Polarization Reversal in AlPO₄-5 Crystals Containing Polar or Nonpolar Organic Molecules: A Scanning Pyroelectric Microscopy Study

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Large AlPO₄-5 crystals containing different polar or nonpolar guest molecules have been studied with scanning pyroelectric microscopy. Calcined crystals are pyroelectric with a polar structure that reverses in polarity at the center of the crystal. Consequently all these crystals are twinned. The temperature dependence of the pyroelectric coefficient reveals a genuine pyroelectric crystal structure, which spontaneous polarization decreases from $30 \,\mu\text{C/m}^2$ to almost zero at a Curie temperature, T_c , of 50 °C. The presence of guest molecules, such as template molecules, adsorbates, or water, modifies the position and sharpness of the phase transition. Short-range interactions between polar guest molecules with the distinct capping faces of the asymmetric lattice were found to be the reason for the bidirectional adsorption (and formation of dipole chains) of polar molecules such as p-nitroaniline (pNA). The specific temperature dependence of the pyroelectric activity of AlPO₄-5/pNA and the observation of a relaxation process were assigned to cooperative motions of the one-dimensional pNA chains. This is in line with theoretical predictions of the coexistence of a solid-like and a liquid-like pNA phase.

1. Introduction

Zeolitic materials are known to be suitable hosts for the ordering and alignment of a multitude of organic guest molecules, for example, various 1,4-substituted aromatic molecules.^{1–3} Most of these molecules can be easily adsorbed and stabilized in the channels and cages of molecular dimensions. The large variety in the pore structure, size, shape, and framework charge density of zeolites enables one to find the optimal combination of host and guest for specific purposes.⁴ Of particular interest is the ability of some zeolites to organize donor—acceptor (D–A) molecules with a macroscopically preferred direction, which gives rise to second harmonic generation (SHG) activity.⁵

Despite the fact that many of these composites have been made, the exact nature of the organizing mechanisms is not clear yet. Parameters influencing (oriented) adsorption are the guest—guest and the host—guest interactions during the different stages of the adsorption process. In this study it will be shown that if AIPO₄-5 is used as a host, the particular structure of the capping faces of the asymmetric lattice has a substantial influence on the ordering of polar molecules.

The lattice of AlPO₄-5 consists of 4-, 6-, and 12-membered rings of T-atoms (alternating Al and P, bridged by O-atoms), which form a hexagonal arrangement of parallel channels, with the 12-membered channel in the [001] direction.⁶ ²⁷Al and ³¹P solid-state NMR confirmed a strict alteration of the Al and P in the lattice. Therefore, if no defects are present, all Al–O–P pairs that are parallel to [001] are pointing in the same direction

(Figure 1a). Taking this asymmetry into account, a polar channel and polar diffusion have been postulated.⁷ This concept could be extended to other microporous AlPO₄ structures like ATV (8-ring), AEL and AFO (10-ring), AET (14-ring), and VFI (18-ring).⁸ However, the idea that the phosphorus is more positive than the aluminum, so that the polarization is pointing in the direction of the phosphorus, is an oversimplification, as will be explained in the Results and Discussion.

Given the presence of strong molecular dipoles arranged in a non-centrosymmetric lattice, AIPO₄-5 should be able to develop a macroscopic spontaneous polarization P_s . Unfortunately, the resulting electrical field, E, is normally compensated by surface charges on the crystal, which make a direct measurement of the spontaneous polarization impossible. However, since these surface charges are real charges of restricted mobility, quick changes of P_s due to fast changes in pressure (piezoelectric effect) or temperature (pyroelectric effect) lead to a measurable change in the net surface charge density $\Delta \sigma = \Delta P_s$. The pyroelectric effect is the basis of the measurements described in this work.

By definition, pyroelectricity originates from the temperature dependence of a spontaneous polarization P_s , which can be expressed by the pyroelectric coefficient p:

$$p = dP_c/dT \tag{1}$$

Crystalline materials which are pyroelectric often also show ferroelectric behavior; i.e. their polarization is switchable by an electric field. The common characteristic of both pyro- and ferroelectric crystals is a Curie temperature, T_c , above which the spontaneous polarization disappears so that the material becomes paraelectric. This phase transition is accompanied by a change in the crystal structure and is further characterized by a maximum in the pyroelectric coefficient, p.

