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The Location and Ordering of Fluoride Ions in Pure Silica Zeolites with Framework Types IFR and STF; Implications for the Mechanism of Zeolite Synthesis in Fluoride Media

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Abstract: Single-crystal X-ray diffraction studies carried out at a synchrotron radiation source have allowed the structure solution and location of fluoride ions inside as-made pure silica zeolites with the IFR and STF framework structures. The local environment of the fluoride has been identified, and unusual ordering of the fluoride ions has been discovered in both cases. The details of the crystal structures are used to suggest structural features that are important in determining the ordering of fluoride ions in zeolites. A mechanism for how the fluoride ordering occurs is suggested for IFR and STF based on the local structure of small cages that make up these zeolites, and the implications for the mechanism of crystal growth are discussed.

Introduction

Zeolites and aluminophosphates are porous, crystalline solids with channels and voids of dimensions similar to those of small organic molecules. Their chemical properties combined with their structural architecture lead to many applications in catalysis, ion exchange, and gas adsorption. Pure silica zeolites are generally prepared in two different ways under hydrothermal conditions, at high pH in the presence of hydroxide (OH^-) ions, or at lower pH in the presence of fluoride (F^-) ions. Aluminophosphate materials, which are isoelectronic with pure SiO_2 materials, can also be prepared with fluoride ions present, usually at near-neutral conditions. The choice of these so-called mineralizers can have a profound influence on the particular solid formed. For pure silica zeolites the major advantages of the fluoride route, which was pioneered by Flanigen and Patton,[1] is that the solids are relatively defect-free,[2] are generally low density, and can be grown as quite large crystals.[3] The lack of defects in a zeolite can have major effects on the hydrophobicity of the material, which can be important in catalytic applications (when the pure silica zeolite is "doped" with catalytic metals such as Ti, Fe, Al, or B).[4,5] The potential advantages of zeolites prepared in fluoride media means that there is driving force for understanding how fluoride ions are involved in controlling the structure and properties of zeolites and aluminophosphates. Camblor and co-workers have led the way in determining how fluoride ions affect the synthesis and have postulated that they perform two main functions during the formation of the zeolite; a mineralizing role in improving the solubility of silicate ions at neutral pHs and a catalytic role in the formation of Si−O−Si bonds.[6] However, it is also clear that the fluoride ions are often incorporated into many of the zeolite and aluminophosphate structures, balancing the positive charge of organic structure-directing cations (SDAs) that are also incorporated into the "as-made" structures. Koller and co-workers, using solid-state NMR spectroscopy, have shown that the fluoride ions are connected to the framework, forming five-coordinated $SiO_{4/2}F^-$ units.[7,8] The fluoride ions therefore introduce a negative charge onto the framework itself. In the hydroxide synthesis of pure silica zeolites, the negative charge on the framework arises from the presence of connectivity defects (e.g., $Si{-}O^-{\cdots}HO{-}Si$ pairs), while in aluminosilicate zeolites substitution of Si(IV) by Al(III) yields a net negative charge on the framework.

As mentioned above, the growth of large crystals in fluoride media has been reported.[3] This property has obvious implications for the ease with which the structures of the materials can be determined by single-crystal X-ray diffraction. Unfortunately, "large" is a relative term, and it is often the case that the crystals prepared are still too small for data collection on laboratory instruments. However, the development of single-crystal X-ray diffractometers at synchrotron sources[9] means that even very small ($>\sim5000\ \mu m^3$) zeolite crystals can now be studied. Recent studies from our group show that the location of fluoride ions can be determined using X-ray diffraction at a synchrotron source and have unambiguously confirmed the presence of five coordinated $SiO_{4/2}F$ units first proposed from NMR experiments.[10,11] This is in marked contrast to connectivity defects

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and framework aluminum ions (at least in high-silica aluminosilicate zeolites), which tend to be randomly or near randomly disordered, making them undetectable by X-ray diffraction when they are in relatively low concentrations.

The crystal structures of pure silica zeolites prepared by the fluoride method indicate that the F^- ions tend to reside inside small cages,[10−13] and are usually connected to a silicon atom that is part of a four-membered ring (i.e., a ring containing four silicon atoms). Depending on the structure and the conditions, the fluoride ion can be connected to one silicon atom in particular or disordered over a number of sites inside the same small cage. NMR experiments indicate that at room temperature this can be dynamic disorder.[7,8] In the clathrasil AST[12] the fluoride ion is located at the center of a $[4^6]$ cage (i.e., a cage made up of six four-membered rings, also known as double four rings[14]). Calculations have shown that this arrangement may act to stabilize this type of cage, adding a "structure-directing" function to the list of possible roles of fluoride in the synthesis of pure silica zeolites. Certainly, this arrangement of fluoride inside $[4^6]$ cages is well-known in aluminum phosphate and gallium phosphate chemistry, and the same structure-directing influence has been proposed,[15] although this is not the case under all conditions.[16,17] In the cases of the pure silica zeolites NON,[13] STT,[10] and IFR[11] the fluoride ions have been located inside $[4^15^46^2]$, $[4^35^4]$, and $[4^35^26^1]$ cages, respectively. Recently, Fyfe and co-workers[18] have used elegant two-dimensional NMR experiments to identify the position of the fluoride ions inside a $[4^15^26^2]$ cage unambiguously in the pure silica version of zeolite MFI (silicalite), a case where X-ray diffraction is more difficult due to twinning problems of the crystal and where different workers have previously given conflicting results.[19] In all the pure silica zeolite cases reported thus far, the fluoride is connected to (or near) silicon atoms that are part of a four-membered ring, perhaps indicating a structure-directing function for the F^- ions similar to that proposed in aluminum and gallium phosphates.

As well as the local structure of the $[SiO_{4/2}F]^-$ units, X-ray diffraction, unlike NMR spectroscopy, also reveals any long-range order in the arrangement of fluoride ions. Remarkably, in the case of zeolite IFR,[11] our crystal structure determination revealed that the material is noncentrosymmetric and polar despite the centrosymmetric nature of the framework. Polar solids show a number of interesting macroscopic properties, including optical nonlinearity (NLO), pyroelectricity, piezoelectricity, etc., and this has led to numerous attempts to incorporate interesting organic molecules inside the pores and cavities of zeolites and other microporous materials,[20] and supramolecular channel inclusion compounds.[21] The major advantage of zeolite-based materials is the combination of inorganic frameworks with dipolar 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 spacegroup to be an active NLO or pyroelectric material.

