Communications

Three-Dimensional Open-Framework Nickel Aluminophosphate $[NiAlP_2O_8][C_2N_2H_9]$: Assembly of One-Dimensional $AlP_2O_8^{3-}$ Chains through $[NiO_5N]$ Octahedra

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The search for new microporous compounds through rational design has received great attention in recent years,[1−4] especially in the aspects of microporous aluminophosphates and related materials.[5−8] These materials show rich compositional and structural diversity compared with the aluminosilicate zeolites.

So far, the main approach to reach the rational synthesis of these target materials is through rational selection of the template agents according to theoretical prediction. Another possible strategy to construct new frameworks is through condensation of a lower dimensional network under suitable conditions. Recently, our lab and others have successfully synthesized a variety of organically templated aluminophosphates with one-dimensional (1-D) chains, two-dimensional (2-D) layers, and three-dimensional (3-D) interrupted open-framework structures built up from Al units (AlO_4, AlO_5, or AlO_6) and PO_4 units by sharing bridging oxygen atoms. Their structures exclusively contain terminal P−OH and/or P═O groups. This leads to a nonunity stoichiometry of Al and P in the framework, such as $AlP_2O_8^{3-}$,[9,10] $Al_2P_3O_{12}^{3-}$,[11−13] $Al_3P_4O_{16}^{3-}$,[14,15] $Al_4P_5O_{20}^{3-}$,[16,17] and $Al_5P_6O_{24}^{3-}$.[18,19] The existence of terminal P−OH and P═O groups indicates that higher dimensional framework can possibly be assembled from a lower dimensional network through condensation. Due to the restriction of Loweinstein's rule, i.e., there is no P−O−P connection allowed, the terminal phosphate groups must be condensed across an extra Al or other metal species.

Transition metal atoms can be incorporated into the frameworks to form many metal substituted aluminophosphates (MeAPOs);[20−22] they have a strong coordination ability to the oxygen atoms. In this work, we have successfully assembled the 1-D $AlP_2O_8^{3-}$ chains into a 3-D open-framework nickel aluminophosphate through the incorporation of transition metal Ni^{2+} ion.

The 1-D $AlP_2O_8^{3-}$ chain compound (**1**) is synthesized using ethylenediamine (en) as a template in an ethylene glycol solvothermal system. The anionic chain, as seen in Figure 1, is made up of linear corner-sharing Al_2P_2 four-membered rings (4-MRs) parallel to the [010] direction. The layers are stabilized by interlamellar $^+H_3NCH_2CH_2NH_3^+$ and NH_4^+ cations as reported before.[23] All AlO_4 tetrahedra each shares four oxygens with adjacent P atoms, whereas all PO_4 tetrahedra each shares only two oxygens with adjacent Al atoms, leaving the other two oxygens terminal. These teriminal P−OH and P═O groups will have the potential to further condense through an extra metal cation to build up a higher dimensional framework.

With the incorporation of Ni^{2+} into the framework, a 3-D open-framework nickel aluminophosphate, designated NiAPO-1, is formed in the same reaction system,

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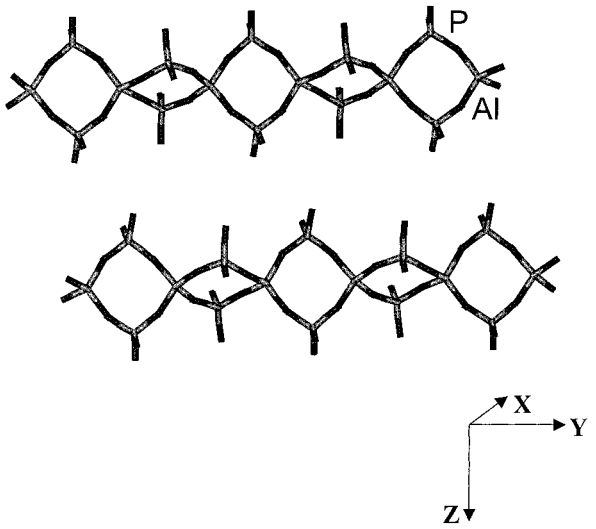

Figure 1. 1-D $[AlP_2O_8]^{3-}$ anionic chains parallel to the [001] direction.

i.e., using ethylenediamine as a template and ethylene glycol as the solvent.[24]

A suitable single crystal with dimensions of 0.06 × 0.05 × 0.03 mm was selected for single-crystal X-ray diffraction analysis. The X-ray powder diffraction pattern of the product is very consistent with the simulated one, proving that the as-synthesized compound is a single phase.