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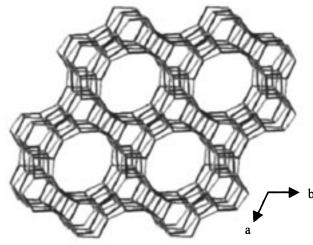


Figure 1. (a, top) Lattice structure of AlPO₄-5. The black tetrahedrons represent the Al atoms and the gray ones the P atoms. The O atoms are omitted for clarity. (b, bottom) Lattice structure showing the large pores, parallel to the c-axis.

Although many zeolite structures are non-centrosymmetric, no experimental evidence of pyroelectricity of a pure zeolite crystal has been published until now. Only recently, pyroelectric activity was found in AlPO₄-5 single crystals loaded with p-nitroaniline (pNA) 9 , which was attributed to a polarization caused by macroscopically aligned polar guest molecules rather than by the host lattice itself.

The pyroelectric properties of pure AlPO₄-5 crystals as well as AlPO₄-5/guest systems will be addressed in the present paper. For this purpose a scanning pyroelectric microscope (SPEM) was utilized, which was recently developed for the study of the polarization properties of organic inclusion compounds. ¹⁰ The SPEM technique combines local heating of a sample at optical resolution with the detection of a pyrocurrent due to the local pyroelectric activity of the sample. Since the heat source is sinusoidally modulated in intensity, an alternating pyroelectric current, I(t), is generated (eq 2); the amplitude of which is

$$I(t) = pA \frac{\mathrm{d}T}{\mathrm{d}t} \tag{2}$$

proportional to the area, A, the pyroelectric coefficient, p, and the time derivative of temperature. Thus, scanning across the surface of a sample yields a micrograph of the pyroelectricity, revealing possible domain structures or other pyroelectric inhomogeneities.

Since the temperature dependence of the pyroelectric coefficient p(T) gives essential information about the origin of the pyroelectric effect, several temperature dependent SPEM experiments have been performed. Knowing the temperature at which p becomes zero (usually the Curie temperature), it is possible to calculate the spontaneous polarization, P_s , at a temperature, T, just by integrating p(T) (eq 3).

$$P_{\rm s}(T) = \int_T^{T_{\rm c}} p(T) \, \mathrm{d}T \tag{3}$$

2. Experimental Section

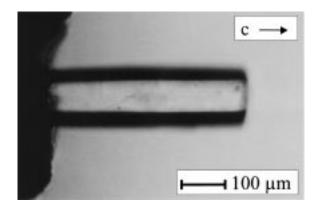
2.1. Materials. Large AlPO₄ -5 crystals of $100-600~\mu m$ were hydrothermally synthesized at about $180~^{\circ} C$ using either conventional¹¹ or microwave heating.¹² Different templates (triethylamine, tripropylamine, and tropine) and reaction mixture compositions were used. For example, $200~\mu m$ crystals were made at $185~^{\circ} C$ in 2 days from a mixture containing $1:1:1.5:450~Al_2O_3:P_2O_5:$ triethylamine: H_2O . To remove the organic template, calcination was performed at $600~^{\circ} C$ for 16~h; the sample was heated and cooled at a rate of $1~^{\circ} C/min$. The removal of the template was verified with Fourier transform infrared (FTIR).

Prior to the loading procedure with guest molecules, the freshly calcined crystals were evacuated at 180 °C for 1 h. Then an evacuated flask with the organic compound was connected to the flask with the zeolite crystals at about 10 °C above the melting temperature of the guest. The two flasks were kept connected for 16 h, after which the crystals were slowly cooled to room temperature. In this way the AlPO₄-5 crystals were filled with *p*-nitroaniline (*p*NA), *p*-dinitrobenzene (*p*DNB), *p*-dichlorobenzene (*p*DCB), *p*-xylene (*p*XYL), *p*-aminoacetophenone (*p*AAP), and *p*-dimethylaminobenzaldehyde (*p*DMAB). Some of the crystals were halved before loading. The degree of adsorption of the organic molecules was verified with FTIR and thermogravimetric analysis (TGA).