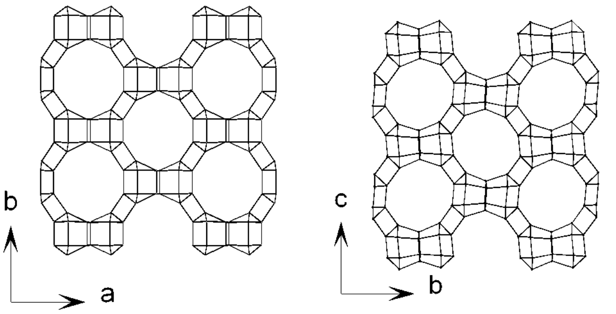

Figure 1. Framework structures of the zeolites studied IFR (left) and STF (right). In this depiction of zeolite frameworks, the solid lines join the centers of the tetrahedra (i.e., the silicon atoms). Oxygen atoms will be near the centers of the lines.

The lowering of nonpolar to polar symmetry in IFR is due to the ordering of fluoride ions inside only half of the possible $[4^35^26^1]$ cages, which in turns leads to ordering of the organic SDAs.[11] Our prediction was that the local structure of the $[SiO_{4/2}F]^-$ units combined with information on their ordering throughout the structure would shed light on the role that fluoride plays in the formation of the zeolite structure. In this contribution we report further investigation of the structure of zeolite IFR, together with X-ray diffraction experiments on a related fluoride-containing pure silica zeolite with the STF framework structure (Figure 1).[22] In both cases the location of fluoride ions has been identified. Zeolite STF has some features that are similar to those of zeolite IFR (see below), and we predicted that long-range ordering of the $[SiO_{4/2}F]^-$ would occur in this zeolite also. The results bear out this prediction, although the manner of ordering is not the same as in zeolite IFR. The impact of these results on the role of fluoride in the formation of these zeolites is also discussed.

Experimental Section

The as-made zeolite with the pure silica framework IFR was synthesized by the previously published method[11] using either benzylquinuclidinium (BQ^+, **1**) or hydroxybenzylquinuclidinium ($BQol^+$, **2**) cations as the structure-directing agents (SDAs). As-made STF was prepared using a slight modification of the published method,[23] with racemic (*R*-,*S*-) *N*,*N*-dimethyl-6-azonium-1,3,3-trimethylbicyclo(3.2.1)-octane ($DMABO^+$, **3**) as the SDA. In this synthesis 6.08 g of TEOS (tetraethyl orthosilicate) are hydrolyzed in 52.84 g of an aqueous solution that is 2.76×10^{-4} mols of the SDA (*N*,*N*-dimethyl-6-azonium-1,3,3-trimethylbicyclo(3.2.1)octane) in hydroxide form per gram of solution. The ethanol (4.37 g) and 48.42 g of water are allowd to evaporate from the mixgure. The resultant mixture is more a solid at this point, and after grinding it to powder, 0.61 g of HF (48%) was added. The mixture was then heated in a Teflon-lined steel autoclave at 150 °C for 38 days under static conditions.

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[22] The structures of zeolites can be named in different ways. For example, zeolites with the IFR framework are also known as MCM-58, ITQ-4, and SSZ-42, and those with the STF type framework SSZ-35 and ITQ-9. In this paper report the framework type of the compound using the International Zeolite Association three-letter code nomenclature. Thus zeolite IFR means a zeolite with the IFR-type framework and so on. Further details can be found in Meier, W. M.; Olson, D. H.; Baerlocher, C. *The Atlas of Zeolite Structure Types*; Elsevier: New York, 1996 or at www.iza-online.org.

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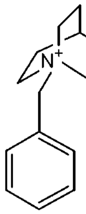

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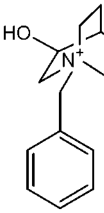

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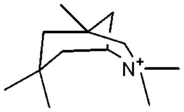

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In both cases the single crystals prepared were too small for data collection on our in house X-ray diffractometers, and therefore microcrystal X-ray diffraction data were collected at low temperature (160 K) using a Bruker AXS SMART CCD area-detector diffractometer on the high-flux single-crystal diffraction station 9.8 at the CCLRC Daresbury Laboratory Synchrotron Radiation Source, Cheshire, UK. The experiments used X-rays of wavelengths of around 0.6−0.7 Å selected by a horizontally focusing silicon (111) monochromator and vertically focused by a cylindrically bent palladium-coated zerodur mirror. The data sets for all experiments covered more than a hemisphere of reciprocal space with several series of exposures, each series with a different crystal orientation and each exposure taken over 0.15° rotation. Corrections were made for the synchrotron beam intensity decay as part of standard interframe scaling procedures. Refinements of the structural models were carried out using standard least-squares procedures. Full structure-determination parameters as well as final agreement factors for both structures are given in Table 1. Full details of the individual refinements, atomic positions, and bond distances can be found in the Supporting Information.

For IFR the structure-directing agents were found to be ordered in the channels of the zeolites, and the correct spacegroup was confirmed as *Im* as we have previously reported.[11] Structural models that removed any or all of the remaining symmetry elements resulted in no improvement in the refinements and a final structural model that was still consistent with Im as the correct spacegroup. Models that included inversion twinning about the polar axes were also tested, but refinement of the twin fractions indicated that no such twinning was present. Refinements against data collected at various temperatures from 30 K up to room temperature revealed the same ordering in all cases. IFR made using BQ^+ and $BQol^+$ revealed the same ordering patterns in all cases

The STF structure is best described in the centrosymmetric space group $P2_1/c$ and the occluded $DMABO^+$ ions are disordered in the channels. Reduction of the symmetry of the model down as low as spacegroup *P*1 did not reveal any ordering of the SDA, and the final model in all cases was still consistent with space group $P2_1/c$. The final refined model of STF included the SiO_2 framework and fluoride ions. Inclusion of the difference Fourier peaks found in the channels into the refinement of the model improved the agreement factors considerably. However, the disorder of the SDA meant that the electron density in the channels of the structure could not be modeled as chemically sensible species and was not modeled in the final refinement. Despite the relatively poor agreement factors in the refinement of the STF model, caused by the disorder of the SDA, the framework and fluoride ions refine well as anisotropic atoms, and there is no doubt that the ordering of the fluoride ions is correct.

