A novel layered aluminophosphate with corner-sharing AlO₆ chains

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The synthesis, Raman spectroscopy and crystal structure of a novel layered aluminophosphate is described. The new phase was derived by the sol-gel method starting from a modified low hydrothermal ALPO₄-34 zeolite synthesis procedure[1]. The structure was solved by direct methods using single-crystal X-ray diffraction. The synthesized layered material, with composition [AlPO₃(OH)F(H₂O)]-(H₉C₄ON), crystallizes in the monoclinic space group P2₁/a with a = 9.2282(5) Å, b = 6.9152(4) Å, c = 14.4615(9) Å, β = 101.57(1)°. Layered aluminophosphates with AlO₆ polyhedra have been previously described [2], although in these compounds Al octahedral share edges. The novel compound has corner sharing AlO₄F(H₂O) chains along [010], where fluorine is at the shared apex, four oxygen atoms are shared with PO₄ tetrahedra and the fifth oxygen is a H₂O group. This kind of aluminophosphate chains is found in nature in tancoite [3]. Chains are linked along [100] through corner sharing with a PO₄ group of the adjacent chain plus hydrogen bonding of the H₂O group. Layers are stacked along c* through hydrogen bonding with a double layer of morpholine (H₉C₄ON) molecules. The chemical stability field of the novel material is strongly dependent from the fluorine/aluminum ratio of the starting gel. At lower fluorine concentrations only ALPO₄-34 and/or AlPO₄ (berlinite) are stable depending on the morpholine content. Crystals growth morphology depends on the supersaturation conditions of the starting gel: at low concentrations crystals are well-developed hexagonal like plate shaped and are very thin. At higher concentrations they show a more elongated morphology. A treatment with H₂CO₃ leads to a complete morpholine removal, as shown by in situ Raman spectroscopy. Powder X-ray diffraction reveals that after morpholine extraction, the material diffract still coherently in two dimensions while a strong broadening is shown for basal planes.


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