2.2. Scanning Pyroelectric Microscopy. Before the scanning pyroelectric experiments, the crystal was coated with a thin absorption layer of black ink to ensure proper surface absorption of the laser light. The crystal was next positioned between two copper electrodes by gluing it with conducting glue onto one of the electrodes with the c-axis of the crystal (the channel direction) perpendicular to the electrode. The second electrode was thermally and mechanically separated by an air gap ($<10 \ \mu m$).

There might be some influence of the glue and ink on the pyroelectric signal, either by adsorption of components or by extracting guest molecules. Therefore some measurements were performed without glue by placing the crystal between the electrodes onto a support of polystyrene foam. The crystals were dipped in the ethanol-based ink for less than 1 s, so some ethanol could be adsorbed in the empty crystals, but no influence was observed.

In the scanning pyroelectric measurements the zeolite crystal is locally heated with a sinusoidally modulated laser diode (LISA HL25/M2, 5 mW, 8 = 635 nm). The laser beam is positioned and focused on the crystal via an optical microscope. The pyroelectric current is amplified by a current amplifier (Keithley 428, 10^8 V/A) and analyzed with a digital lock-in amplifier (Stanford Research 850). By scanning with the laser beam across the surface, a two-dimensional image of the pyroelectricity could be obtained with a sensitivity of 10^{-14} A and a lateral resolution of $10~\mu m$. However, most crystals were characterized by scanning along the c-direction of the crystal,



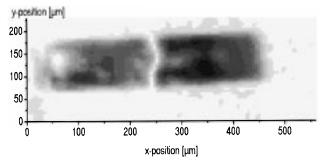


Figure 2. (a, top) 450 μ m calcined AlPO₄-5 crystal and (b, bottom) pyroelectric image of the same AlPO₄-5 crystal.

with a step size of 5 or 10 μ m, at a frequency of 1000 Hz, whereas for some of the crystals a two-dimensional image was taken.

Temperature dependent scanning pyroelectric measurements were performed in a nitrogen atmosphere between 25 and 200 °C.

3. Results and Discussion

3.1. Polarization and Lattice Structure of Calcined AlPO₄-5. A two-dimensional pyroelectric image of a calcined AlPO₄-5 crystal is shown in Figure 2b. This image reveals the true shape and dimensions of the crystal. The left (gray) part denotes a positive current and the right (black) part a negative current. In all pyroelectric images of calcined AlPO₄-5 crystals both halves of the crystals give an opposite pyroelectric current, indicating a polarization reversal in the middle of a crystal. This implies that there is also a reversal in the lattice structure, which means that the c-axes for both sides of the crystal are pointing in the opposite direction. Apparently, all these crystals have a twinned structure. This could not be observed with X-ray diffraction (XRD) because there is only one symmetry plane in the center of the crystal. However, it is possible in priciple to determine the absolute direction of the polar axis of half a crystal by X-ray anomalous scattering.

To obtain direct evidence of the polarization in half-crystals, several of them were aligned in an electric field of 5 kV/cm using comb electrodes. The crystals were suspended in silicone oil to facilitate their movement and orientation. It has already been shown that large AlPO₄-5 crystals will align parallel to an electric field, ¹³ but in principle this will happen for every rod-shaped dielectric. All half-crystals, however, orient with the broken side (the original center of the crystal) toward the positive electrode. This means that the crystal endings are positively charged and that the polarization is directed toward the end of the crystal. If we combine this observation with the (positive) sign of the pyroelectric current, these results imply a

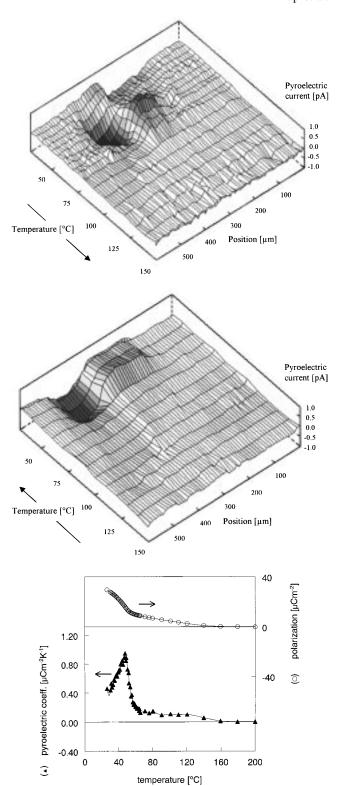


Figure 3. Temperature dependent SPEM of calcined AlPO₄-5: (a, top) first heating run (with water); (b, middle) cooling run; (c, bottom) pyroelectric coefficient (absolute value) and spontaneous polarization as a function of temperature.

negative sign of the pyroelectric coefficient as expected for pyroelectric crystals (usually the polarization decreases with temperature).

