Crystal structure of MAPO-20 sodalite: theoretical analysis of three-color ordering of Mg, Al and P in a sodalite unit

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Abstract: The crystal structure of synthetic MAPO-20 with the sodalite topology, including a possible position for encapsulated tetramethylammonium species (TMA), was determined at room temperature by X-ray single-crystal diffraction, and at room temperature, 200 K and 20 K by neutron powder diffraction. Unit cell composition: Mg2Al4P6O24·2(CH3)4N, Mr=682.7, cubic, Pm3n (223), a = 9.0437 (8) Å (X-ray). Because refinement in P43n of the room-temperature data gave no improvement over that in Pm3n, the framework must be fully expanded at room temperature. The short C-O distances (3.05–3.20 Å) indicate weak hydrogen bonding between framework oxygen and the hydrogens in the encapsulated molecule. Broadening of peaks in the neutron data at 20 K suggests a transition to non-cubic symmetry. MAPO-20 is a derivative of ALPO-20, which has strict alternation of Al and P over the tetrahedral vertices. One third of the Al atoms are substituted by Mg. Theoretically, there are many ways to accomplish this substitution. A three-color mathematical enumeration of the 4 Mg, 8 Al and 12 P atoms over the 24 vertices of the truncated octahedron yielded 27 distinct models and 18 mirror images. No diffraction evidence for long-range order was obtained from the present study. The nuclear magnetic resonance data of Barrie & Klinowski (1989) can be explained by local order of several types in which no 4-ring contains 2 Mg.

Key-words: sodalite, MAPO-20, crystal structure, framework ordering.

Introduction

The geometrical relationships and chemical bonding between an inorganic framework and an encapsulated organic species are important for the synthesis and applications of microporous materials (Flanigen et al., 1988; Pluth & Smith, 1989). Most of the new microporous aluminophosphates contain organic material encapsulated during synthesis (Wilson et al., 1982). Included among them is ALPO-20, which has the same framework topology as the natural mineral sodalite, (Na3Al4Si6O24)6H2O: structure determination by Pauling, (1930, and Löns & Schulz, 1967). The present paper describes the crystal structure of MAPO-20, a synthetic magnesium aluminophosphate with encapsulated tetramethylammonium ion (TMA) prepared by Barrie & Klinowski (1989). These authors concluded from magic-angle-spinning nuclear magnetic resonance spectra of 27Al and 29P that the Mg, Al and P atoms have a specific type of ordering. We use X-ray and neutron diffraction studies coupled with a theoretical analysis of three-color topochemistry of the sodalite unit to place limits on the ordering.

There is a large literature on materials with the sodalite structure. Some recent structure determinations are: Beagley et al. (1982), synthetic LiCl, KCl and NaCl sodalites with cubic symmetry; Depmeier (1988a, b), synthetic (Ca,Sr)4Al12O24(S,Mo,W)3O8 sodalites with cubic and pseudocubic symmetries; Felsche et al. (1986, 1987), Na8Al2Si6O24·8H2O with hydrogen bonding, and the anhydrous product with a relaxed framework; Hassan & Buseck (1989), no-sean with incommensurate modulations; Hasha et al. (1988), SAPO-20, (Al0.4Si1.3P0.4)O2 to (Al0.36Si0.8P0.12)O2 synthetic silicaluminosilicates.

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