Table 1. Crystal Structure and Refinement Details for As-Made Zeolites [F,BQol]-IFR and [F,DMABO]-STF

sample title	[F,BQol]-IFR	[F,DMABO]-STF
chemical formula	$Si_{16}O_{32}{\cdot}F{\cdot}C_{14}H_{19}(OH)N$	$Si_{16}O_{32}{\cdot}F{\cdot}C_{12}H_{23}N$
unit cell		
a (Å)	18.5710 (8)	7.4573 (2)
b (Å)	13.4943 (6)	18.0966 (5)
c (Å)	7.7153 (3)	14.0233 (4)
β (deg)	102.302 (1)	99.254 (1)
cell volume (Å^3)	1889.08 (4) at $T = 30$ K	1867.84 (9) at $T = 150$ K
wavelength	0.6448 Å	0.6892 Å
Z	2	2
symmetry	monoclinic *Im*	monoclinic $P2_1/c$
unique reflections	2360	5279
observed reflections [$F^2 > 2\sigma(F^2)$]	2258	4269
number of parameters	322	226
wR($F^2_{\text{observed data}}$)	0.129	0.263
$R(F_{\text{observed data}})$	0.048	0.094
$S(F^2_{\text{all data}})$	1.096	1.101

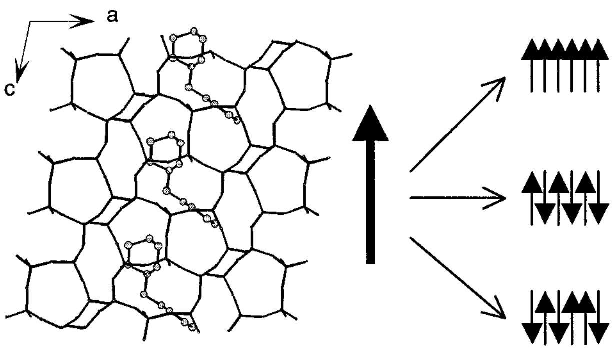

Figure 2. Head-to-tail ordering of benzylquinuclidinium SDA species inside one of the channels of IFR and a schematic of how this orientation (indicated by the large arrow) can produce noncentrosymmetric (top), ordered centrosymmetric (middle) and disordered centrosymmetric (bottom) structures when expanded into three dimensions. The strict parallel and strict antiparallel arrangements are favored by strong lateral interactions between adjacent channels.

Results and Discussion

The structure of zeolite IFR The structure of as-made zeolite IFR was originally solved from powder X-ray diffraction data in the centrosymmetric spacegroup *I*2/*m*.[6] Subsequently however, we have shown that the correct spacegroup is *Im*, with a noncentrosymmetric ordering of the fluoride ions and SDAs as shown in Figures 2 and 3.[11]

There are two polar directions in space group *Im*; parallel to the *a* and *c* unit cell directions. For the symmetry of the overall structure to be noncentrosymmetric the templates occluded in the channels of IFR must be ordered parallel with each other in one channel *and* in adjacent channels. Ordering of templates so that they all point in the same direction in one channel is perhaps not surprising. The benzylquinuclidinium templates are asymmetric, having a positively charged quinuclidinium end and a π-electron-rich benzyl end. There is therefore the potential for stacking of the template in a head-to-tail fashion (Figure 2) similar to that seen for many donor−acceptor type guests that are incorporated into microporous[20] or inclusion compounds.[21] However, computer modeling of a slightly different template inside zeolite IFR indicated that head-to-tail, head-to-head, and tail-to-tail orientations have similar energies.[24] On the basis of this report we would not expect the SDAs to be ordered in any one channel. The ordering of SDAs inside any one zeolite channel is not the only requirement for a polar noncentrosymmetric structure. There must also be ordering between adjacent channels. That is, all of the SDAs in the bulk material must be aligned parallel to each other. Ordered alignment of chains antiparallel or a disordered arrangement of channels with 50% of the channels pointing “up” and 50% pointing “down” would lead to centrosymmetric arrangements. Hulliger and co-workers[21] have explained that for channel alignment it is the lateral interactions (i.e., those between molecules in different channels) that are most important in determining whether a structure will be polar or not. Since the centers of the channels in IFR are

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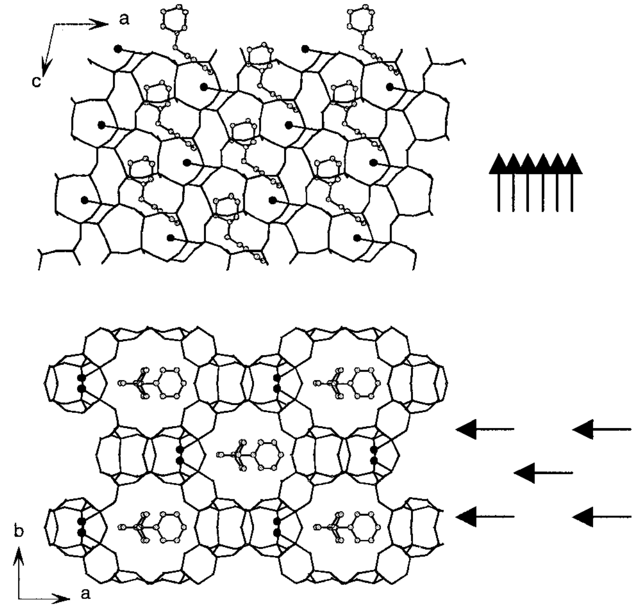

Figure 3. Two views of the structure of as-made benzylquinuclidinium-fluoride-IFR; viewed perpendicular (top) and parallel (bottom) to the channels. The SDA species are ordered in the two polar directions, parallel to the channels in a head-to-tail manner and the SDAs in adjacent channels all pointing in the same direction. The arrows on the right indicate the polar ordering in the channels of the structure (the arrowhead representing the quinuclidine end of the SDA). Fluorine, carbon, and nitrogen are shown as black, gray, and hatched spheres, respectively. The silica framework is shown as a line drawing.

separated by approximately 13.5 Å, it is unlikely that there is any interaction between SDA molecules in adjacent channels strong enough to cause the SDAs to all point the same way.[21] The IFR host itself is topologically centrosymmetric, and there should be no inherent advantage in having one channel containing ordered parallel SDAs over one containing ordered antiparallel SDAs or any situation in between.

