Spontaneous Polarization and Orientational Dynamics of Polar Rod-like Molecules in Host/Guest Materials

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ABSTRACT
The polar domain structure and dynamics of host/guest materials which include polar rod-like molecules were investigated by pyroelectric and dielectric techniques. Using scanning pyroelectric microscopy (SPEM), spatially resolved information on a μm scale was obtained of the 3-D domain structure of the polarization caused by an acentric host lattice and/or the polar arrangement of dipolar guest molecules. Two classes of pyroelectric host/guest materials were examined with SPEM: (1) an inorganic host (zeolite AlPO₄-5) which was loaded with p-nitroaniline (PNA) guest molecules by an adsorption process, and (2) an organic channel-type inclusion material, which establishes its macroscopic polarity by cocrystallization of perhydrotriphenylene (PHTP) with the polar guest 1-(4-nitrophenyl)piperazine (NPP). Despite great differences in the chemical composition and morphology, both types of host/guest systems revealed 180° macro-domains, of which the particular shape and sign of the polarization were in accordance with models about crystal growth and/or directed adsorption of polar molecules. In order to assess the molecular dynamics of the included guest molecules, frequency dependent local pyroelectric measurement, based on SPEM, and broad-band dielectric relaxation spectroscopy were performed. Whereas guest molecules included in PHTP channels show no rotational dynamics, we found several relaxation processes in PNA-loaded AlPO₄-5 crystals, which were assigned to local and cooperative relaxation modes of molecular chains of the hydrogen-bonded PNA guest molecules.

1 INTRODUCTION
Channel-type inclusion compounds and zeolite based host/guest systems are promising materials for crystal engineering of stable and highly efficient 2nd order nonlinear opticaly active and pyroelectric materials. Their common feature is the ability to establish a noncentrosymmetric arrangement of hyperpolarizable molecules in structural voids, either by co-crystallization of guest and host molecules (inclusion crystals cf. Figure 1(a) to (c) or due to directional adsorption of guest molecules in zeolite channels (cf. Figures 1(d) to (f) and 2). The molecular mechanisms for polar growth in inclusion compounds [1], as well as for directed adsorption of p-nitroaniline (PNA) molecules in AlPO₄-5 [2], have been investigated in the last few years, leading to
the understanding of the key mechanisms [3, 4].

Figure 1. Schematic representation of two different polar host/guest structures and their building units. above: (a) stack of 2 PHTP molecules, (b) guest compound NPP and (c) lattice model of a PHTP-NPP inclusion crystal; below: (d) view on the AlPO4-5 framework along the channel axis, (e) structure of PNA and (f) illustration of the channel system of AlPO4-5 filled with PNA guest molecules.

In order to study the polarization direction and possible domain structures of the macroscopic polarization in polar materials, we have applied a new scanning probe technique based on local pyroelectric measurements (SPEM). After a brief description of the experimental technique, we will discuss the pyroelectric information obtained for polar inclusion crystals and PNA-loaded zeolites, which yielded details on the growth process of the (guest) host crystal or peculiarities of the adsorption behavior of AlPO4-5.

Not much is known about the molecular dynamics of polar host/guest materials, except that full reorientation of the included polar guest molecules by 180° flips is practically impossible for steric reasons. The very absence of such a relaxation process of the guest molecules in both zeolite-based and PHTP-based host/guest systems makes them attractive as polar materials. This can be rationalized easily for PHTP inclusion crystals, where rod-like guest molecules like 1-(4-nitrophenyl)piperazine (NPP) are tightly packed in the PHTP channels and are stabilized by van der Waals forces and e.g. guest-guest hydrogen bonds. In contrast, the formation of polar order in the nano-porous zeolite AlPO4-5 during the filling process requires sufficient molecular mobility for diffusion of PNA guest molecules over macroscopic distances along rigid tubes of diameter \( \sim 0.73 \) nm. Polarized Fourier transform infrared (FTIR) measurements have shown that restricted torsional fluctuations of the PNA molecules from the c-axis (channel axis) exist and that the mean fluctuation angle and the degree of H-bonding between PNA molecules are temperature dependent even at room temperature [5].

