The Structure of Zeolite CSZ-1 interpreted as a Rhombohedrally Distorted Variant of the Faujasite Framework

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In contrast to earlier suggestions that the structure of CSZ-1 corresponds to the theoretical hexagonal structure 6 of Breck, evidence from a combination of techniques demonstrates that it is instead topologically similar to the faujasite framework, differing in having rhombohedral, rather than cubic, symmetry.

Crystallizations from $Cs_2O{\cdot}Na_2O{\cdot}SiO_2{\cdot}Al_2O_3{\cdot}H_2O$ gels yield, at relatively low caesium levels, a high-silica polymorph of faujasite (FAU) known as CSZ-3,[1] and at higher caesium contents a large-pore zeolite designated CSZ-1.[2] Both materials exhibit a platelet morphology. Preliminary powder X-ray diffraction data from CSZ-1 were interpreted on the basis of a hexagonal unit cell with $a = 17.4$ and $c = 28.4$ Å,[2] implying a correspondence with the theoretical structure designated as 'Structure 6' by Breck,[3,4] which is generated from that of faujasite by recurrent twinning across every adjacent layer in the [111] direction. Crystallographic twinning across <111> planes in FAU[5] and FAU-related[6] materials has been observed by high resolution electron microscopy (h.r.e.m.) and by selected area electron diffraction. Recent electron microscopy studies of 'CSZ-1-type materials'[7] were also interpreted in terms of recurrent twinning, akin to the structure 6 model.[2,7,8] We have now examined a range of CSZ-1 materials using h.r.e.m., selected area electron diffraction, powder X-ray diffraction, ^{29}Si magic angle spinning (m.a.s.) n.m.r. spectroscopy, and structure modelling. In contrast to previous suggestions,[2,7,8] we conclude that CSZ-1 is not Breck's structure 6, but instead is topologically similar to faujasite. It is, however, distinct in having rhombohedral, not cubic symmetry.

High resolution lattice imaging and electron diffraction demonstrate that CSZ-1 and FAU-framework materials are structurally related. Electron diffraction patterns of CSZ-1, CSZ-3, and a platelet (Na,K)-zeolite Y, viewed along the platelet [111] axes, are remarkably similar (Figures 1—3). The principal difference is that the $<4\bar{4}0>$ spot intensities are systematically weaker in the CSZ-1 pattern. Structure factor calculations indicate that weaker $<4\bar{4}0>$ intensities can be expected when caesium occupies sites outside the sodalite cages in the FAU framework such as the open 6-ring window site (site II). The presence of caesium at sites (such as I′ or II′) within the sodalite cages does not strongly affect the $<4\bar{4}0>$ intensities. Extensive ammonium-exchange of CSZ-1,† which

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† 40% of the original caesium content is retained in this material.

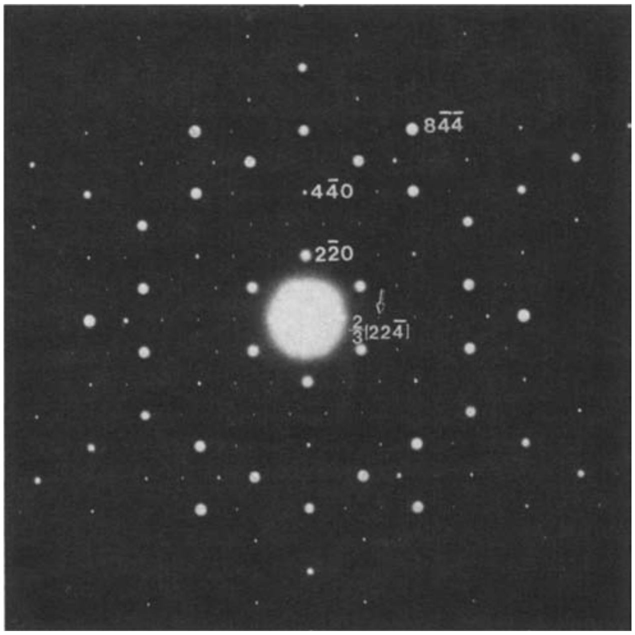

Figure 1. [111] diffraction pattern of CSZ-1.

