

# The synthesis of the new zeolite, ERS-7, and the determination of its structure by simulated annealing and synchrotron X-ray powder diffraction

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The new zeolite ERS-7 (EniRicerche-molecular-Sieve-7), which was synthesized within a narrow temperature and compositional range using *N,N*-dimethylpiperidinium as a structure directing agent, has a structure consisting of 17-sided (4<sup>6</sup>5<sup>4</sup>6<sup>5</sup>8<sup>2</sup>) picnic-basket-shaped cages connected by 8-membered ring windows.

The discovery of new zeolites is closely linked to the use of increasingly complex and novel structure directing agents (SDAs). The syntheses of extra-large pore UTD-1<sup>1</sup> and CIT-5<sup>2</sup> zeolites, for example, were recently accomplished by using Cp<sub>2</sub>Co<sup>+</sup> and N(16)-methylsparteinium, respectively. Because of the lack of selectivity typical of many SDAs, good results may also be achieved by carefully controlling other synthesis parameters. This is the case with the 'simple' *N,N*-dimethylpiperidinium cation, which was reported to favor the crystallization of ZSM-51 (NON).<sup>3</sup> By systematic investigation of different synthesis parameters (*i.e.* temperature, crystallization time, and the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>, SDA/SiO<sub>2</sub>, OH<sup>-</sup>/SiO<sub>2</sub> and H<sub>2</sub>O/SiO<sub>2</sub> molar ratios), we have obtained several known microporous framework compounds (MOR, MTW, LEV, NON),<sup>‡</sup> together with the hitherto unknown ERS-7 phase.<sup>4</sup>

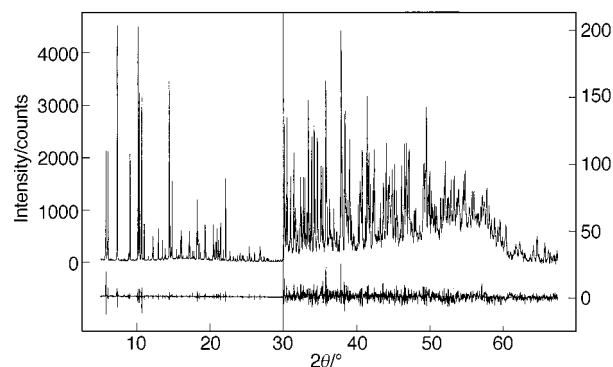
To synthesize ERS-7, a reaction mixture with the composition 0.2SDA : 0.3Na<sub>2</sub>O : 0.04Al<sub>2</sub>O<sub>3</sub> : 1SiO<sub>2</sub> : 40H<sub>2</sub>O was prepared by using sodium silicate (Carlo Erba, 27 wt.% SiO<sub>2</sub>, 8 wt.% Na<sub>2</sub>O) and Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·16H<sub>2</sub>O as sources of silica and aluminium, respectively. Aqueous *N,N*-dimethylpiperidinium hydroxide (30 wt.%) was synthesized by refluxing an ethanol solution of 1,5-dibromopentane and dimethylamine; the bromide salt obtained was filtered, washed with ethanol, dried under N<sub>2</sub>, dissolved in demineralized water and finally exchanged to the OH<sup>-</sup> form by electrodialysis. The reaction mixture was then charged in a Teflon-lined stainless steel autoclave and heated under autogeneous pressure at 170 °C for 7 days.

The pure and well crystallized ERS-7 product was only obtained in a narrow range of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratios near 25. Increasing the aluminium content in the reaction mixture resulted in the formation of LEV (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 15) or a small amount of an unidentified crystalline phase (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 20). Pure MTW was obtained when the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio was increased to 80, while NON crystallized from reaction mixtures containing little (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 214) or no aluminium. If instead, the SDA/SiO<sub>2</sub> molar ratio was decreased, MOR was formed as a product. At 155 °C, ANA crystallized first, while ERS-7 started to appear only after 7 days, the pure phase being obtained after 14 days with the consumption of ANA. Similar kinetics were observed at 170 °C, with MOR forming first, and ERS-7 completely crystallizing after 5 days.