Recently, dielectric spectroscopy on AlPO4-5/PNA crystals has revealed a strong relaxation process that was assigned to cooperative motions of the one-dimensional PNA-chains [6], since the relaxation time followed a Vogel-Fulcher-Tammann (VFT) behavior. In the present paper we describe results from (dynamic) pyroelectric experiments on the same materials, which allow the study of individual crystals. A comparison between dielectric and pyroelectric relaxation times will be made.

2 MATERIALS AND SAMPLE PREPARATION

2.1 ZEOLITE SAMPLES

Large AlPO4-5 crystals were synthesized in Teflon™ lined autoclaves with triethylamine as a template. To remove the organic template, the crystals were calcined at 700°C for 48 h. The removal of the template was verified with FTIR measurements, the crystal structure was checked by X-ray diffraction. Freshly calcined crystals were filled with PNA from the vapor phase at 155°C for \( \sim 4 \) h. This procedure resulted in an average degree of filling with PNA molecules of \( \sim 5 \) wt% as verified by FTIR and thermogravimetric analysis.

2.2 PREPARATION OF PHTP INCLUSION COMPOUNDS

In this study, inclusion crystals based on perhydrotriphenylene (PHTP) and the donor/acceptor (DA) disubstituted chromophore NPP were investigated. Needle-shaped crystals of 1 to 3 mm in length and 0.2 to 0.5 mm in thickness were obtained by crystallization from solution, resulting in crystals with a nearly hexagonal cross section. The needle axis corresponds to the channel axis. Further details concerning the crystal growth and the sample preparation are described in [7].

3 EXPERIMENTAL SETUP

3.1 SCANNING PYROELECTRIC MICROSCOPY

A schematic representation of the SPEM equipment is shown in Figure 3. The sinusoidally modulated beam of a laser diode is focused by use of the objective of a conventional microscope onto the blackened surface of a pyroelectric crystal. The charges generated are collected on a metal plate that is connected to a current amplifier (Keithley 428, conversion factor \( 10^9 \) to \( 10^{10} \) V/A). A digital lock-in amplifier (Stanford Research 850) provides the sinusoidal modulation voltage and phase sensitive analysis of the response. In order to perform the scanning of the sample surface the whole sample/electrode system is
mounted on a motorised X-Y-displacement unit. More experimental
details are given in [8].

![Experimental setup of SPEM.](image)

**Figure 3.** Experimental setup of SPEM.

To ensure a high resolution of the pyroelectric measurements, two
requirements must be fulfilled

1. high optical resolution, i.e. small spot size of the laser beam ($d \approx 5 \mu m$),

2. short thermal diffusion length $\mu = \sqrt{K/\pi f}$ ($K$ is the thermal dif-

To match these conditions for polymers and organic crystals ($K \approx$
$10^{-9} m^2/s$) frequencies in the kHz range are necessary (case a in Fig-

4). However, if low frequencies are used – which cause semispher-

ical heat profiles (case b in Figure 4) – one can probe the pyroelectric

To perform temperature and frequency dependent pyroelec-

tric experiments on individual AlPO$_4$-5/PNA crystals, the SPEM setup

was combined with a hot/cool stage (Linkam THM 600), which was

modified by a sample holder for accurate crystal positioning. A laser

spot of $\approx 50 \mu m$ in diameter was adjusted such that the crystal was

heated close to the free end of the crystal. According to [9] this re-

sulted in probing the pyroelectric activity in a volume of the crystal,

the size of which depends on the modulation frequency. Consequently,

doing the domain contributing to the pyroelectric response varied from the ir-

radiated crystal’s half (at high frequencies, $f > 100$ Hz) to the whole

crystal (at low frequencies). Since both halves are pyroelectric with op-

site sign, low frequencies result in a decrease of the pyroelectric re-

sponse due to the influence of the bipolar polarization profile. For this

reason the practically usable frequencies were limited to range from

2 Hz to 2 kHz.

![Thermal profiles for different thermal diffusion lengths in rod-

like samples between oversized electrodes. The situation on the far left (a)

ensures the highest possible thermal resolution.](image)

**Figure 4.** Thermal profiles for different thermal diffusion lengths in rod-

like samples between oversized electrodes. The situation on the far left (a)

ensures the highest possible thermal resolution.

