Babelite: the Random Member of the ABC-D6R Family of Zeolites

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A newly synthesised zeolite of the ABC-family of double six-membered ring crystalline structures, babelite, is composed of an infinite random stacking of double six-ring layers in an ordered hexagonal array.

A one-dimensionally random molecular sieve of the chabazite family has not been seriously considered theoretically[1] though DLS-refinement[2] and lattice-energy calculations[3] on all known and many hypothetical ordered lattices indicate that all packing sequences for double six-rings are geometrically and energetically feasible. Haphazard stacking of D6R layers produces a unique distribution of cage structure. Unlike the amorphous molecular sieves, these cavities are well defined 7 Å diameter cylindrical voids. The feature that differentiates babelite from the fully ordered zeolites is the length of the cavities. In babelite the cages continuously increase stepwise in 5 Å segments. Access to all cavities is *via* eight-membered ring pore openings. In addition to its use as an adsorber and catalyst, this unusual material may represent a new and zeolitic example of spatial chaos.

Babelite crystallises from aluminosilicate gels containing a range of SiO_2/Al_2O_3 ratios, between 10 to 28, in the presence of both sodium and lithium cations. Adding very small amounts of lithium cations to a fresh sodium aluminosilicate gel result in the crystallisation of this phase. Compositions under which babelite has been found to crystallise in the presence of lithium are: $Na/Na + Li = 0.9$; $Na_2O/SiO_2 = 0.4$–0.5; $SiO_2/Al_2O_3 = 10$–28. Large amounts of lithium however suppress crystallisation. In the absence of lithium, the faujasite structure is preferred. A batch composition resulting in the crystallisation of the babelite phase is: 8.64 $NaOH : 0.96\ LiNO_3 : 10\ SiO_2 : 2Al(OH)_3 : 250\ H_2O$. Crystallisation occurs readily at 100 °C after three days.

The use of lithium cations in the formation of zeolite structures has not been thoroughly investigated though crystallisation of mixed phases of faujasite and EMC-2 have been suggested to occur from Na/Li containing gels.[4–7] Synthetic chabazite, a well known ordered double six-layer structure in this family, was first prepared hydrothermally by Barrer and Baynham in 1956 from a potassium aluminosilicate gel.[8]

The resulting crystals of babelite exhibit a spherical morphology around 6 μm in diameter composed of very small plate-like crystals. The SiO_2/Al_2O_3 ratio of babelite is similar to that found in synthetic chabazite. Double six-membered ring structures contain only one symmetrically equivalent T-atom site. The presence of only one site in babelite is verified by the ^{29}Si NMR confirming the stacking of only double six rings. The molecular sieving properties of this material were also explored. Babelite readily adsorbs water and oxygen nearly equivalent to the amounts adsorbed by chabazite. Hexane is adsorbed but cyclohexane is not. Such results are consistent with the presence of 4 Å diameter windows formed by the interconnecting layers throughout the structure. The random nature of the stacking in this material does not adversely affect its thermal stability. The ammonium cation forms of babelite and chabazite exhibit similar stability's upon thermal treatment.

The unusual X-ray powder diffraction pattern of synthetic babelite is shown in Fig. 1(*a*). The broad and misshapen lines intermixed with sharp reflections observed for this material is reproducible from sample to sample. Random stacking in the *c* direction is expected to result in a distinct X-ray powder diffraction pattern containing both sharp and broad lines. This diffraction pattern matches well the simulated diffraction pattern for a random stacking of the double six-ring layers and is shown in Fig. 1(*b*) for comparison. The simulated XRD pattern of babelite was calculated using the DIFFAX[9–11] software. In spite of the fact that the calculation is based on a pure SiO_2 lattice while the material contains both framework aluminium and ammonium cations in addition to silica, there is a good agreement between the calculated and observed diffraction pattern. Simulated diffraction patterns of other possible stacking sequences could not be fit to the observed X-ray diffraction pattern of babelite.

Though bonding in the zeolites occurs in all three dimensions, the ABC-D6R structures can be visualised as a close packing of double six rings analogous to the packing of spheres in a metallic solid. The double six ring layers are represented by AA, BB, and CC differing from one another by a 120° rotation about the *c* axis. In gmelinite the sequence is AABB, in chabazite, AABBCC, and in $AlPO_4$-52, it is AABBCC-AACCBB.[12,13] Babelite is represented by a non-repeating stacking sequence of AA, BB, and CC where AA may be followed by either BB or CC, BB randomly followed by either

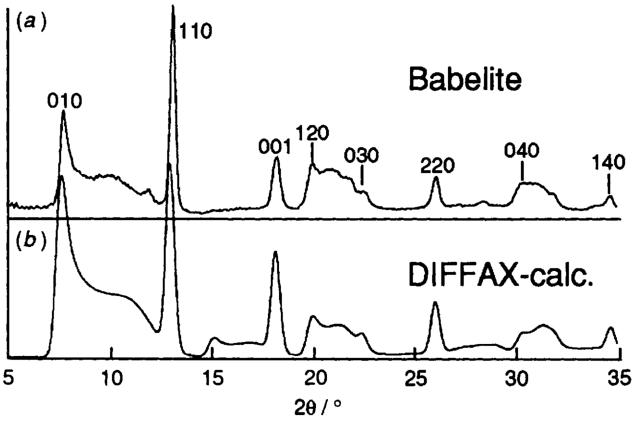

Fig. 1 The X-ray powder diffraction pattern of NH_4-babelite measured at 200 °C (*a*), and calculated pattern of a pure SiO_2 babelite lattice (*b*)[11]

