

Control of Structural Ordering in Crystalline Lamellar Aluminophosphates with Periodicity from 51 to 62 Å

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The self-assembly of polymeric inorganic materials in the presence of organic species has led to the synthesis of many novel microporous materials such as aluminosilicate zeolites and microporous aluminophosphates.^{1–4} Recently, a new family of mesoporous materials with pore sizes beyond 100 Å have been prepared through the templating of lyotropic liquid crystal phases.^{5–8} Much of the work has been focused on silicate materials, but there has been an increasing interest in extending mesoporous materials into other compositional domains such as aluminophosphates and transition metal oxides.^{9,10}

One of the most distinct structural characteristics of mesostructured materials is their amorphous wall structure. For example, for 1-D ordered MCM-50 type lamellar phases, even though the interlayer spacing is well defined, there are no registries between adjacent layers. The amorphous nature of the inorganic wall is also true for hexagonally ordered mesostructures with 2- or 3-D ordering or cubic phases with 3-D ordering. In short, these materials have no periodic ordering in any direction at the atomic scale. The reason for the formation of these amorphous walls is in part related to the loosely assembled structure of micelles and liquid crystals compared to smaller and more rigid molecular templates. As a result, the communication between self-assembly processes occurring at different ends of micelles or liquid crystals is not adequate to generate atomically ordered structures.

To enhance communication between polymerizing species so that the information about the structural ordering at one location can be transmitted to other sites, one synthesis strategy is to use long-chain diamines as templates. One advantage of these diamines is that they can form relatively strong N–H···O type hydrogen bonding with the inorganic host and the information about such an interaction can be passed from one end of the structure to the other side through the C–C backbone.

Here, we report hydrothermal syntheses and characterizations of four crystalline lamellar aluminophosphates denoted as UCSB-50, UCSB-51, UCSB-52, and UCSB-53. These materials have the same inorganic composition and architecture, but they have different interlayer spacings because of the different chain lengths of diamines. One of the most distinct features of these

phases is that adjacent inorganic sheets are in perfect registry despite the large interlayer distance (equal to $1/3$ of the c axial length). The periodicity along the hexagonal c axis is unusually long and ranges from approximately 51 to 62 Å.

UCSB-51 was synthesized by preparing a mixture of aluminum isopropoxide (3.17 g), 85% H₃PO₄ (3.48 g), ethylene glycol (25.30 g), and 1,10-diaminododecane (1.68 g). The mixture had a pH of 7.0 and was subsequently heated at 180 °C for 4 days in a Teflon-coated steel autoclave. UCSB-50, -52, and -53 could be synthesized under similar conditions, but with 1,9-diaminononane, 1,11-diaminoundecane, or 1,12-diaminododecane as the structure-directing agent, respectively. Qualitative elemental analyses were performed on a JEOL JSM-840A scanning electron microscope equipped with an X-ray energy dispersive system. The thermal analysis in the static air on UCSB-51 shows that the loss of lattice water molecules happens at temperatures between 100 and 150 °C whereas the decomposition and burning of diamine molecules occur at temperatures between 250 and 650 °C. The total observed weight loss at 800 °C is 44.0%, in agreement with the calculated value of 43.3%.

The inorganic sheet in UCSB-50, -51, -52, and -53 consists of four- and six-membered rings (excluding bridging oxygen atoms, Figure 1) and is oriented perpendicularly to the rhombohedral c axis.¹¹ Because there is a terminating P=O group on each of the three phosphate groups (PO₄³⁻), all phosphate groups are 3-connected to other parts of the sheet. In comparison, two-thirds of Al sites are 4-connected as in zeolites and one-third of Al sites are 6-connected in a pattern similar to Zr⁴⁺ in well-known layered zirconium phosphates. Thus, mathematically, the inorganic sheet is a mixed 3-, 4-, and 6-connected 2-D net. To our knowledge, such a novel net has not been previously observed in other materials.¹² The structural details obtained here may help elucidate structures of noncrystalline, mesostructured aluminophosphates.

The inorganic sheets are separated by monolayers of diamines perpendicular to the c axis with an interlayer distance equal to