Temperature dependent measurements up to 200 °C show a maximum in the pyroelectric current at 50 °C (Figure 3b,c). Above this temperature a low activity remains, which completely disappears only above 150 °C. This behavior is entirely

TABLE 1: Charges on Al, P, and O in AlPO₄-5 Calculated with Different Models

Al	P	O	ref
0.55	0.23	-0.19	17
1.4	3.4	-1.2	18
1.23	0.3	-0.38	19
2.2	2.4	-1.15	20

reversible upon cooling and subsequent heating cycles. So it is clear that a pyroelectric to paraelectric transition occurs, at which the spontaneous polarization disappears. Below 50 °C AlPO₄-5 might even show ferroelectric behavior, i.e. a switchable polarization. This will be subject of further experiments. The sharp maximum in the pyroelectric current is a strong indication for the occurrence of a phase transition of the lattice. This phase transition was also observed with temperature dependent XRD measurements.14

The magnitude of the polarization was calculated using eq 3, in which 200 °C was used as the upper integration limit (Figure 3c). This results in a value of about 30 μ C/m² for the spontaneous polarization of the crystal at room temperature. The polarization of the crystal is directly related to the dipoles in the lattice. However, although the structure of AlPO₄-5 was established by single crystal X-ray diffraction already in 1983,7 important uncertainties still remain. The model that all Al-O-P bonds in the channel are pointing in the same direction, with phosphorus more positive than aluminum, and that consequently the polarization is pointing in the direction of the phosphorus is too simple.

The first point of discussion is that the dipoles of the other Al-O-P bonds are neglected in such a model. These dipoles have a component in the opposite c-direction (Figure 1). Thus, it depends on the exact angles and positions of these dipoles whether these effects will cancel out or that instead a net polarization will remain instead.

Another uncertainty is the position of the bridging oxygen. According to the proposed space group P6cc, the oxygen lies almost exactly between P and Al. Because this would give an almost linear Al-O-P entity, other researchers have tried to find a more likely configuration. One method is to use a microdomain model with tilted tetrahedra, in which all T-O-T bonds are close to 150°. This is consistent with partial covalency.⁷ Reduction of the symmetry from the experimentally determined P6cc to P6 allows for the full optimization of the O(2) position, also resulting in Al-O-P angles much closer to those generally observed ($\sim 160^{\circ}$). The same is found when using the orthorhombic space group Pcc2.¹⁶

The third point of debate is the charge on the different atoms. Depending on the model used, either Al or P is more positively charged. A few examples are shown in Table 1. When a high degree of covalency is assumed, the aluminum is more positively charged due to a larger electronegativity of the phosphorus. A partial-charge ion model predicts a more positively charged phosphorus. There is still no consensus which model gives the best description of the actual structure.

What can be concluded from this discussion is that it is not straightforward to derive the resulting dipole moment from the available structure analyses. Even the direction is difficult to predict. However, it is undoubtedly clear from the pyroelectric and alignment measurements that, at room temperature, a small net dipole moment remains. If a value for the spontaneous polarization of 30 μ C/m² is used, it can be calculated that there is a dipole moment of about 0.1 mD (5 \times 10⁻³⁴ Cm) per oxygen surrounded T-atom. For a unit charge this corresponds to a displacement of the order of 10^{-15} m. This value can be an

average of larger changes, of course, but it emphasizes that the resulting polarization is quite small as compared to strong pyroelectric materials (e.g. LiTaO₃, 0.2 C/m²).