Single-crystal X-ray diffraction analysis gives that NiAPO-1 crystallizes in the monoclinic space group $P2_1/c$, with lattice parameters a = 8.542 (2) Å, b = 15.564 (3) Å, c = 7.627(2) Å, and β = 110.60(1)°.[25] NiAPO-1 has the empirical formula $[NiAlP_2O_8][C_2N_2H_9]$.

In contrast to previous Ni-substituted microporous aluminophosphates, a stoichiometric mixing of Ni and Al in the framework has been found in NiAPO-1. Figure 2 shows the framework structure viewed along the [001] direction, which contains 8-MRs with the template agents protruding into the 8-MR openings. The 1-D

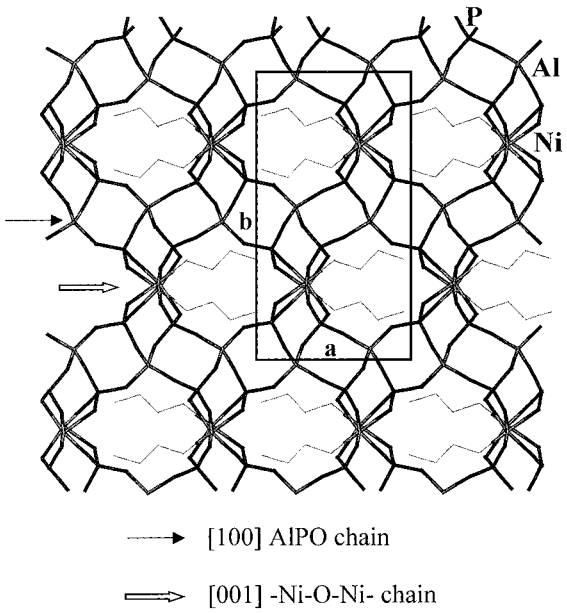

Figure 2. Framework structure of NiAPO-1 viewed along the [001] direction.

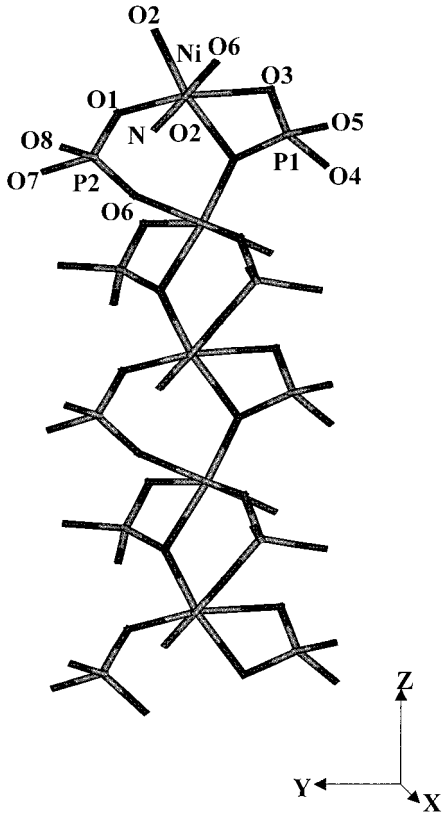

Figure 3. −Ni−O−Ni− chain running along the [001] direction, showing the connectivity of Ni octahedra with the phosphates and amino groups of the template molecules.

$AlP_2O_8^{3-}$ chains parallel to the [100] direction are assembled through octahedral Ni atoms, which coordinated to the terminal oxygens of the 1-D $AlP_2O_8^{3-}$ chains and the amino groups of the template.

The 1-D $AlP_2O_8^{3-}$ anionic chains and the −Ni−O−Ni− chains are cross-linked with each other. Figure 3 is the −Ni−O−Ni− chain running along the [001] direction, showing the connectivity of the octahedral Ni atoms with the phosphates and the ethylenediamine template. The Ni atoms connect with each other via an

(24) Large single crystals of NiAPO-1 were synthesized in a solvothermal system in which ethylene glycol was used as a solvent and ethylenediamine as a template agent. Typically, a certaint amount of nickelous acetate $Ni(OAc)_2$ and aluminum triisopropoxide $(i\text{-pro})_3Al$ were first dispersed into ethylene glycol (EG) with stirring, and then phosphoric acid (H_3PO_4, 85 wt % in water) was added dropwise to form a gel. Finally, ethylenediamine (en) was added to the above mixture. The gel molar composition was 1.0:0.2:2.0:5.0:100, $Ni(OAc)_2$:$(i\text{-pro})_3Al$:H_3PO_4:en:EG. The reaction mixture was further stirred for 1−2 h until it was homogeneous and then was sealed in a Teflon-lined stainless autoclave and heated at 180 °C for 20 days under autogenous pressure. The resulting product containing large light green single crystals was filtered, washed thoroughly with deionized water, and dried at ambient temperature.