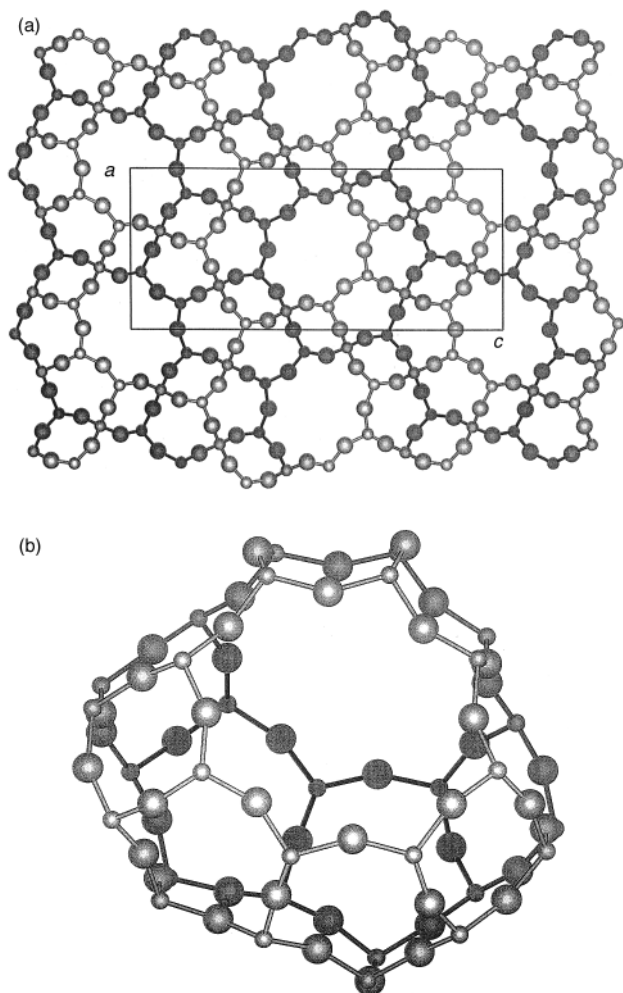
The framework structure of ERS-7 was determined by simulated annealing.<sup>5</sup> As implemented by MSI for zeolite-like structures,<sup>6</sup> the simulated annealing algorithm required the unit cell dimensions, the space group symmetry, the total number of T-sites (or more precisely, the number of cationic framework

atoms) in the unit cell, and the number of crystallographically independent T-sites. High resolution synchrotron X-ray powder diffraction data were collected at room temperature on dehydrated template-free H<sup>+</sup> ERS-7§ at beamline X7A of the Brookhaven National Synchrotron Light Source. The first 30 large reflections were indexed with the TREOR90 software package<sup>7</sup> to obtain a primitive orthorhombic unit cell ( $M_{30} = 50$ ,  $F_{30} = 242$ ). The space group *Pnma* was selected as a starting-point based on the unambiguous determination of extinction class and the absence of significant second-harmonic-generation emission. The framework density was determined by measuring the density of an ERS-7 precursor (2.04 g cm<sup>-3</sup> using a Micromeritics AccuPyc 1330 helium displacement pycnometer) and then correcting for the thermogravimetric loss of H<sub>2</sub>O and SDA trapped inside the pores (15.5 wt.% using a Mettler TG50 thermobalance) as well as the Na<sup>+</sup> content (1.2 wt.% from elemental analysis); the final value was 1.70 g cm<sup>-3</sup> which corresponds to 48.1 T-sites per unit cell.

Assuming 48 total T-sites and *Pnma* symmetry, simulated annealing runs with different initial random seeds were performed for each possible number of symmetry-independent T-sites, from 6 to 12. From the 1000 runs that assumed 6 symmetry-independent T-sites, 373 unique framework topologies were generated. The correct structure was identified among these by geometry optimizing<sup>8</sup> the simulated structures, sim-