3.2. AlPO₄-5 Crystals with Guest Molecules. 3.2.1. *Water.* The pyroelectric response along the *c*-axis of a calcined AlPO₄-5 crystal was measured as a function of temperature. The result of the first heating run is displayed in Figure 3a. Around 50 °C the sign of the current changes. After a maximum, at about 60 °C, the current decreases and drops below the noise level at 80 °C. Decreasing the temperature from 150 °C to ambient, the current comes back again at 70 °C and shows a maximum at 50 °C. A change of sign is not observed anymore (Figure 3b). The next heating cycles are reversible, showing the same pattern as during the cooling run.

At the start of the measurement the crystal contained about 20% (w/w) water. During the first heating run, this water is desorbed from the crystal. Most of the water desorbs from the zeolite at a temperature of about 50 °C as could be observed with FTIR and TGA. So, the change in sign of the pyroelectric signal is due to the removal of water from the pores. Above this temperature and also during the cooling run the crystal shows the same pyroelectric response as a dry crystal.

The difference in the pyroelectric signal of dry and waterfilled AlPO₄-5 crystals can have different causes. The water is present in the zeolite as both physisorbed water and chemisorbed water, coordinated to Al. ²⁷Al and ³¹P solid-state NMR measurements established that, upon hydration, up to 40% of the tetrahedral aluminum changes to octahedral aluminum by coordination with two water molecules.²¹ A small amount of the aluminum can also be five-coordinated. According to these measurements the water is randomly distributed over the different aluminum atoms. These five- and six-coordinated aluminum atoms are still connected to P (the framework). This structural transition is reversible by dehydration. Powder XRD measurements showed that the lattice is distorted due to the (coordinated) water by reduction of the Al-O-P bond angles,²² resulting in a small change of the unit cell: dry, a = 13.78 Å, $c = 8.38 \text{ Å}, V = 1378 \text{ Å}^3; \text{ wet, } a = 13.71 \text{ Å}, c = 8.44 \text{ Å}, V =$

Therefore two effects of water on the pyroelectric signal can be distinguished. The first is the altered signal of the lattice due to the changed angles and positions of the atoms. The second one is the introduction of the strong water dipoles (\approx 2 D), which also give a pyroelectric signal if there is some degree of order. Because of the asymmetric lattice and the bonding to aluminum atoms, it can be expected that the water molecules are somewhat oriented. From alignment experiments it follows that the crystals with adsorbed water have an opposite polarization compared to the dry crystals.

The fact that most water desorbs around 50 °C could be due to the phase transition of the lattice from pyroelectric to paraelectric. The spontaneous polarization of the lattice at lower temperatures also gives an explanation why the crystal is remarkably hydrophilic in spite of the neutral framework. On the other hand, the water molecules also influence the framework and thus the phase transition.

3.2.2. Templates and Nonpolar Molecules. The presence of the usual templates and of nonpolar molecules in the channels has only a minor influence on the pyroelectric signal (Figures 4 and 5). The maximum in the temperature dependent measurements is often slightly shifted in temperature, and also the temperature where the signal becomes zero is somewhat different. This is probably due to a small distortion of the lattice by the incorporated molecules. It has been shown with XRD

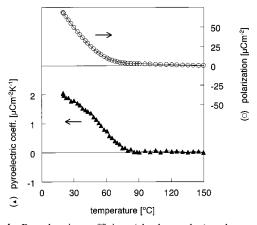


Figure 4. Pyroelectric coefficient (absolute value) and spontaneous polarization as a function of temperature of AlPO₄-5 with a template (TPA).

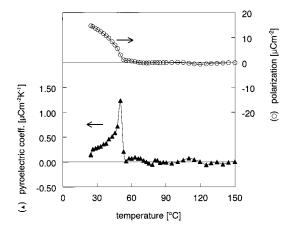


Figure 5. Pyroelectric coefficient (absolute value) and spontaneous polarization as a function of temperature of AlPO4-5 with *p*-dinitrobenzene.

that the cylindrical channel of as-synthesized material is slightly scalloped (9.96 \times 10.08 Å), whereas that of the calcined material is circular within the experimental error (10.01 Å).²³ Also a shortening of c upon calcination has been found. It can be seen in Figure 5 that the pyroelectric behavior of AlPO₄-5 filled with p-dinitrobenzene is almost the same as that of the calcined crystals. Only the maximum is somewhat shifted in temperature. Obviously, these molecules have only a small influence on the phase transition temperature of the lattice. The influence of a template is somewhat larger. In AlPO₄-5 with tripropylamine (TPA) there is no clear maximum in the pyroelectric current, but the pyroelectric coefficient steadily increases with decreasing temperature (Figure 4). The interaction of the bulky TPA with the lattice is probably larger than that of pDNB, thus influencing the phase transition of the lattice. Besides, the TPA molecule itself has also a dipole moment that might influence the pyroelectric signal.