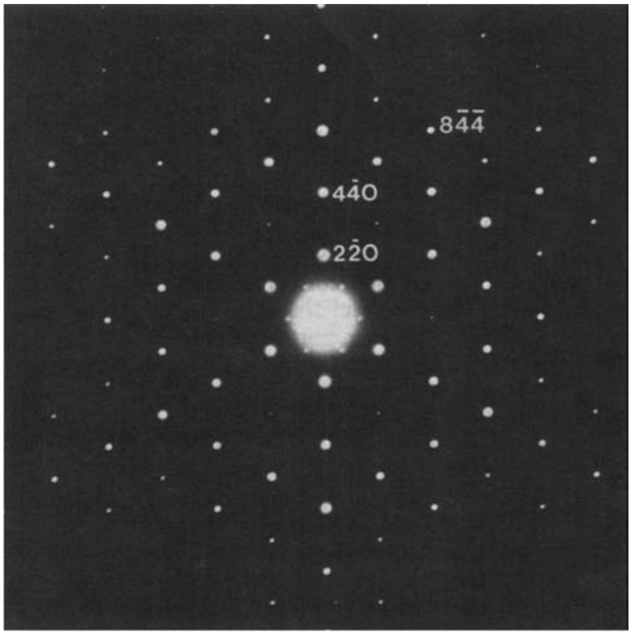

Figure 3. [111] diffraction pattern of platelet (Na, K)-zeolite Y.

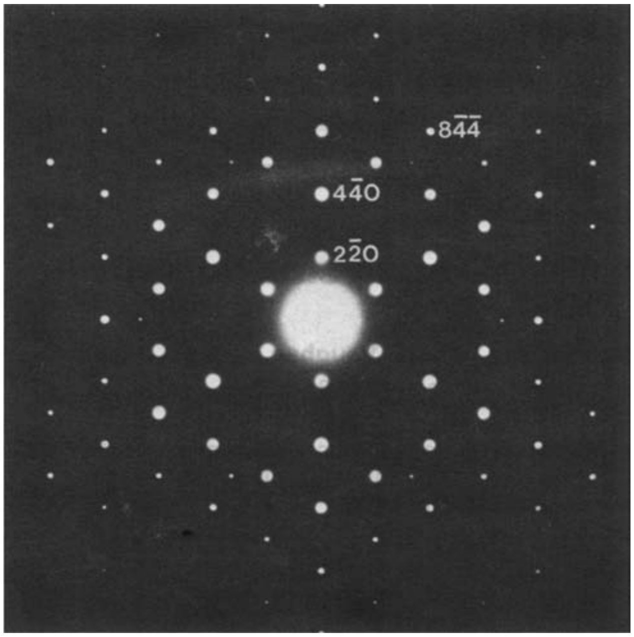

Figure 2. [111] diffraction pattern of CSZ-3.

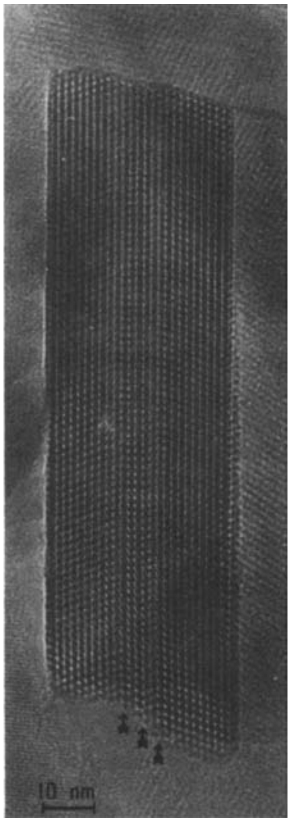

Figure 4. [$1\bar{1}0$] structure image of a CSZ-1 platelet, showing twin planes near the centre.