The energetic interactions controlling polar ordering have been formulated in an equation relating the net polarization of dipolar molecules in a nonpolar inclusion compound on the basis of the growth of a crystallite by formation of an adlayer of dipolar molecules at a surface.[21] This is a very similar situation to the incorporation of dipolar benzylquinuclidinium SDAs in the essentially nonpolar IFR framework. The equation is

$$x(\mathrm{u})/x(\mathrm{d}) = \exp[(\Delta E_{\mathrm{f}} - \gamma z_{\mathrm{l}} \Delta E_{\mathrm{l}})/RT] \qquad (1)$$

where $x(\mathrm{u})/x(\mathrm{d})$ is the ratio of polarization "up" to "down", ΔE_{f} is the difference in energy between head-to-head and tail-to-tail orientations of the SDA in one channel, ΔE_{l} is the difference in energy between parallel and antiparallel orientations of SDAs in neighboring channels, z_{l} the number of nearest neighbor channels, and γ is a scaling factor, which lies between 1 and 2 and depends on the model used for the calculations. Zones and co-workers calculated no energy difference between head-to-head and tail-to-tail orientations (i.e., $\Delta E_{\mathrm{f}} \approx 0$) of the SDA used to prepare the borosilicate version of zeolite IFR.[24] The SDAs in neighboring channels are ~13.5 Å apart, precluding most polarization-induced interactions, and therefore ΔE_{l} will also be approximately zero. Given these two values of the interaction energies, eq 1 yields a ratio of polarization, $x(\mathrm{u})/x(\mathrm{d})$, of one, and thus predicts a nonpolar, centrosymmetric structure for the incorporation of the benzylquinuclidiunium SDAs into the nonpolar IFR framework. The calculation that $\Delta E_{\mathrm{f}} \approx 0$ is somewhat surprising, given that the quinuclidine end of the SDA is positively charged, and placing two positive charges in close proximity is expected to be less favorable than having them separated by a larger distance. However, even if there are some favorable head-to-tail interactions of the SDA giving rise to $|\Delta E_{\mathrm{f}}| > 0$, the dominating factor in eq 1 is the lateral energy, ΔE_{l}, by virtue of the scaling factor, γ, being greater than 1 and nearest neighbor number, z_{l}, usually being >2 (even at a surface). Therefore, spontaneous polarization of a growing crystallite, while not being completely unknown in cases where $\Delta E_{\mathrm{l}} \approx 0$ (see the review by Hulliger and co-workers for examples[20]), is much less probable than in cases where there is a relatively large value of ΔE_{l}. The pertinent questions in the case of the observed polar structure of [BQ,F]-IFR are what mechanism accounts for the strict head-to-tail ordering of the SDAs in one channel, and how is the information on the orientation of the SDA from one channel to the next transmitted? This effect can be traced to the location of the fluoride inside the cages in IFR.

The X-ray diffraction experiment (confirmed by second harmonic generation experiments) showed conclusively that, in IFR, there is parallel ordering of the SDAs in adjacent channels leading to an overall noncentrosymmetric structure.[11] It also revealed that the fluoride, as part of a pentacoordinate $[\mathrm{SiO}_{4/2}\mathrm{F}]^-$ 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. This ordering of the fluoride provides the mechanism by which the orientation of the SDAs in one channel is controlled and then transmitted to the next channel. The location of the organic SDA is strongly affected by the position of the fluoride ion because it is the negative charge on the F^- that balances the positive charge on the cationic SDA. As the SDA is asymmetric, with the positive charge localized primarily on the quinuclidine unit, this end of the SDA will orient itself so as to maximize electrostatic interaction with the negatively charged $[\mathrm{SiO}_{4/2}\mathrm{F}]^-$. The ordering of the template parallel to the *a*-axis is aided in this case by the bent conformation of the SDA inside the channel (Figure 3). The alternative orientation of the template, which is necessarily present in the centrosymmetric model, will have the positive charge on the template significantly further away from the fluoride ions and thus will be energetically less favorable. The orientation of the SDA is therefore intimately connected with the ordering of the fluoride ions into the $[4^35^26^1]$ cages; an ordered arrangement of F^- will lead to an ordered noncentrosymmetric arrangement of SDAs in adjacent channels as shown in Figure 3.

There are two possible structural reasons for the ordering of fluoride ions. The structure of IFR consists of fused $[4^35^26^1]$ cages, two cages sharing a common four-membered ring face (marked B in Figure 4). Since the negatively charged fluoride ions are located inside the cages, having both cages occupied by fluoride would lead to the negative charges being approximately 5.5 Å apart, a situation that may be electrostatically unstable (assuming that the negative charge remains localized on the fluoride ion). The second reason can be found in the distortions of the framework structure caused by the presence of the five-coordinated $[\mathrm{SiO}_{4/2}\mathrm{F}]^-$ units. Camblor and co-workers[2] have suggested that fluoride incorporation into the pure silica structure is most stable when the fluoride ion is connected to a silicon atom that is a part of a four-membered ring. In the IFR structure, the fused $[4^35^26^1]$ cages are linked to each other via four-membered rings (marked A in Figure 4). However, the arrangement of fluorine ions means that at no time are there two $[\mathrm{SiO}_{4/2}\mathrm{F}]^-$ units connected to the same four-membered ring (4MR). This is not too surprising since, as detailed below, the

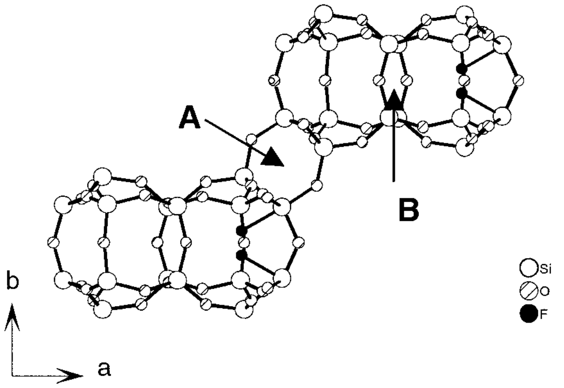

Figure 4. Four of the $[4^35^26^1]$ cages from IFR showing how they are fused together to form pairs through a shared 4MR (marked **B**) in the crystallographic a-direction and how they are linked through a 4MR (marked **A**) in the *b*-direction. The strict alternation of F-containing and empty cages is also clearly seen. The fluoride ions in each cage are disordered (50% occupancy for each site) across the mirror plane perpendicular to *b*.

local structure of the $[SiO_{4/2}F]^-$ is markedly distorted from the tetrahedral. The local distortion leads to the O−Si−O angle making up one corner of the 4MR being reduced by almost 20°, from tetrahedral ($\sim$109°) to trigonal bipyramidal ($\sim$90°). Given the rather inflexible nature of small rings, having two distorted units as part of the same 4MR would necessarily introduce excess strain into the structure. Simple energy minimization calculations carried out using the Materials Studio Software[25] on linked $[4^35^26^1]$ cages show that having two $[SiO_{4/2}F]^-$ units on the same 4MR is energetically unfavorable compared to an arrangement where only one corner of a 4MR contains a five-coordinate silicon atom. Since different pure silica zeolites have very similar thermodynamic stabilities (covering only $\sim$7 kJ mol^{-1}),[26,27] we suggest that even very small changes in lattice energy are significant enough to play an important role in determining the long-range order of fluoride ions inside zeolites such as IFR.

From the results of our structural studies on zeolite IFR, we propose the following structural features of a material that will lead to ordering of fluoride ions:

The zeolite structure must contain small cages suitable for incorporation of fluoride ions (almost all zeolites have such cages).

