A New Family of Crystalline, Three Dimensionally Ordered, Microporous Structures

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Summary Theoretical arguments, supported by preliminary electron microscopic evidence, reveal that solids with a composition $A_xB_xC_{m-x}O_{2m}\cdot nH_2O$ (where A is an exchangeable monovalent cation, B is typically Al or Ga, C is typically Si or Ge, and x, m, and n are integers the magnitudes of which are governed by the size of the unit cell) possess novel structures with tunnel diameters of molecular dimension; such structures may be generated by recurrent twinning at the unit-cell level.

Principally for practical purposes there is considerable interest in designing and engineering ordered porous materials possessing pore diameters in the 5—20 Å range. It is an extra advantage if the open frameworks are negatively charged and accommodate exchangeable cations, as do the zeolites, which are hydrophilic. There are also advantages when the framework is essentially neutral, as in the so-called porotectosilicates of which ZSM-5 and ZSM-11 are renowned examples; these tend to be hydrophobic and oleophilic. Both classes are of great importance in heterogeneous catalysis and in the science and technology of molecular separation. In this note we report the discovery of a new type of tunnel structure that may be generated by recurrent twinning of the faujasite structure (Figure 1). The new structure constitutes the archetype of a large family of materials covering a range of chemical compositions: in principle they may be hydrophilic or hydrophobic.

The mineral faujasite [idealized composition $(Na_2,Ca,Mg)_{29}Al_{58}Si_{134}O_{384}\cdot 240\ H_2O$] is cubic with a = 24·7 Å. The faujasite structure consists of cuboctahedra (at the 24 vertices of which there are either SiO_4^{4-} or AlO_4^{5-} tetrahedra) linked *via* hexagonal prisms (so-called 'double six rings'). The synthetic zeolites X and Y have the same framework structure as faujasite, but with different values of the Si : Al ratio from 1·0 : 1 (X) to beyond 1·5 : 1 (Y). Very recently it has been demonstrated[1] that the Si : Al ratio may be greatly increased, to beyond 100 : 1 for example, while still retaining the faujasite framework structure. It is also known that in zeolites X and Y Ga and In may enter the tetrahedral sites occupied by Al and Ge, and Sn may enter the tetrahedral sites occupied by Si.

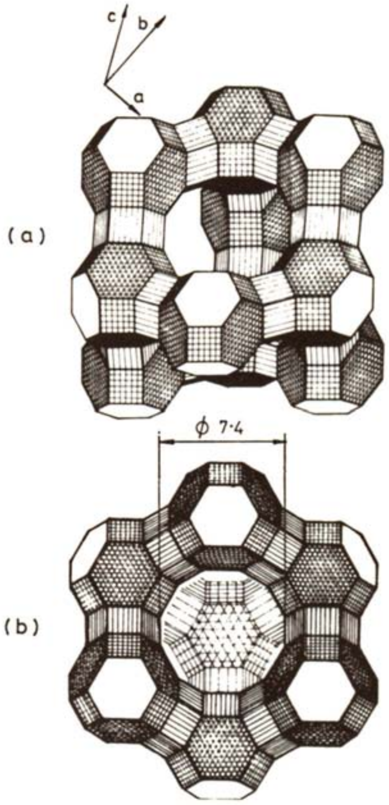

Figure 1. (a) Polyhedral model of the faujasite structure showing cuboctahedra connected by hexagonal prisms ('double-six' connectivity). (b) View of the same structure along [111]. The aperture to the supercage is 7·4 Å.