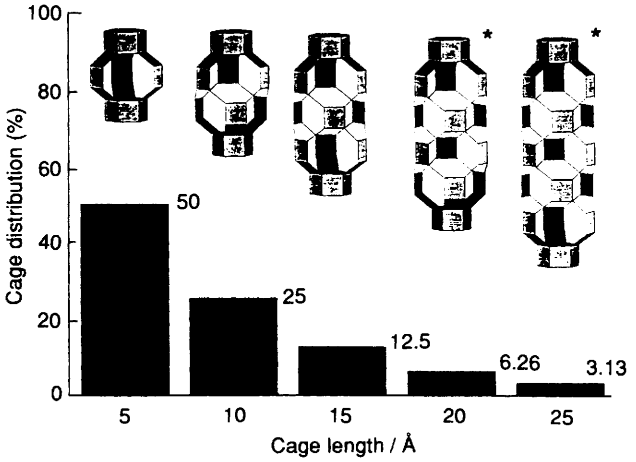

Fig. 2 Babelite contains a discrete distribution of cages. All cages have a constant diameters of 7 Å and lengths consistent with the cages found in gmelinite (5 Å), chabazite (10 Å) and $AlPO_4$-52 (15 Å). New cage types are indicated by*. The probability of finding a cage with specific length of *n*-double layers is proportional to 2^{-n}.

AA or CC, and CC randomly followed by either AA or BB, *ad infinitum*. Repeated stacking of the same layer, *e.g.* AA–AA, is not allowed. All structures in the double six ring family have maximum hexagonal symmetry and show an identical 001 topological projection except for gmelinite as it is lacking the CC layer.

Since the unit cell of babelite is undefined in the *c* direction, a sub-cell, that comprises the single stacking layer, AA, is defined as a tool to index the sharp lines in the diffraction pattern. This allows the calculation of the *a* axis (a = 13.7 Å) and the layer thickness (c = 4.9 Å). Sub-cell indexing of the diffraction lines in babelite are given in Fig. 1. The value calculated for *a* compares well with the other double six member ring containing structures, gmelinite (a = 13.8, c = 10.0 Å), chabazite (a = 13.8, c = 15.0 Å) and $AlPO_4$-52 (a = 13.7, c = 29.0 Å).[12] The large *a* dimension is a further indication that this material has no single six-membered rings in the stacking sequence as a contraction in this dimension would be expected for materials containing both single and double six member rings.[1,12]

The most unique feature found in the babelite structure is the presence of cages of regularly varying length all accessible through eight member ring windows. The length of a cage is defined by the distance between two identical layer sequences where all intervening sequences are of the other two layer types. The cage size in babelite changes in well defined 5 Å steps. The probability of finding a cage with the specific length of *n*-double layers is proportional to 2^{-n}. This implies that 50% of the sequences are gmelinite type (two-double layers), 25% chabazite-type (three-double layers), 12.5% AFI-type (four-double layers), 6.25% new five-double layer, 3.12% of new six-double layer long cage, and so on with even longer cages. The types and distribution of cages in babelite are illustrated in Fig. 2. Unlike the three-dimensionally amorphous molecular sieves like amorphous SiO_2 and carbon, babelite exhibits uniformity in pore-openings (4 Å) and also a uniformity in cages, in the way that the size of every cage is known exactly. In the three-dimensionally amorphous materials, both opening and cage sizes will have a continuous gausian distribution.[14] In fully ordered ABC-6 zeolite stacking of the AABBCC type, a single cage type would be present. The distinct distribution of cages in babelite is a singular product of completely random stacking of the D6R layers. This order from randomness is expected to impart distinctive bulk adsorptive and diffusional properties to this material.

Faulted domains have been observed embedded in other zeolite structures[15–18] and near random stacking has been noted for the molecular sieve, zeolite beta.[9,10,19–21] Unlike babelite, faulting in beta may occur in two directions.[10] The two ordered end members of beta have never been synthesised and only one type of faulted beta phase is presently known.[22] The presence of stacking faults in this material does not generate unique cage structures nor does faulting impart special zeolitic properties as expected for babelite. Three ordered ABC-D6R polytypes are known and other less faulted phases have been described with properties differing from that of babelite.[23,24]

In applications such as adsorption and ion exchange, babelite should show unique separation coefficients owing to its discrete exponential change in the size of the cages. Understanding these completely random structures and learning how to control the degree of faulting should provide valuable insight into the mechanism of how these commercially valuable microporous materials grow. Such knowledge may ultimately lead to the generation of new ABC-D6R phases with stacking sequences and cages larger than those presently known.

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