The cages must be arranged in pairs that are relatively close together so that incorporation of fluoride into two neighboring cages is electrostatically unfavorable.

The pairs of cages must be connected together by 4MRs, so that incorporation of five-coordinate silicon atoms in different cages but part of the same 4MR is geometrically unfavorable.

The number of single cages present in the structure must be at least twice as many as the number of monopositive structure-directing agents needed to fill the pores.

The last structural feature is a requirement for charge balance in the structure. If the number of cages is twice the number of positive charges present in the structure then the fluoride ions need only fill half the cages to achieve charge balance, affording the possibility of different order/disorder schemes in how the cages are occupied by fluoride.

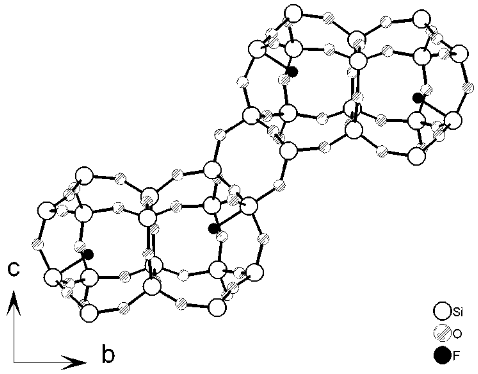

Figure 5. Ordering of fluoride ions inside zeolite STF fom X-ray diffraction. Each fluoride site has a crystallographic occupancy of 50%. Note that the 4MR joining the cages in the *c*-direction (marked **A**) has only one fluoride ion linked to it. This ordering is repeated throughout the structure. However, there is no strict alternation of fluoride-containing and empty cages as there is in IFR (cf. Figure 4).

One zeolite structure in particular, STF, does seem to have all the necessary features listed above. To test our hypotheses we reexamined, by X-ray diffraction, the structure of as-made fluoride containing STF.

The Structure of STF The framework structure of STF has similar structural features to zeolite IFR, and it was postulated that a similar ordering of fluoride ions might be revealed in X-ray diffraction experiments. Both structures can be described in a similar fashion, they contain fused small cages that are arranged into columns, the columns then being linked by single 4MR and 6MR units. The columns are linked in such a way as to form one-dimensional channels in both zeolites (Figure 1). The topological symmetry of both frameworks is *I*2/*m* (standard setting: *C*2/*m*), and their framework density (as calculated by distance least-squares) is almost identical: 17.2 and 16.9 tetrahedral atoms per 1000 Å^3 for IFR and STF, respectively.[28] The differences between the structures are mainly in the nature of the cages themselves: IFR contains $[4^35^26^1]$ cages (Figure 4), while STF contains $[4^15^26^2]$ cages (Figure 5), and the pores in IFR and STF are defined by 12MR and 10MR openings, respectively (Figure 1). Another major and important difference in the two structures is their framework symmetry. Pure silica IFR retains its monoclinic topological symmetry of *I*2/*m* when calcined (i.e., when the fluoride and organic SDA have been removed) while the calcined STF framework structure is triclinic.[29] Low symmetry (triclinic) calcined STF has been calculated to be $\sim$5kJ mol^{-1} more stable than the high-symmetry framework.[23] In the as-made fluoride-containing material reported here the crystallographic symmetry is monoclinic with centrosymmetric spacegroup $P2_1/c$. The hypothesis that the similar structural features of STF would lead to a similar noncentrosymmetric ordering as seen in IFR is therefore proven to be incorrect. However, the basic structural features of STF *are* similar to those of IFR, and the important question to be answered is why there is a centrosymmetric ordering of fluoride and SDAs in the STF structure. This can be traced to two features. The SDA used to prepare STF (DMABO) is chiral, but the solution used to synthesize the samples contains a racemic mixture of the two enantiomers. While each individual molecule is asymmetric, there is no π-electron-rich end of the molecule, and thus, the formation of strong head-to-tail interac-

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[25] *Materials Studio*; MSI Inc: San Diego, 2000.

[26] Camblor, M. A.; Diaz-Cabanas, M. J.; Cox, P. A.; Shannon, I. J.; Wright, P. A.; Morris, R. E. *Chem. Mater.* **1999**, *11*, 2878.

[27] Piccione, P. M.; Laberty, C.; Yang, S. Y.; Camblor, M. A.; Navrotsky, A.; Davis, M. E. *J. Phys. Chem. B*, **2000**, *104*, 10001.

[28] See the International Zeolite Association website http://www.iza-online.org for further details.

[29] Wagner, P.; Zones, S. I.; Davis, M. E.; Medrud, R. C. *Angew. Chem., Int. Ed.* **1999**, *38*, 1269.

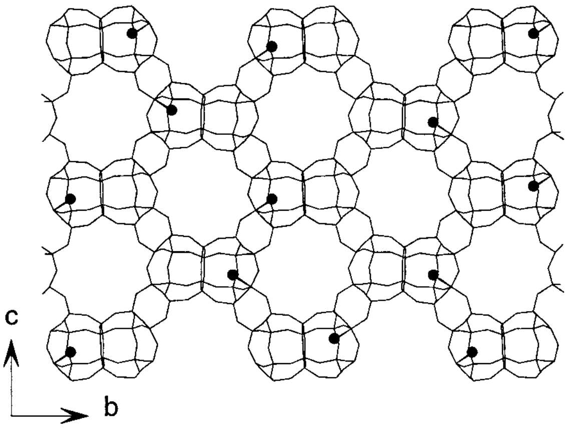

Figure 6. An arrangement of fluoride ions (black spheres) in zeolite STF that has only one of any two fused cages occupied by fluoride and no 4MR with more then one fluoride ions attached to it. The "average" of this arrangement gives the structural model refined in the X-ray diffraction experiments (Figure 5). The difference between this model and the situation in IFR is the intracage ordering of fluoride ions in STF means there is no requirement for strict alternation of empty/filled cages in the crystallographic *c*-direction.

tions is even less likely than is the case for the benzylquinuclidinium cation in IFR. Therefore, there might not be such strong energetic reasons to have the head-to-tail type ordering in one channel, and if both enantiomers are occluded into the same crystal, either disordered in the same channel or in different channels, then the resulting structure will be centrosymmetric.