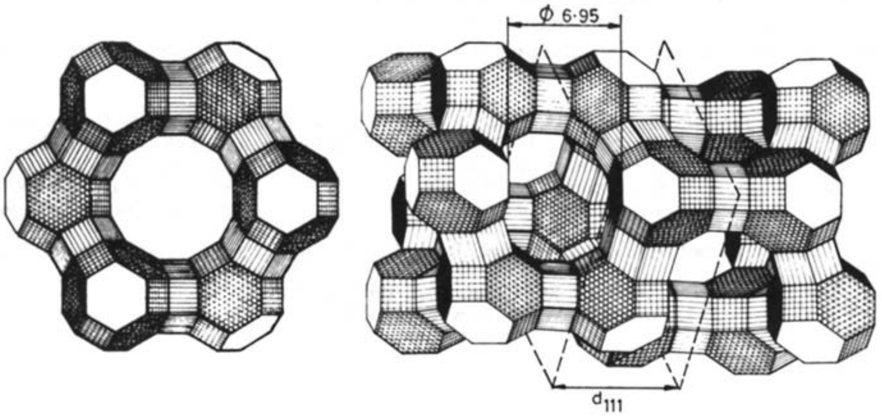

Figure 2. The faujasite structure with two consecutive (111) twin planes which are denoted by dashed lines. Note slight change in shape and size of the apertures which intersect the tunnel that lies along [111]. At the left is the view along the [111] tunnel.

During the course of high resolution electron microscopic studies of Na–Y and La–Y zeolites, we noted that recurrent twinning on (111) takes place. The effect of inserting two consecutive twin planes into the faujasite structure is illustrated in Figure 2. The parent structure,[2] which consists of an array of 'supercages,' each with a free diameter of *ca.* 13 Å, separated by apertures with a diameter of 7·4 Å, is converted by recurrent twinning into a tunnel structure. The diameter of the tunnel varies between 7·4 and 13 Å. Intersecting these tunnels which run along ⟨111⟩ are apertures which are elliptical with dimensions of 6·9 and 7·4 Å. The new structure is hexagonal. Figure 3 emphasises the essential changes in connectivity of the cuboctahedra at the twin plane. The regular, untwinned faujasite structure may be represented by ···· △△△△ ···· where each △ denotes a building unit repeat along ⟨111⟩ (*i.e.* 14·2 Å). The sequence ··· △/▽/△/▽/△ ··· signifies that a twin lamella, ▽, bounded by a pair of {111} twin planes, denoted by slashes, is inserted along every alternate unit cell repeat along ⟨111⟩. If the number of twin planes introduced in this way is n, the length of the tunnel in the new structure is $14{\cdot}2 \times (n + 1)$ Å + 6·95 Å. The second term in the sum accounts for twice the distance between the extreme (111) plane and the wall of the supercage, with which the tunnel terminates at each end. (The new structure described here has a certain kinship with, but is distinct from, the so-called 'structure 6' discussed as a theoretical possibility by Breck[3].) A sequence such as ···· △△/▽/△△/▽ ··· signifies that a twin lamella is introduced between flanking pairs of regular repeat units along ⟨111⟩. This gives rise to a new structure composed of interconnected 'hypercages' which are 49·6 Å in length and a diameter which again varies between 13 and 7·4 Å. This new structure has been identified by high resolution electron microscopy, by selected area electron diffraction, and by optical diffractometry.

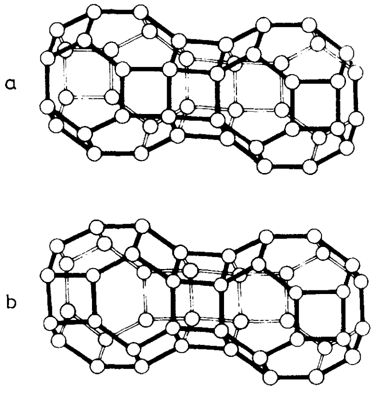

Figure 3. (a) The faujasite structure. In (b) there is a (111) twin plane, perpendicular to the paper, intersecting the hexagonal prisms.

It can be shown by similar arguments that recurrent twinning at the unit cell level can convert other well known open structures into new microporous variants (compare ref. 4); mechanical deformation of parent structures covering a range of initial compositions is currently being explored as a means of effecting such conversions.

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