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# Imposition of Polarity on a Centrosymmetric Zeolite Host: The Effect of Fluoride Ions on Template Ordering in Zeolite IFR

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The need for polar solids for use as nonlinear optical (NLO) materials has led to numerous attempts to incorporate interesting organic molecules inside the pores and cavities of zeolites and other microporous materials.[5] The major advantage of this approach is the combination of inorganic frameworks with optically active organic molecules to produce very robust functional materials with many potential applications. A major obstacle to this work is the need for the final material to crystallize in a noncentrosymmetric space group to be an active NLO material. This paper describes how fluoride, added as a mineralizer to a zeolite synthesis, leads to crystallization in a polar noncentrosymmetric space group for zeolite IFR, a framework whose topological symmetry is centrosymmetric and therefore nonpolar. This also leads to a noncentrosymmetric ordering of the organic template molecule in the channels, which is vital if materials with good NLO properties are to be prepared. The reasons for this ordering can be traced to the influence of the fluoride ion on the structure of the framework. When the fluoride ions and templates are removed by calcination, the framework symmetry is centrosymmetric.

It has been known for a number of years that pure silica zeolite phases can be prepared hydrothermally in the presence of fluoride ions as mineralizers.[6] However, it is only recently that NMR and X-ray diffraction studies have indicated that $F^-$ can interact strongly with the framework silicon atoms, giving rise to pentacoordinated $[SiO_{4/2}F]^-$ in a number of pure silica phases.[7] Purely siliceous zeolite IFR can be prepared from fluoride-containing media using benzylquinuclidinium ($BQ^+$) or benzylhydroxyquinuclidinium ($BQol^+$) cations as templating (structure directing) agents.[2b,8] The structure of calcined IFR (i.e., where the template and fluoride have been thermally removed) was originally solved from powder X-ray diffraction, and showed the framework topology to be centrosymmetric (monoclinic space group $I2/m$).[9] The framework structure consists of small $[4^35^26^1]$ cages linked together to form a unidimensional channel system. Further powder diffraction studies identified the fluoride ion positions in the as-made material as being inside the small cages and also identified possible template positions.[10] However, because of the inherent problems of powder X-ray diffraction, further details of the structure could not be determined with any great precision. Subsequently, small crystals (approximately 20$\mu$m × 20$\mu$m × 10$\mu$m) of both [BQ,F]-IFR and [BQol,F]-IFR were prepared suitable for single-crystal X-ray diffraction studies using the microcrystal X-ray diffraction station at the CCLRC Synchrotron Radiation Source, Daresbury Laboratories, UK. Data were collected at a range of temperatures from 30 up to 370 K and all showed essentially the same results.

Refinements of the centrosymmetric $I2/m$ models against data collected using both [BQ,F]-IFR and [BQol,F]-IFR crystals were unsatisfactory. For example, in the [BQol,F]-IFR case at 30 K, the refinement stopped with the agreement factor, $R_1$, of approximately 9%. Lowering of the symmetry to polar space group *Im* produced a much-improved refinement with a final residual agreement factor of 4.5%.[11] The difference in agreement factors between the centrosymmetric and polar space group refinements is clearly significant, and indicates that the polar model is the correct one. In addition, the hydrogen atoms of the template were located in the difference Fourier maps and further refinement revealed only very small residual electron density peaks that could not be modeled as any extra/disordered template atoms.

A powdered sample of [BQol,F]-IFR frequency doubled the light from a Nd:YAG (1064 nm) laser to such an extent that the resulting green light (532 nm) was visible to the naked eye. This demonstration of NLO properties is proof that the crystal structure is indeed noncentrosymmetric.

The final model, illustrated in Figure 1, indicated that the template is ordered in a noncentrosymmetric arrangement within the pores of the zeolite. It also revealed that the fluorine, as part of a pentacoordinate $[SiO_{4/2}F]^-$ unit, is only present in one of the two possible $[4^35^26^1]$ cages, although disordered over two possible sites within the cage it occupies. Single-crystal X-ray diffraction experiments on the [BQ,F]-IFR sample, despite the crystals being of slightly lesser quality than the [BQol,F]-IFR ones, show the same arrangement of template and fluoride ions. The reason the fluoride and templates order in such a fashion is not altogether apparent at first sight. There is no obvious significant interaction between neighboring templates that might account for the ordering, such as the dipolar "head-to-tail" interactions that can order *p*-nitroaniline inside zeolite pores.[1d] In fact, the location of the template is more likely to be affected by the position of the fluoride ion, since it is the negative charge on the $F^-$ that balances the positive charge on the cationic template. As the templates are asymmetric, with the positive charge localized primarily on the quinuclidine unit, it is this end of the template that is most strongly attracted by a region of negative charge. This strong, electrostatic interaction will lead to the template being oriented so that the quinuclidinium end of the molecule is as close to the negatively charged $F^-$ ion as possible. The alternative orientation of the template, which is necessarily present in the centrosym-

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(7) Example crystal data for [BQol,F]-IFR, $Si_{16}O_{32}\cdot F\cdot C_{14}H_{19}(OH)N$: unit cell $a = 18.5710(8)$ Å, $b = 13.4943(6)$ Å, $c = 7.7153(3)$ Å, $\beta = 102.302(1)°$, $V = 1889.08(4)$ Å$^3$ at $T = 30$ K, $Z = 2$, monoclinic spacegroup *Im*, $\rho_{calcd} = 2.1$ g cm$^{-3}$; 4955 integrated intensities ($2.48° < \theta < 28.08°$, $\lambda = 0.6448$ Å), 2360 unique, 2258 observed [$F^2 > 2\sigma(F^2)$]. Final refinement (322 least-squares parameters) converged to $wR(F^2_{\text{obsd data}}) = 0.129$, $R(F_{\text{obsd data}}) = 0.048$, $S(F^2_{\text{all data}}) = 1.096$.