3.2.3. Polar Molecules. The temperature dependent measurements of crystals with adsorbed p-nitroaniline show a lowand a high-temperature plateau with a (phase) transition at 100 °C (Figure 6). The signal of the high temperature plateau is significantly higher than that at low temperatures. It should be mentioned that the pyroelectric coefficient measured at 25 °C ($p = 1.5 \ \mu\text{C m}^{-2} \ \text{K}^{-1}$) agrees very well with data reported earlier. The polarization, shown in Figure 6, was calculated using an upper integration limit of 150 °C. Because the pyroelectric signal is still larger than zero at this temperature,

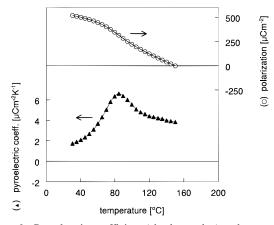


Figure 6. Pyroelectric coefficient (absolute value) and spontaneous polarization as a function of temperature of AlPO₄-5 with pNA.

this approximation will give a value. However, this value is much too low.

Especially at high temperatures there is a large difference between the pyroelectric signal of the calcined and the pNA filled crystals. The signal of the composite has two components: one of the lattice and one of the pNA. The signal of the lattice might also depend on the presence of the inclusion compound. The unit cell of AlPO₄-5 indeed increases upon loading with pNA.24 However, as could be seen from other molecules (e.g. p-DNB), this has only a small influence on the pyroelectric signal of the lattice. Therefore, the major part of the current will be due to the polar guest molecules. The origin of the pyroelectric signal of these molecules is the temperature dependence of the fluctuation angle,9 which predicts a negative sign of the pyroelectric coefficient. From this model it can be concluded that the pNA molecules are oriented with the NO₂ groups toward the center of the AlPO₄-5 crystal. This orientation was confirmed by alignment in an electric field of halfcrystals filled with pNA.

Two aspects of the pNA filled AlPO₄-5 crystals, the adsorption process and the phase transition, will now be discussed in more detail.

Adsorption Process. The reason why pNA molecules form ordered chains in AlPO₄-5 has been a point of debate. It has been proposed that the polar structure of AlPO₄-5 could be the origin of this ordering.⁴ Other authors suggested that it is an intrinsic property of the pNA to enter a zeolite channel with a specific side in front. The latter explanation seemed to be confirmed by pyroelectric measurements, which show a polarization reversal in the center of the crystal, and thus hint to chains with an opposite direction in both halves of the crystal.⁹

However, from the measurements presented here it appears that the empty crystals also show a polarization reversal. Therefore both explanations could be right. In order to be able to distinguish between the two mechanisms, two half-crystals were filled with pNA. If the preferred direction is controlled by the polar structure of the lattice, all pNA molecules will point in the same direction in the crystal (Figure 7c). If, however, the direction had been caused by the specific adsorption, this would again result in a polarization reversal in the center of the sample (Figure 7b).

For these half-crystals no polarization reversal was observed, so all pNA molecules are lined up in one direction. Therefore, the polarization field originating from the host lattice seems to give the proper explanation for the specific adsorption. However, at the loading temperature of pNA (150 °C) the AlPO₄-5

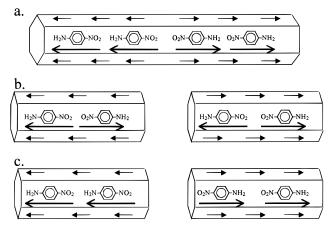


Figure 7. Dipole alignment in AlPO₄-5: (a) pNA in whole crystals, (b) half-crystals showing a polarization reversal, and (c) half-crystals with no polarization reversal. The small arrows indicate the lattice polarization; the large arrows represent the strong dipole moments of the pNA molecules. Dipole vectors point from negative to positive charge.

lattice is not pyroelectric anymore (Figure 3), so most likely the polarization is also zero and, thus, has no influence on the

However, one fact that is related to the asymmetric structure has still not been taken into account; the surfaces of both ends of a half-crystal are not identical in structure. Both sides terminate with another crystal plane, as can been seen in Figure 1, which will result in two chemically distinct surfaces. At one side the aluminum atoms are completely surrounded by the lattice, while the phosphor atoms are exposed, whereas at the other side the reverse is the case. It should be emphasized that even at temperatures above T_c , at which the polarization vanishes, the two surfaces remain different.

