13.65	14	3	3	0	39.47	10
0	2	1	15.88	19	0	4	5	42.14	8
2	0	2	18.79	13	5	0	5	48.24	8
2	1	1	20.48	73	1	3	7	49.90	12
1	1	3	21.60	17	2	5	3	50.42	6
0	3	0	22.31	8	6	1	2	51.67	7
1	2	2	22.81	18	0	0	9	53.07	6
1	0	4	24.32	21	0	7	2	53.65	9
2	2	0	25.81	24	1	6	4	55.78	8
0	2	4	27.52	21	7	1	0	58.91	9
3	1	2	29.32	13	6	2	4	60.80	7
0	1	5	30.02	16	7	1	3	62.44	6
2	1	4	30.51	47	4	2	8	63.90	6
2	0	5	31.25	12	5	4	4	65.30	7
3	2	1	32.74	11	5	5	0	67.06	8
1	0	4	33.18	11	4	5	5	68.48	4
4	1	0	34.37	12	2	7	7	78.88	4

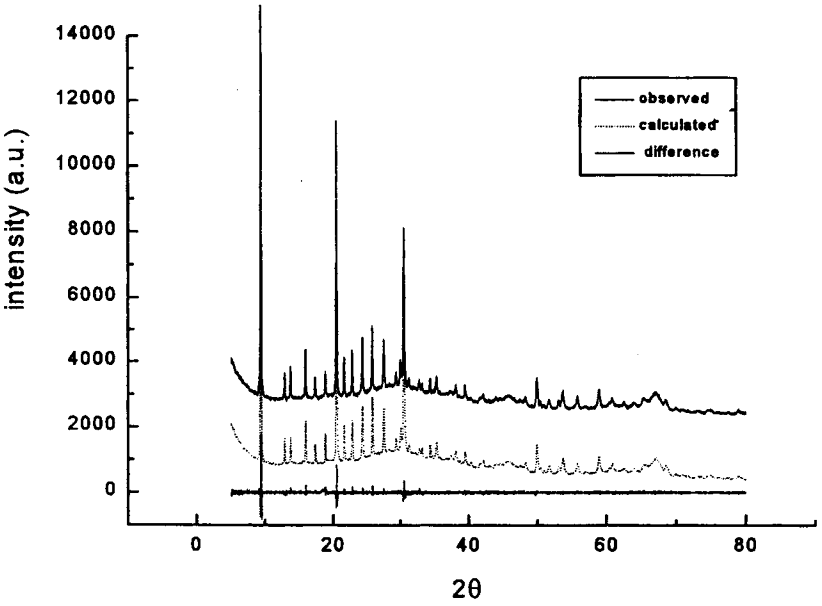

Fig. 1. XRD spectra after Rietveld refinement of ZnAPO-34, observed, calculated and difference spectra.

$a = 13.827_1$ Å and $c = 15.401_3$ Å. These parameters present a small difference compared to previous literature results concerning a structure without any Ca content [9,10]. The fractional atomic coordinates, thermal isotropic parameters (Å^2) and Wyckoff position for this compound are given in Table 2. The position (36*i*) is assumed the same for Al, P and Zn, and their combined occupancy is practically 100%. Nevertheless, the low content of Zn atoms within the structure made it difficult to locate their exact positions, therefore it cannot be excluded that Zn is part of the structure. The same considerations apply for Ca atoms. The sample stoichiometry after Rietveld refinement is: $P_{2.25}Al_{8.66}Ca_{0.43}Zn_{0.87}O_{24} \cdot 13H_2O$.

The Al and P atoms occupy identical tetrahedral

Table 2
Fractional atomic coordinates, thermal isotropic parameters (Å^2) and Wyckoff position for ZnAPO-34

Atom	*X*	*Y*	*Z*	*B*	*N*	Wyckoff	Atoms/cell
P	0.3350	0.1040	0.4380	0.3500	0.1880	36*i*	6.76
Al	0.3350	0.1040	0.4380	0.5300	0.7220	36*i*	26
Ca	0.1180	−0.0050	0.4730	0.3000	0.0454	36*i*	1.3
O_1	−0.2620	0.2620	0.0000	0.5500	1.0000	18*h*	18
O_2	−0.009	0.3250	0.1670	0.5500	0.5000	36*i*	18
O_3	0.2150	0.2150	0.4670	0.5500	0.5000	36*i*	18
O_4	0.09967	0.09967	0.1267	0.5500	0.5000	36*i*	18
Zn	0.3350	0.1040	0.4380	1.3000	0.0720	36*i*	2.6
$(H_2O)_1$	0.1090	0.1090	0.3530	0.9000	0.5000	36*i*	18
$(H_2O)_2$	−0.1667	−0.1667	0.3330	0.9000	0.1666	36*i*	6
$(H_2O)_3$	0.0000	0.0000	0.2000	0.9000	0,1666	36*i*	6
$(H_2O)_4$	0.0000	0.0000	0.4150	0.9000	0.1666	36*i*	6