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- (11) Crystal data for all four compounds: rhombohedral, space group $R\bar{3}$, $Z = 3$, temp = 298 K, transparent plate, Bruker SMART diffractometer, Mo K α radiation ($\lambda = 0.71073$ Å), $2\theta_{\max} = 45^\circ$, refinement on F^2 . Crystal data for UCSB-50: [NH₃(CH₂)₉NH₃]₇(H₂O)₈ [Al₁₃(PO₄)₁₈H], $a = 16.593(2)$ Å, $c = 51.617(9)$ Å, $V = 12307.3(3)$ Å³, $0.31 \times 0.20 \times 0.040$ mm³, $\mu = 0.34$ mm⁻¹, $R(F) = 7.30\%$, $R_w(F^2) = 21.8\%$, GOF = 1.02 for 228 parameters and 2518 unique reflections with $I > 2.0\sigma(I)$. Crystal data for UCSB-51: [NH₃(CH₂)₁₀NH₃]₇(H₂O)₈ [Al₁₃(PO₄)₁₈H], $a = 16.538(2)$ Å, $c = 55.622(9)$ Å, $V = 13174(3)$ Å³, $0.24 \times 0.23 \times 0.026$ mm³, $\mu = 0.32$ mm⁻¹, $R(F) = 7.29\%$, $R_w(F^2) = 24.2\%$, GOF = 1.06 for 228 parameters and 2598 unique reflections with $I > 2.0\sigma(I)$. Crystal data for UCSB-52: [NH₃(CH₂)₁₁NH₃]₇(H₂O)₈ [Al₁₃(PO₄)₁₈H], $a = 16.574(2)$ Å, $c = 58.493(8)$ Å, $V = 13915(3)$ Å³, $0.37 \times 0.20 \times 0.026$ mm³, $\mu = 0.31$ mm⁻¹, $R(F) = 6.26\%$, $R_w(F^2) = 21.4\%$, GOF = 1.05 for 228 parameters and 2849 unique reflections with $I > 2.0\sigma(I)$. Crystal data for UCSB-53: [NH₃(CH₂)₁₂NH₃]₇(H₂O)₈ [Al₁₃(PO₄)₁₈H], $a = 16.536(3)$ Å, $c = 62.22(2)$ Å, $V = 14735(6)$ Å³, $0.40 \times 0.20 \times 0.013$ mm³, $\mu = 0.29$ mm⁻¹, $R(F) = 7.78\%$, $R_w(F^2) = 23.9\%$, GOF = 1.03 for 228 parameters and 2687 unique reflections with $I > 2.0\sigma(I)$.
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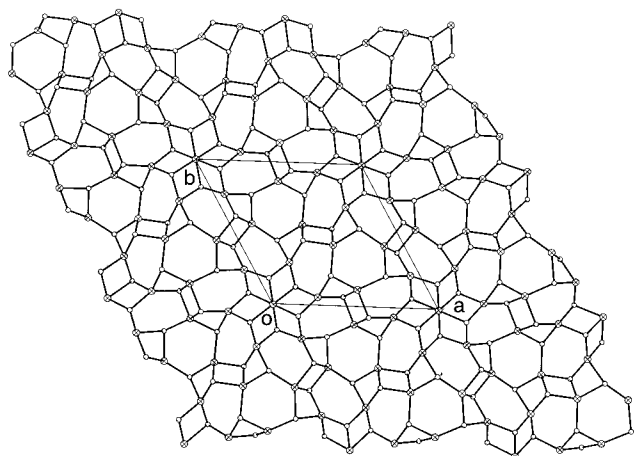


Figure 1. Projected down the crystallographic c axis, a mixed 3-, 4-, and 6-connected 2-D net. Larger circles represent aluminum sites, and smaller circles represent phosphorus sites. The terminal and bridging oxygen atoms are omitted for clarity.

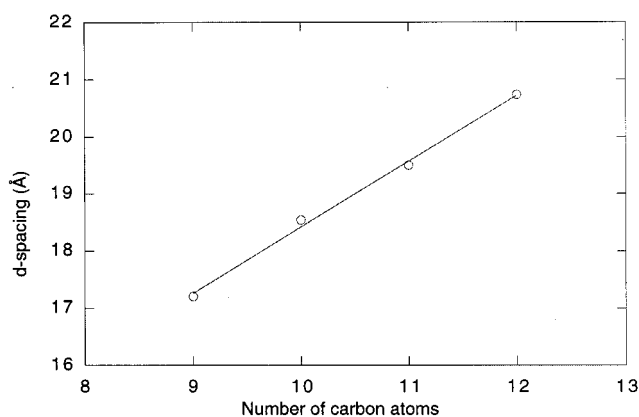


Figure 2. Approximate linear relationship between the number of C atoms in a diamine and the interlayer spacing.

$\frac{1}{3}$ of the c axial length, i.e., between approximately 17 and 21 Å. The interlayer distance is consistent with the d spacing of the strongest peak observed in the X-ray powder diffraction of each sample. An approximate linear correlation is observed between the chain length of diamines and the interlayer spacing (Figure 2). Sayari et al. reported the synthesis of lamellar aluminophosphates with d spacing from 20 to 36 Å using primary or tertiary amines with a long alkyl chain such as $C_{12}H_{25}NH_2$.¹³ Using $C_{10}H_{21}NH_2$, Ozin et al. reported the synthesis of lamellar

aluminophosphates with an approximate d spacing of 29 Å.¹⁴ Both hexagonal and lamellar mesostructured aluminophosphates have been made by Feng et al. using the cationic surfactant $C_{16}H_{33}(CH_3)_3NBr$. None of these materials, however, possesses the periodic ordering in any direction at the atomic scale. A similar lack of the atomic-level ordering is also observed in transition metal oxides or lamellar silica prepared from neutral diamines.^{15,16}

The success of our synthetic strategy is supported by structural features such as the location of diamines. While it is difficult to determine the atomic positions of all carbon atoms in the backbone, the terminal nitrogen atomic positions are well defined. Also the carbon atoms that are directly attached to the nitrogen atoms can be readily located. The ordering of nitrogen atoms is clearly due to the strong interaction between amine groups and the inorganic sheet. In addition to the electrostatic interaction, the $N-H\cdots O$ type hydrogen bonding plays an essential role. The presence of the hydrogen bonding is supported by the short $N\cdots O$ distance. The shortest $N\cdots O$ distances for three ordered N-atom positions in UCSB-50 are 2.76, 2.82, and 2.83 Å, respectively.

In conclusion, organic diamines have been employed in a strategy that is designed to enhance host-guest interactions and also to promote the effective communication between different interaction sites. A new family of lamellar aluminophosphates with large interlayer separations and with 3-D periodicity at the atomic scale have been obtained. The formation of these new materials is driven by several factors including nanoscale phase separation and hydrogen bonding. It is expected that the synthesis strategy described here can be extended to include even larger structure-directing agents and to more complex inorganic systems so that mesoporous materials with atomically ordered frameworks can be more readily prepared.

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Supporting Information Available: Tables of crystal data, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters and four figures showing ORTEP diagrams. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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