The other reason is the arrangement of fluoride ions in the structure. The parallel arrangement of SDAs in adjacent channels in IFR can be traced back to the strict alternation of fluoride-containing and empty [$4^35^26^1$] cages. The X-ray diffraction structure of STF shows no such ordering. However, rather than the fluoride ions being disordered over two sites in the IFR cage (intracage disorder), the fluoride ions in STF are localized onto one silicon atom. That there is no hopping of fluoride from one silicon to another (i.e., no dynamic disorder) is confirmed by NMR experiments. The localization of the fluoride ion onto only one of the silicon sites must be a consequence of the lower symmetry of the STF cage when compared to the IFR cage, otherwise there would be two equivalent silicon atoms per cage, and there would be similar two-fold disorder. The presence of this intracage ordering in STF leads to a strict alternation parallel to the crystallographic *c*-axis, where only one silicon in each four-ring has a fluoride attached to it (Figures 5 and 6), thus confirming that the structure avoids having two fluoride ions attached to the same 4MR. However, the fluoride ions do show some intercage disorder, with the fluoride ions occupying either one of the two fused [$4^15^26^2$] cages (50% probability of each). This is in marked contrast to zeolite IFR, which shows intracage disorder between two [$SiO_{4/2}F$]$^-$ units related by a mirror plane and strict alternation of occupation of the fused [$4^35^26^1$] cages.

However, the results of intercage order and intracage disorder for IFR and intracage order and intercage disorder for STF lead to the same general conclusions. In STF it is easy to draw arrangements of fluoride ions where there is occupation of only one of the two fused cages and only one silicon atom per 4MR has a fluoride attached to it (Figure 6), yet the overall structure is still (on average) centrosymemtric. Therefore, the different ordering of fluoride ions in the two structures does not necessarily invalidate the general features needed for ordering to occur, just that there are several possible fluoride-ordering schemes compatible with these features.

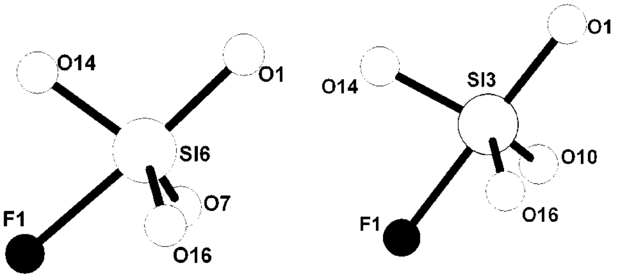

Figure 7. The "average" geometry (as measured by X-ray diffraction) of the [$SiO_{4/2}F$]$^-$ units in IFR (left) and STF. The similar distortion from tetrahedral toward trigonal bipyramidal coordination in IFR and STF is consistent with the similar fluoride occupancy for these two sites. Selected bond distances and angles for the IFR (atom numbering schemes refer to the structural models reported in the Supporting Information) 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)°. Selected bond distances and angles for STF: Si3−F1, 1.867 (8) Å; Si3−O1, 1.664 (4) Å; Si3−O10, 1.617 (4) Å; O1−Si3−F1, 178.9 (3)°; O1−Si3−O10, 99.3 (2)°.

Unlike the IFR structure, the lowering of symmetry caused by the intracage ordering of fluoride ions does not lead to an ordering of the structure-directing agents inside the channels. There is still at least two-fold disorder of the organic cations, and they could not be satisfactorily located from the X-ray diffraction experiments.

Local Structure of [$SiO_{4/2}F$]$^-$ Units In both IFR and STF the fluoride ions incorporated into the frameworks are successfully located by single-crystal X-ray diffraction techniques. As expected from the previous X-ray diffraction studies and predictions, all of the fluoride ions in the pure silica materials are found to be inside small cages. In neither case, however, is there a fully occupied fluoride ion site. In IFR this partial occupancy reflects the fact that there are two possible silicon atoms suitable for the formation of [$SiO_{4/2}F$]$^-$ units in each cage, and there is statistical (and possibly dynamic) disorder between these possible sites. For zeolite STF, there is only one identifiable [$SiO_{4/2}F$]$^-$ unit per cage, and the static disorder is then between cages. Given the fact that all of the fluoride ions show some disorder, the local environment around the silicon in a [$SiO_{4/2}F$]$^-$ unit measured by X-ray diffraction is necessarily an average one. The average consists of trigonal bipyramidal (tbp) and tetrahedral silicon, the components weighted by the occupancy of the fluoride ion at that particular site (Figure 7). This makes it very difficult, by X-ray diffraction, to determine the actual local structure of the [$SiO_{4/2}F$]$^-$ unit. In the structures of IFR and STF, where the fluoride occupancy is 0.5, the environment around the silicon in the [$SiO_{4/2}F$]$^-$ units is similar, showing a definite elongation of the axial Si−O bonds. There is also a decrease of the O_{eq}−Si−O_{ax} angles (e.g., the O1−Si6−O7 angle in IFR coordination in Figure 7) toward 90° and an increase of the O_{eq}−Si−O_{eq} (e.g., O7−Si6−O14 angle for IFR, Figure 7) toward 120°. Where the occupancy of the fluoride ion is less, as in STT,[10] CHA,[30] and FER,[30] the tetrahedral component dominates, and there is very little distortion toward a tbp structure. The Si−F interatomic distances vary from 1.867 (8) Å for STF to 1.92 (1) Å for IFR. These are slightly shorter than the bond distance in fluoride-containing silica MFI as measured by solid-state NMR (2.08 ± 0.03 Å)[18] but are longer than those resulting from calculations on other fluoride-

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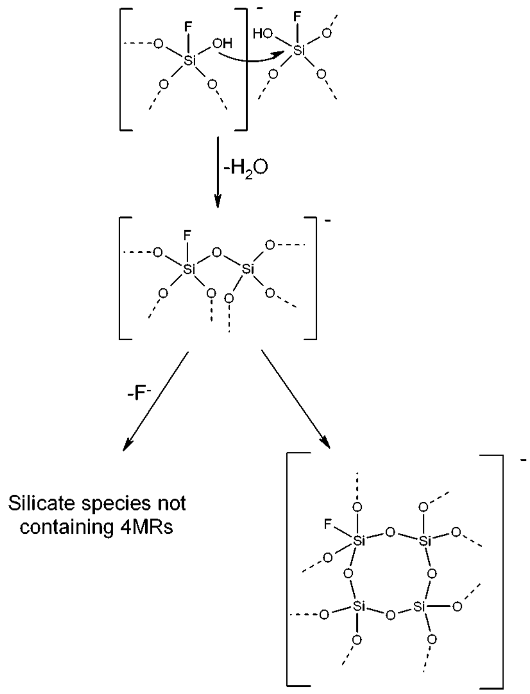
(30) Villaescusa, L. A.; Bull, I.; Wheatley, P. S.; Lightfoot, P.; Morris, R. E. Unpublished results.