(25) Crystal structure data for $[NiAlP_2O_8][C_2N_2H_9]$: F_w = 336.74, monoclinic, space group $P2_1/c$ (No. 14), a = 8.542(2) Å, b = 15.564(3) Å, c = 7.627(1) Å, β = 110.60(1)°, V = 949.1(3) Å^3, T = 293(2) K, Z = 4, ρ_{calcd} = 2.357 Mgm^{-3}, $F(000)$ = 680, μ(Mo Kα) = 2.506 mm^{-1}, θ_{max} = 23.30°. Goodness-of-fit on F^2 was 1.044, R_1 [for $I > 2\sigma(I)$] = 0.0281, wR_2 = 0.0746. Data/restraints/parameters = 1259/0/181. A suitable single crystal was selected for single-crystal X-ray diffraction analysis. Structural analysis was performed on a Siemens SMART CCD diffractometer using graphite-monochromated Mo Kα radiation (λ(Mo Kα)) = 0.71073 Å). The data were collected at a temperature of 20 ± 2 °C. Date processing was accomplished with the SAINT processing program (SMART and SAINT (software packages), Siemens Analytical X-ray Instruments, Inc., Madison, WI, 1996). Direct methods were used to solve the structure using the SHELXTL crystallographic software package (SHELXL, version 5.1, Siemens Industral Automation, Inc., 1997). Hydrogen atoms were located by a difference Fourier map and were added to the structure factor calculation. All non-hydrogen atoms were refined anisotropically.

O(2) bridging atom to form an infinite zigzag chain. Each Ni atom coordinates with one N atom of the ethylenediamine template with a Ni−N bond length of 2.077 Å. Each Ni atom shares five oxygens with adjacent P atoms, two of which bridge one P(1) atom. The Ni−O bond distances are in the range of 1.999−2.224 Å. It is noted that the O(2) atom is a μ_3-O, which bridges two Ni atoms and one P(1) atom. Two Ni atoms and one P(2) are connected through oxygen atoms to form a 3-MR, which is rarely observed in 3-D open-framework structures. Magnetic measurement of NiAPO-1 suggests that NiAPO-1 is paramagnetic with a magnetic moment of 2.2 μ_B, consistent with a Ni^{2+} d^8 spin state. The unique −Ni−O−Ni− chains might lead to some interesting magnetic properties,[26,27] which will be further studied.

The template molecule not only acts as a ligand for Ni atom, but also plays a charge balance role in its monoprotonated state for the negatively charged $[NiAlP_2O_8]^-$ macroanion. Thermogravimetric analysis shows that the template molecules decompose in the region 270−450 °C with a weight loss of 17% (theoretical value: 18%). X-ray powder diffraction analysis shows that NiAPO-1 transforms to an amorphous phase above 450 °C. ICP analysis gave the content of Ni, Al, and P is 17.1%, 7.6%, and 17.6% (Calcd. Ni, 17.4%; Al, 8.0%; P, 18.4%), respectively. Elemental analysis gave the content of C, H, and N as 6.5%, 2.5%, and 7.2%. (Calcd. C, 7.1%; H, 2.7%; N, 8.3%), respectively. The composition of $[NiAlP_2O_8][C_2N_2H_9]$ generated from chemical analysis is in agreement with the empirical formula given by single-crystal X-ray diffraction analysis.

In conclusion, using Ni^{2+} transition metal ion, a 1-D aluminophosphate chain can be successfully assembled by connecting the terminal oxygens with Ni octahedra. It is possible that the 1-D $AlP_2O_8^{3-}$ chain species are first formed during the crystallization followed by its assembly around the Ni^{2+} cations and the template molecules. Further investigation of the formation mechanism is underway. The successful synthesis of NiAPO-1 demonstrates that many types of new 3-D open-frameworks can be assembled by lower dimensional networks that contain terminal oxygen groups via transition metal cations. This work will further assist in the rational design and synthesis of target materials.

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Supporting Information Available: Tables of crystal data, structure solution and refinement, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for NiAPO-1. This material is available free of charge via the Internet at http://pubs.acs.org.

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