Usually, the sorption process of a molecule into a zeolite pore is divided into three steps.^{25,26} First the molecule is adsorbed on the external surface, where a surface layer is formed. In the second step the molecule moves into the pore opening. The last step consists of intracrystalline diffusion. The first two steps are very sensitive to the composition and structure of the surface, thus resulting in a specific adsorption process.

Quite remarkable is the sharp polarization reversal at the center of the pNA filled crystal. It would be expected that if the molecules enter the crystal from both sides, there would be a region near the center where the chains from both sides show some overlap. There are two explanations why this is not observed. The first explanation is that because of a large amount of defects, which is often observed in the core of a single crystal, the diffusion in the center of the crystal is diminished. Another possibility is that the defects give larger holes in which the pNA molecules can reorientate.

Phase Transition. Based on thermodynamic models two physical states of pNA in the AlPO₄-5 channels have been proposed.²⁷ This theory predicts the coexistence of a solidlike and a liquid-like phase up to a critical temperature of about 90 °C. At higher temperatures no different phases exist any more. Temperature dependent IR measurements have shown that a decrease in the amount of hydrogen bonds takes place between 100 and 200 °C.²⁸

Temperature dependent SPEM measurements clearly show a phase transition around 90 °C (Figure 6). This value should not be confused with the theoretical critical temperature! Combining the pyroelectric experiments with the IR results, the following model can be used to describe the behavior of pNA

in the AlPO₄-5 pores: At low temperatures most pNA molecules are connected by hydrogen bonds forming long chains. In that situation the torsional fluctuation of the molecules from the c-axis is restricted because it comprehends a cooperative motion of many molecules. Since the pyroelectric coefficient is related to this fluctuation angle,9 the pyroelectric response is also quite low. At high temperatures the hydrogen bonds are broken and only single pNA molecules are still present. The fluctuation angle will be much larger, being only limited by the confined space of the pores. This gives a higher pyroelectric coefficient, as can be seen in Figure 6.

Around 90 °C the hydrogen bondings start to break up, leading to spatial inhomogeneities in the chains and a coexistence between free pNA molecules and short pNA chains. A small change in temperature will turn pNA molecules from the "polymeric" state into separate molecules, thus showing a fast change in the polarization and a maximum in the pyroelectric coefficient. A quantitative model for the pyroelectric response of the pNA/AlPO₄-5 system will be presented in a forthcoming paper.

4. Conclusions

SPEM measurements on calcined AlPO₄-5 crystals show that the lattice is pyroelectric with a polarization reversal at the center of the crystals, which is evidence for a twinned structure. The measurements also revealed a phase transition at 50 °C of the AlPO₄-5 lattice from a pyroelectric to a paraelectric state. The spontaneous polarization of the lattice is about 30 μ C/m² at 25 °C, which is quite low as compared to strong pyroelectric materials such as LiTaO₃.

The presence of guest molecules, such as template molecules, adsorbates, or water, modifies the position and sharpness of this phase transition. This can be ascribed to a deformation of the lattice and to an ordering of the (polar) molecules in long chains.

Short-range interactions between polar guest molecules and the distinct capping faces of the asymmetric lattice were found to be the reason for the bidirectional adsorption (and formation of dipole chains) of polar molecules, such as p-nitroaniline. The specific temperature dependence of the pyroelectric activity of AlPO₄-5/pNA and the observation of a relaxation process were assigned to cooperative motions of the one-dimensional pNA chains. This is in line with theoretical predictions of the coexistence between a solid-like and a liquid-like pNA phase.

Similar behavior is expected for other nonsymmetric microporous AlPO4 structures loaded with a variety of polar molecules.

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