**Fig. 1** Experimental and difference XRD patterns from the Rietveld refinement of the ERS-7 structure. The scale of the high angle data is expanded to better illustrate its detail.  $R_{wp} = 6.11\%$ ,  $R_p = 5.60\%$ ,  $\chi^2 = 1.566$ ,  $R_B = 3.28\%$ , 1407 reflections, 12491 data points. A total of 195 parameters were refined: scale (1), profile shape (6), positional parameters (56), anisotropic thermal parameters (112), and 20 evenly spaced background points with linear interpolation between points. Lattice parameters were refined during the LeBail fit to the profile, but fixed during the model refinement due to slight oscillation. The pseudo-Voigt profile shape of Thompson *et al.*<sup>10</sup> was used including the asymmetry correction of Finger *et al.*<sup>11</sup> Refined profile parameters were  $U = 0.597$ ,  $V = -0.057$ , and  $W = 0.008$  (degrees squared), Lorentzian strain broadening = 0.005°, anisotropic (011) strain broadening = 0.131, and S/L = 0.013 (H/L was fixed at the measured value of 0.011). The thermal ellipsoid of O9 has one slightly negative root.



**Fig. 2** (a) The [010] projection of ERS-7 showing the 8-membered ring channels. Final values for the lattice parameters were  $a = 9.79976(4)$ ,  $b = 12.41163(6)$ ,  $c = 22.86063(11)$  Å, and  $V = 2780.561$  Å<sup>3</sup>. (b) Schematic representation of the 17-sided ( $4^65^46^58^2$ ) 'picnic-basket'-shaped cage.

ulating their X-ray diffraction (XRD) patterns and visually comparing them to the experimental XRD pattern; it also had the overall best (lowest) figure of merit (value of the cost function) of any topology generated. The structure model was then refined by the Rietveld technique from the synchrotron data using the GSAS<sup>9</sup> software package, resulting in the fit to the XRD data shown in Fig. 1. Each Si atom is 4-coordinated. The total number of symmetry-independent oxygens is 14. The range of Si–O bond lengths was 1.573 to 1.623 Å (avg. = 1.595 Å), and the O–Si–O and Si–O–Si bond angle ranges were 105.0° to 111.3° (avg. = 109.5°) and 139.3° to 171.4° (avg. = 155.4°) respectively.

The framework structure of ERS-7, shown in Fig. 2(a), can be described as having a one-dimensional 8-membered ring channel system running along the  $b$  axis, with large side-pockets along the sides of the channel. The structure can be assembled entirely by 17-sided ( $4^65^46^58^2$ ) picnic-basket-shaped cages ( $9.0 \times 7.6 \times 8.2$  Å) that share 6 and 8-membered ring faces, such that the channel system runs through the 'basket-handles' while the pockets form the 'basket bottoms' [Fig. 2(b)]. The 8-membered ring channels are consistent with our observations that ERS-7 adsorbs H<sub>2</sub>O and methanol, but not  $n$ -hexane. The

cages connected to these channels explain the fact that while  $N,N$ -dimethylpiperidinium is too large to fit into the 8-membered ring channel ( $7.4 \times 6.2$  Å), it can still be removed upon decomposition at high temperature without damaging the framework. The ERS-7 framework can also be viewed as consisting of chains of smaller 11-sided cages that share 6-membered ring faces along the  $a$  axis, but connect in the  $b + c$  and  $b - c$  directions by additional 4-rings rather than by corners, edges, or faces.

The synthesis of ERS-7 demonstrates that the preparation of new zeolites is related not only to the use of increasingly complex SDAs but also to the systematic screening of the synthesis parameters. The use of simulated annealing to solve the structure of a fairly complex new zeolite demonstrates its importance as an alternative approach when single crystals are unavailable.

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## Notes and References

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‡ Synthesis products were identified by X-ray powder diffraction using a Philips PW1710 vertical diffractometer.

§ Synchrotron XRD data were collected at room temperature over the range  $5^\circ \leq 2\theta \leq 67.45^\circ$  in steps of  $0.005^\circ$  while the sample (in capillary) was rotated at *ca.* 1 Hz. For data collection, a double-crystal Si[111] monochromator set for  $\lambda = 1.1528$  Å, a Ge[220] analyzer, horizontal incident and receiving slits of 13 mm and 16 mm respectively, and a sample-detector distance of 700 mm were used. Dehydrated template-free H<sup>+</sup> ERS-7 (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 16.7) was prepared by calcining at 550 °C for 5 h under flowing air, repeated ion exchange in an ammonium acetate solution at 60–70 °C, drying at 120 °C, calcining again in air and then under  $10^{-5}$  Torr vacuum, and flame-sealing in a quartz capillary. CCDC 182/932.

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