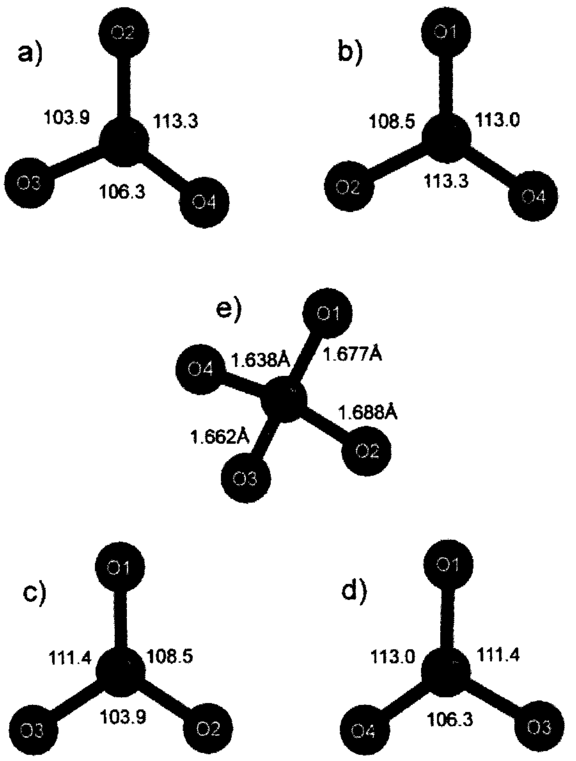

Fig. 2. (a–d) Measurements of angles, (e) distances for ZnAPO-34 tetrahedra.

Table 3
ZnAPO-34 Rietveld parameters

Unit cell contents	$P_{2.86}Al_{11}Ca_{0.55}$ $Zn_{1.1}O_{24} \cdot 13H_2O$
Refined pattern 2θ range	5–80°
Step scan increment (2θ)	0.02°
Wavelength (λ)	1.54060, 1.54443
Volume (Å^3)	2550.2
Calculated density (g/cm^3)	1.91
No. of profile data steps	4250
No. of contributing reflections	433
$R_P = (\Sigma \lvert I_o - I_c \rvert)/(\Sigma I_o)$	3.03
$R_{WP} = (\Sigma w_i[I_{io} - I_{ic}]^2)/(\Sigma w_i I_{io}^2)^{1/2}$	4.18
R expected $= R_{WP}/\{(\Sigma w_i[I_{io} - I_{ic}]^2)/(n_{obs} - n_{var})\}^{1/2}$	3.27
S	1.28
D–W D	1.45
Zero point	0.0009

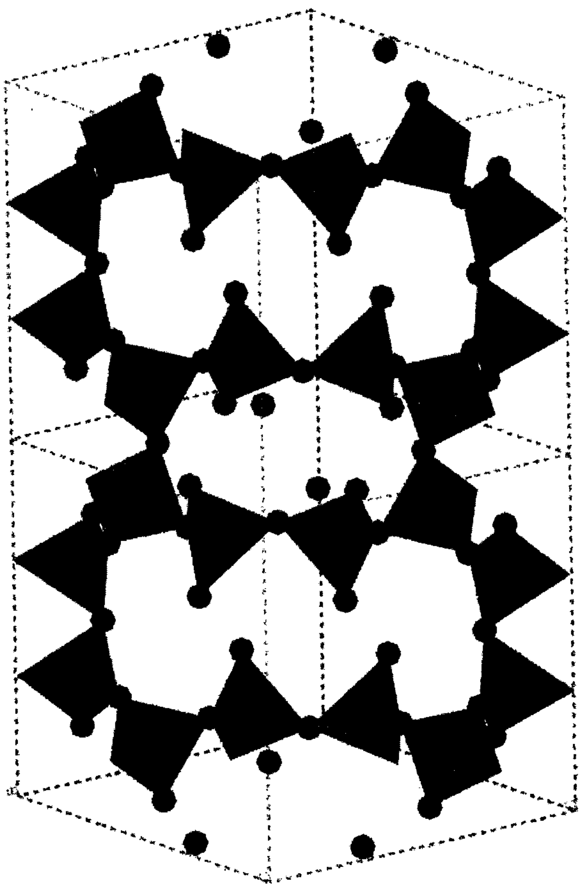

Fig. 3. ZnAPO-34 crystal model, tetrahedral space distribution can be observed.

sites in the structure, the bond distances and angles for this site are shown in Fig. 2 and Fig. 3 illustrates the crystal model, where tetrahedral space distribution can be observed.