Scheme 1. Role of Fluoride Ions in "Catalyzing" the Formation of Si−O−Si Bonds (After Camblor et al.)[2,6]



containing silica zeolites.[31] Examination of the thermal parameters of the silicon atoms in STF shows that the longest axis of the anisotropic displacement parameters on the $[SiO_{4/2}F]^-$ silicon is parallel to the Si−F bond, indicating that there is some static disorder present. The real Si−F bond distance in this case is therefore probably shorter than the measured one. The range of measured Si−F bond distances from diffraction and NMR experiments and that calculated from DFT methods indicates that the bonding in these materials varies, depending on the nature of the structure being investigated. It should be noted that there is no dynamic disorder in the STF structure and that the disorder in IFR will have been "frozen out" by the low temperature (30 K) of the data collection; thus, variation in Si−F distances is not due to averaging of motion between sites.

Implications for Mechanism of Synthesis of IFR and STF. The growth of a zeolite crystal, whether it is polar or nonpolar, occurs at a surface. The mechanism of the formation of a crystallite must take into account the primary confinement of the silica framework, SDA, and fluoride species at a crystallite−nutrient interface. We are not in a position from X-ray diffraction experiments to elucidate the whole mechanism; many further experiments are needed. However, we are in a position to make some comment on how the rather interesting ordering phenomena in zeolites STF and IFR might occur.

The role of fluoride ions in the synthesis of pure silica materials has been discussed by Camblor and co-workers.[2,6] They identified a number of roles that fluoride ions can play, including as a mineralizing agent (enhancing solubility of silica species at low pH). Also, fluoride ions can catalyze the formation of Si−O−Si bonds as shown in Scheme 1. In addition, there is now evidence from both X-ray diffraction reported here and NMR spectroscopy that the fluoride ions tend to remain bonded to one of the silicon atoms in a 4MR. Whether this is a structure-directing phenomenon, selectively forming 4MRs at the expense of other silicate species (or secondary building units), is open to question. However, there is no doubt now that in the final solid it is very common to see the fluoride connected to a silicon atom of a 4MR, and we can presume that this is a stable configuration.

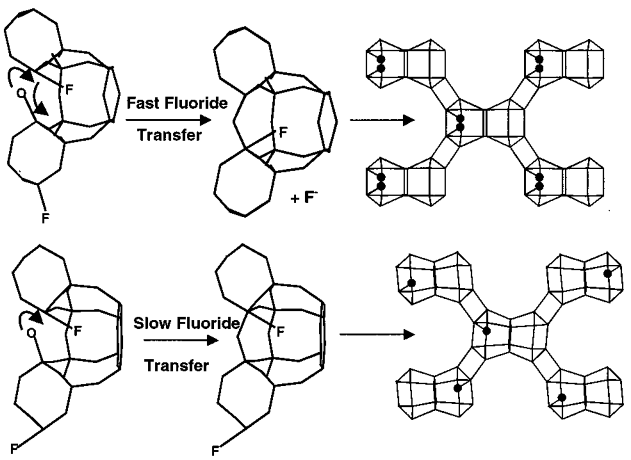


Figure 8. Proposed mechanisms for the ordering of fluoride ions in zeolite IFR (top) and STF (bottom) during synthesis. As cages are formed from condensation of silicate species at a crystallite surface, fluoride ions are incorporated into the solid when they are connected to 4MRs. If there are two sites of equal stability in one cage, as is the case in IFR, then fluoride transfer can take place, preventing fluoride ions on an incoming 4MR from being incorporated into the structure because of the strain of having two fluoride ions connected to the same 4MR. In the case of STF, no such fluoride transfer takes place (or it is very energetically disfavored), and the incoming 4MR can now have a fluoride connected to it. As the fused cages are formed in both cases, electrostatic interactions between fluorides in neighboring cages are unfavorable, and only one of each pair of fused cages can contain a fluoride ion.

The ordering of fluoride ions seen in zeolites IFR and STF is remarkable in that it is different in each zeolite. Particularly intriguing is how these ordering effects come about. While it is possible that fluoride ions can diffuse through the six-ring windows in the materials, it is unlikely that they will move through the four-membered rings that connect the cages. Therefore, it is most likely that the fluoride ions order during the synthesis of the material. Two features of the STF structure are particularly intriguing: the tendency of the pure silica calcined material (i.e. where the fluoride and organic SDA have been removed) to distort from its topological symmetry to a much lower symmetry and the ordering of the fluoride ions inside the cages of the as-made material. This tendency to distort to lower symmetry must be important in determining the energetics of ordering of the fluoride ions.

In STF, there is only one identifiable fluorine site per cage (at 160 K). In IFR there are two, related by a crystallographic mirror plane. Furthermore, NMR spectroscopy has shown that disorder inside the IFR cage is dynamic and that no such disorder is present in STF, which agrees with the X-ray diffraction results. This difference in ordering within one cage allows us to suggest a mechanism for the way by which the long-range ordering of fluoride occurs during the synthesis of IFR and STF as shown in Figure 8. The $[SiO_{4/2}F]^-$ units are most stable as part of 4MRs and inside small cages. As the 4MRs are incorporated into the structure, the fluoride ions direct the building of small cages around them. The exact nature of the cage will depend on a number of factors, including the interactions with the organic structure-directing agents. As the STF structure forms and begins to grow, there is only one silicon atom to which the fluoride ion attaches in any one $[4^1 5^2 6^2]$ cage. The next 4MR to attach to the same cage can also have a

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(31) Attfield, M. P.; Catlow, C. R. A.; Sokol, A. A. Manuscript in preparation.

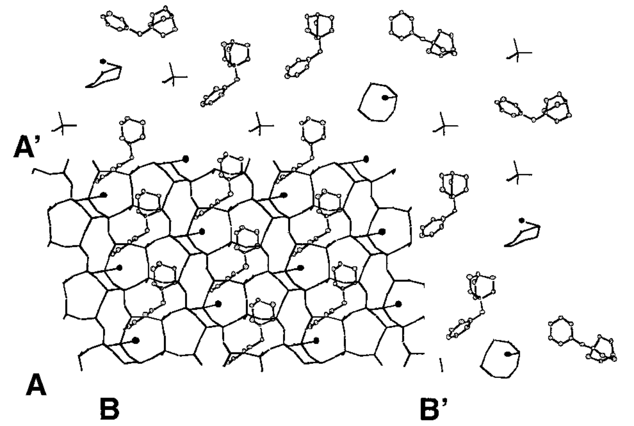

Figure 9. Schematic view of preferential crystal growth of IFR at the A′ (001) and B′ (100) surfaces compared to the A (00−1) and B (−100) surfaces from a randomly oriented nutrient. Silica and silicate species are shown as line drawings, carbon, fluoride, and nitrogen atoms by gray, black, and white spheres, respectively.

fluoride attached, as long as it not inside the same cage as the first, which would be electrostatically unfavorable. Alternatively there is no requirement for this 4MR to have a fluoride attached. As the structure grows further, the location of fluoride ions in the fused cages is determined by whether the first cage to form contains a fluoride ion. The result is the ordering scheme seen for STF.