is expected to remove the readily exchangeable caesium cations, such as those at site II, does indeed restore the <$4\bar{4}0$> intensities, rendering an electron diffraction pattern similar to that of the platelet FAU materials (Figures 2,3). The faint spots at ostensibly superlattice positions, such as 2/3 ($22\bar{4}$), are visible in all the patterns and are insensitive to crystal tilting. Therefore, they do not represent superlattice reflections, but are associated with streaking of higher order Laue zone spots along the [111] direction. The streaking derives from the thinness of the platelets, and such spots are most pronounced in CSZ-1 where the crystals are characteristically thinnest. High resolution electron micrographs of CSZ-1 zeolites taken with the beam parallel to the [$1\bar{1}0$] axis show that the layer stacking along the [111] direction, normal to the platelet surface, is predominantly faujasite-like in character (Figure 4). Twin planes, marked by changes in stacking direction, are observed characteristically near the centre of each platelet. Such twin planes are found to be no more prevalent in CSZ-1 than in FAU materials with similar (platelet) morphologies such as CSZ-3.[1] A *single* unit cell of Breck's structure 6 would

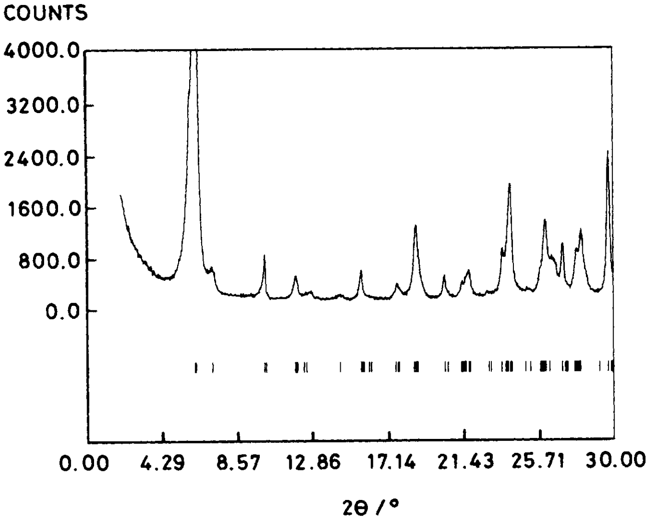

Figure 5. Powder *X*-ray diffraction patterns of CSZ-1. Tick marks show positions of Bragg peaks for rhombohedral indexing (see text).

require adjacent twin planes, and even one such occurrence of recurrent twinning has not been observed in these materials.

Other physical characterization methods reveal CSZ-1 zeolites to be quite distinct from FAU materials. ^{29}Si M.a.s. n.m.r. measurements show broad, unresolved features, suggesting the presence of more than one crystallographic silicon site. I.r. spectra exhibit two different modes in the 600—630 cm^{-1} region (in contrast with FAU materials that show a single framework mode in the region 565—580 cm^{-1}), and CSZ-1 materials have markedly different sorption selectivities.

All the above experimental observations can be rationalized on the basis that CSZ-1 has the same sodalite cage connectivity as the FAU framework, but differs in having rhombohedral rather than cubic symmetry. The powder *X*-ray diffraction patterns of CSZ-1 zeolites, which are consistent with the unit cells of neither the FAU framework (space group $Fd\bar{3}m$, a = 24.6 Å), nor structure 6 ($P6_3/mmc$; a = 17.4, c = 28.4 Å), can be indexed satisfactorily on the basis of a rhombohedral cell derived from the cubic (FAU) cell by a slight elongation along the [111] body diagonal (that is parallel to the platelet axis). Least-squares optimization of the rhombohedral lattice constants for a representative CSZ-1 material with Si/Al = 2.8, gives a_{rh} = 17.37(2) Å and α_{rh} = 59.43(4)° (Figure 5). Similar results from a range of CSZ-1 materials indicate a general correlation between the extent of the distortion and the framework composition, the distortion being greater at lower Si/Al ratios. With this reduction in symmetry, the single T-site of the FAU framework gives rise to a minimum (in space group $R\bar{3}m$, No. 166) of four crystallographically inequivalent T-sites, consistent with the ^{29}Si m.a.s. n.m.r. and i.r. results.

Minor crystallographic distortions in zeolite systems[9] are relatively common, although they are generally reversible. In contrast, dehydration–rehydration and/or ion-exchange does not effect a transformation of the rhombohedral CSZ-1 structure to cubic symmetry. The origins of this unusual structural characteristic, which could possibly arise from an elastic stress field associated with the twin planes, or from composition gradients associated with inaccessible caesium cations, are being further explored.

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