Finally, Table 3 shows the Rietveld output parameters after the structure refinement.

Some differences between the XRD pattern reported in this paper and that reported recently by Novak et al. [8] are observed; particularly (113) and (116) planes which could not be seen in Novak's XRD pattern.

We have observed the samples by SEM, looking for the morphology and composition of the crystals. The observations show two different crystal morphologies, Fig. 4. The first one occurs in 33%

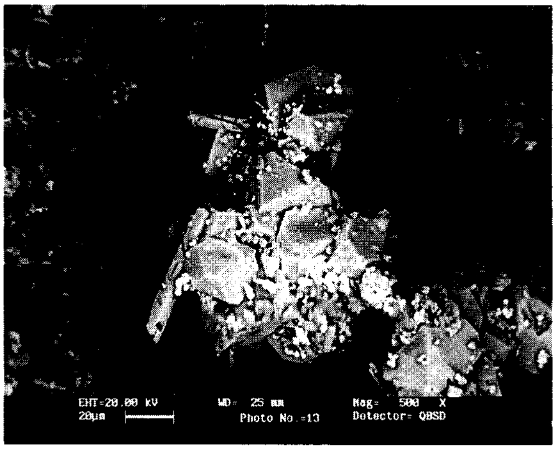

Fig. 4. SEM image of characteristic ZnAPO-34 crystals (back-scattering electron mode).

of the cases, is characterized by a needle-like shape and flat faces (stick), and presents two slightly different chemical compositions, mainly revealed in their Ca content, that we called type 1 and type 2. The second one occurs in 66% of the cases, is characterized by bulkier shape and flat faces (particle), and also has differences in Ca content, Fig. 5.

These composition differences do not necessarily imply the existence of two phases, since all diffraction peaks are compatible with a single structural model which fits properly the experimental data. Indeed, these kinds of compounds present a very wide solid solution. The limits of the solution were not studied in this work.

To conclude, we have prepared ZnAPO-34 by a new synthesis route. In this compound, a better determination of lattice parameters (by the Rietveld method) has been made, and several associated crystal morphologies are reported.

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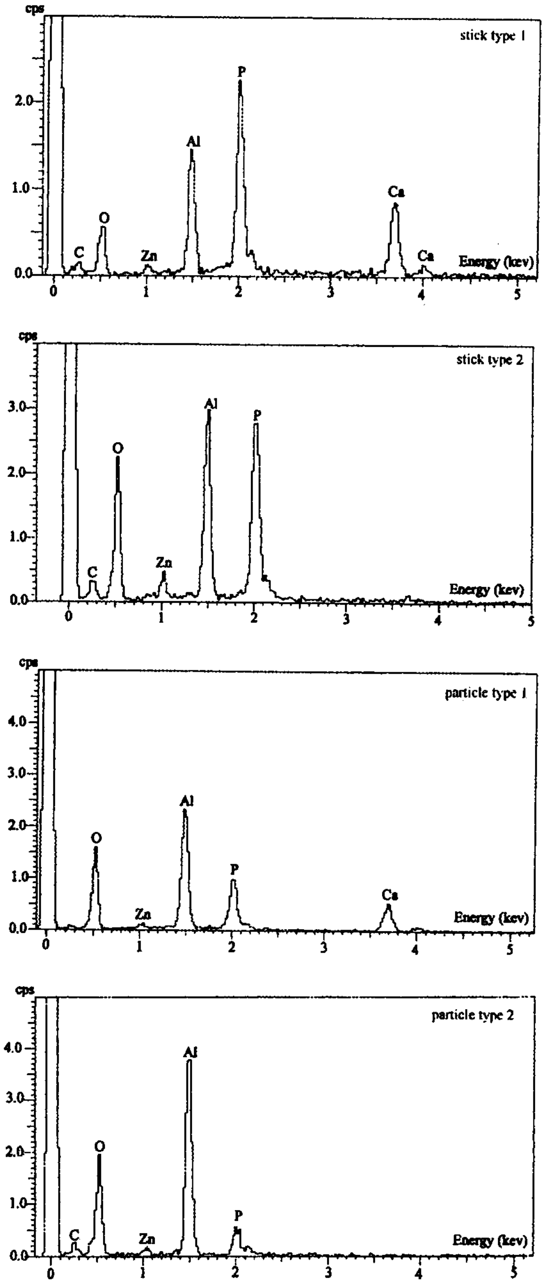

Fig. 5. EDS spectra corresponding to sticks and particle morphologies.

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