The $[4^35^26^1]$ cages in IFR have two positions equally likely to contain a fluoride ion. Fast fluoride transfer (as shown by NMR) between the two sites as the structure is forming will mean that the 4MRs attaching to a formed cage cannot contain a fluoride ion, as this would mean that at some point in time the 4MR would have two fluoride ions attached to it, which we believe to be unfavorable. There is the possibility of concerted motion of all F^- ions to retain only one fluoride on any 4MR at any instant in time. However, for this to occur, the cages would need to be formed faster than the rate of transfer of fluoride between the sites, otherwise the fluoride ion in the forming cage would be lost back into the nutrient phase. The X-ray diffraction experiment shows that this does not occur, as there is strict alternation of cages with and without fluoride in IFR. The ordering of filled/empty cages in IFR would also suggest that the cages are not formed in the nutrient phase and then laid down on the solid, but are formed around the fluoride ions as the solid grows. This is because the fluoride that is released from the 4MR ring as the structure is formed (Figure 8 top) could not escape if it was already entrapped in a fully formed cage, and the strict alternation of filled/empty $[4^35^26^1]$ cages could not happen. The difference between the two ordering schemes can therefore be traced to the possibility of dynamic disorder of fluoride ions inside the IFR cage, while no disorder is present in the STF cage.

The schematic mechanism illustrated in Figure 8 indicates how the fluoride ion ordering schemes in IFR and STF might be controlled by the dynamic disorder of fluoride ions inside a cage as the structure is formed. However, the actual growth of a crystal is a surface effect. Zeolites are often described as growing by a laying-down of successive adlayers of silica and SDA from a disordered nutrient system (which might be a solution or gel phase). Figure 9 shows how such a layered growth mechanism might lead to the polar structure seen in zeolite IFR. In the diagram the surfaces perpendicular to the polar directions of a growing crystallite, (001), (00−1), (100), and (−100), are designated A′, A, B′, and B, respectively. The head-to-tail ordering of the SDA inside one channel of the zeolite means that surface A′ (terminated by the quinuclidine end of the SDA) is not equivalent to surface A (terminated by the benzyl end). Equivalent surfaces would result if new channels, formed by deposition of subsequent adlayers of SDA and silica at B and B′, were of the opposite orientation. However, the long-range ordering of the fluoride ions inside the cages makes surfaces B and B′ not equivalent, surface B′ being terminated by fluoride-containing cages, and surface B, by empty cages. Adsorption of SDA molecules at the “fluoride”-terminated surface should be more favorable if the SDA is in the correct orientation (to maximize the interaction between positive SDA and negative fluoride). The orientation of SDAs in IFR that maximizes this favorable interaction has, because of the ordering of the fluoride, the same orientation as that of the SDAs in adjacent channels. In this way the polarity of the structure is propagated parallel to both the a and c directions of the unit cell.

In STF, the intracage ordering of the fluoride onto one silicon means that there is no long-range requirement for ordering between filled and empty cages. This leads to an overall centrosymmetric arrangement of the fluoride ions, and even if there is a head-to-tail interaction inside one channel (parallel to the *a*-axis), the two surfaces perpendicular to the other polar direction (the 010 and 0−10 surfaces) would be equivalent (Figure 6) with no possibility of polarity being propagated parallel to the *b*-axis. The structure of STF is therefore centrosymmetric.

Most zeolites with unidimensional channel systems grow with needlelike morphologies, which can be explained by preferred deposition of the SDA along the direction of a channel that already exists. The deposition of new SDAs perpendicular to this direction to form new channels is less favored, and the growth in this direction is slower.[32] Indeed crystals of IFR containing aluminum (rather than fluoride) as the source of negative framework charge grow as long needlelike crystals as expected. However, the morphology of the fluoride-containing IFR has a much lower aspect ratio, indicating that the formation of new channels is quicker in the fluoride-containing material than it is in aluminum-containing Al-IFR.[33] The change in morphology between F-IFR and Al-IFR is also probably a consequence of the location of fluoride ions inside the $[4^35^26]$ cages. This distributes the negative charges all around the channels, which presumably favors the adsorption of the SDA, making formation of new channels at surface B′ more favorable than is the case for Al-IFR. There is no constraint for aluminum ions to be sited inside the small cages, and this probably means the negative charges are not necessarily so favorably disposed for the adsorption of SDAs as they are in F-IFR. While this effect is quite obvious for Al-IFR, the incorporation of boron into zeolite IFR[24] yields crystal morphologies that are more difficult to rationalize and may indicate that boron and aluminum are not incorporated into the frameworks in the same manner.

Conclusions

Single-crystal X-ray diffraction experiments at the Daresbury synchrotron source have allowed us to solve the crystal structures of as-made zeolites IFR and -STF, both of which have been shown to contain fluoride ions. The local structure of each fluoride ion has been determined and compared to the results from NMR and DFT calculations. However, the disorder present

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(32) Gies, H. In *Inclusion Compounds*; Atwood, J. L., Davis, J. E. D., McNicol, D. D., Eds.; Oxford University Press: U.K., 1991; Vol. 5, p 1.

(33) Villaescusa, L. A.; Barrett, P. A.; Kalwei, M.; Koller, H.; Camblor, M. A. *Chem. Mater.* **2001**, *13*, 2332−2341.

in both structures does complicate the description of this local structure. The long-range ordering of fluoride ions in IFR and STF has also been identified, and this can be traced back to electrostatic and geometric requirements to keep fluoride ions from being too close to each other and having only one fluoride attached to a 4MR at any one time. The ordering schemes are different in the two structures, which can be explained by dynamic disorder of two sites for fluoride in each IFR cage, while there is only one available fluoride site in each STF cage. The structural information gathered from the X-ray diffraction experiments have allowed us to propose mechanisms for how this ordering occurs during the synthesis if the zeolites. The results we have described here show the value of obtaining good quality single-crystal X-ray diffraction data on these quite complex materials, and how even information on the average bulk structures can allow one to comment on details of the crystallization mechanism.

In the growth of polar host−guest crystals using centrosymmetric host materials, the ordering of the guest molecules is normally controlled by the guest−guest interactions. In the case of IFR, however, it is probably the specific location of the fluoride ions that controls the orientation of the guest molecules.

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Supporting Information Available: Details of the crystal structure determinations (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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