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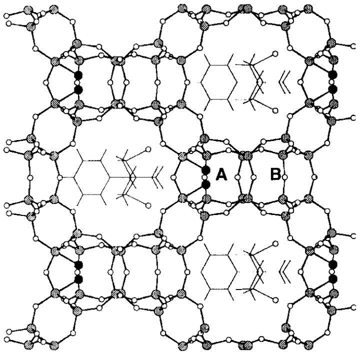

**Figure 1.** The structure of [BQol,F]-IFR viewed parallel to the crystallographic *c* axis. The Si, O, and F atoms are depicted as dark gray, open, and black spheres, respectively. The $BQol^+$ cation template is represented as a line drawing with the oxygen of the hydroxide group as an open sphere. The $[4^35^26^1]$ cage occupied by F is labeled **A**, the unoccupied cage **B**.

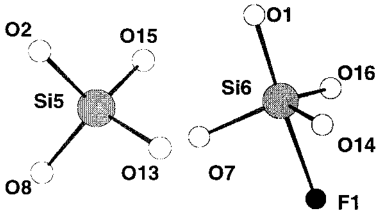

**Figure 2.** The tetrahedral coordination polyhedron around Si5 (left) and the almost trigonal bipyramidal coordination around Si6 (right). These two silicon atoms would be equivalent by symmetry in the centrosymmetric *I*2/*m* model. Selected distances and angles (at 30 K): Si6−F1, 1.92(1) Å; Si6−O1, 1.678(6); Si6−O7, 1.625(4) Å, O1−Si6−F1, 176.4(4)°, O1−Si6−O7, 99.3(4)°. Si5−O bond distances are in the range 1.603(6) to 1.634(6) Å, and O−Si5−O angles range from 107.9(4)° to 111.0(4)°.

metric model, will have the positive charge on the template significantly further away from the fluoride ions. The arrangement of the template is therefore intimately connected with the ordering of the fluoride ions into the $[4^35^26^1]$; an ordered arrangement of $F^-$ will lead to ordered templates.

Why the fluoride orders into only one of the two possible $[4^35^26^1]$ cages is thus the important question in determining the structure of the as-made IFR materials. There are two possible reasons for this. One is a simple electrostatic effect in which the negatively charged $[SiO_{4/2}F]^-$ units arrange themselves as far away from each other as possible, which requires ordering of the fluoride ions. The second reason can be found in the distortions of the framework structure caused by the presence of the five-coordinated $[SiO_{4/2}F]^-$ units. Figure 2 shows the coordination polyhedra around two of the eight crystallographically independent silicon atoms in the polar structure. These two silicon atoms are equivalent by symmetry in the centrosymmetric *I*2/*m* model, and the large differences in bond lengths and angles between these two polyhedra adds significant weight to the assertion that the polar model is the correct one. The Si6-centered polyhedron is much nearer a trigonal bipyramid than a tetrahedron, as would be expected for the $[SiO_{4/2}F]^-$ unit. The coordination around the seven other silicon atoms in the structure is tetrahedral.

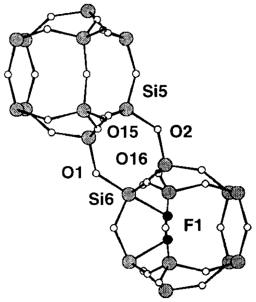

**Figure 3.** Two $[4^35^26^1]$ cages from the structure of $BQol^+$-ITQ4 linked by a single four-ring unit, illustrating the presence of fluorine in only the lower cage. Atom shading as for Figure 2.

The distortion of the Si6 coordination polyhedron also has an effect on the single four-ring (containing oxygens O1, O2, O15, and O16) that links the $[4^35^26^1]$ cages together (Figure 3). The fluorine in the lower cage causes the O1−Si6−O16 to be distorted from tetrahedral (109.7°) to 102.4(3)°, and the Si6−O1 distance is elongated to 1.678(6) Å, which is about 0.07 Å longer than that expected for a Si−O bond. The presence of another fluorine in the upper cage, bonded to Si5, would distort the single four-ring even further by similarly decreasing the O2−Si5−O15 angle to an extent that would strain the small four-ring unit to an unfavorable degree. Therefore, accommodation of $F^-$ into one cage necessarily requires that the next is empty, the next-but-one then has $F^-$ present, and so on. A combination of this distortion and electrostatic effects probably causes the fluorine to order into one cage only, which in turn causes ordering of the templates, thus requiring the overall polar noncentrosymmetric structure.

This work represents the first time that the distortion of a silica zeolite framework by fluoride has been experimentally verified by using diffraction. That the presence of fluoride causes such a dramatic change of symmetry and ordering of the organic template may have an effect on how future optically active composite materials of this kind are designed.

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**Supporting Information Available:** Listings of refinement details, atomic coordinates, thermal displacement parameters, and bond lengths and angles (PDF). Supporting Information is also available in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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