### 3.2 PYROELECTRIC SPECTROSCOPY

In order to perform temperature and frequency dependent pyroelec-
tric measurements on individual AlPO$_4$-5/PNA crystals, the SPEM setup

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sponse due to the influence of the bipolar polarization profile. For this

reason the practically usable frequencies were limited to range from

2 Hz to 2 kHz.

![Pyroelectric images obtained on various AlPO$_4$-5 crystals: (a)

crystal (1 to 1 pA; $f = 2000$ Hz, $\Delta y = 10 \mu m$), (b) single domain crystal grown on a substrate (black

= 0, white = positive current), (c) abnormally grown crystal showing 3 po-

larization reversals, (d) asymmetrically grown and incompletely calcined

crystal; the black area within the white part probably indicates residuals

from the organic template, (e) cross section of an abnormally grown crystal

with core exhibiting a polarization opposite to that of the outer regions. In

all Figures (except (b)) the pyroelectric current is shown on a gray scale,

reaching from black (negative current) via half-gray (zero) to white (posi-

tive current).](image)

**Figure 5.** Pyroelectric images obtained on various AlPO$_4$-5 crystals:
(a) complete (twinned) empty crystal (-1 to 1 pA; $f = 2000$ Hz, $\Delta x/$
$\Delta y = 10 \mu m$), (b) single domain crystal grown on a substrate (black

= 0, white = positive current), (c) abnormally grown crystal showing 3 po-

larization reversals, (d) asymmetrically grown and incompletely calcined

crystal; the black area within the white part probably indicates residuals

from the organic template, (e) cross section of an abnormally grown crystal

with core exhibiting a polarization opposite to that of the outer regions. In

all Figures (except (b)) the pyroelectric current is shown on a gray scale,

reaching from black (negative current) via half-gray (zero) to white (posi-

tive current).

### 3.3 DIELECTRIC SPECTROSCOPY

For dielectric measurements, PNA loaded AlPO$_4$-5 crystals were put

between circular brass electrodes of 20 mm in diameter, resulting in a

moderately packed layer ($\approx 40\%$vol packing density) with a thickness

of $\approx 85 \mu m$ of preferentially planar oriented crystals. Preparation took

place either in vacuum or under flowing gaseous nitrogen. Dielectric

experiments were performed using a combination of three dielectric

measurement systems covering a broad frequency range from $10^{-2}$ Hz
to $10^9$ Hz:

1. a frequency response analyzer (Schlumberger 1260) equipped with a

custom made dielectric interface (developed by TNO) for frequencies

between $10^{-2}$ and $10^9$ Hz,
2. a Hewlett-Packard 4284 A precision LCR-meter for frequencies between $10^3$ and $10^4$ Hz, and
3. a Hewlett-Packard rf-analyzer HP4291 A for the frequency range from $10^6$ to $1.8 \times 10^6$ Hz.

The sample was placed in a nitrogen cryostat (Novocontrol), the temperature of which was controlled with a stability of better than ±50 mK.

4 POLAR DOMAINS IN ZEOLITES FILLED WITH DIFFERENT GUEST MOLECULES

The SPEM measurements on empty crystals of aluminophosphate AlPO$_4$-5 with channel-like nanopores always revealed a polarization reversal in the middle part of these crystals (Figure 5(a)) [10]. This behavior can be ascribed to the crystallization process, in which the crystals grow freely from a seed into opposite directions with one particular absolute configuration. However, a single domain crystal is formed when the crystal is grown from a substrate (Figure 5(b)).

In some cases, especially after fast crystallization, deviating crystal shapes and complex domain structures were found. This can be caused, for example, by the presence of more defects, intergrowth of crystals in the early stage, dendritic growth, or secondary nucleation. A few examples are shown in Figures 5(c) to (e). Because the material grows with the polarization direction always the same as the growth direction, the SPEM images contain information about the growth history of the sample. In other words, the domain structure after growth represents the frozen-in evolution of the growth process. Figure 5(e) shows a cross-section of a crystal in which the core of the crystal has an opposite polarization compared to that of the surface region. The SEM images of samples from different stages in the crystallization process confirm that these parts actually grew in an opposite direction.

5 POLAR DOMAIN STRUCTURE IN PHTP BASED INCLUSION COMPOUNDS

Another successful application of SPEM was the characterization of the 3-dimensional polarization distribution in a polar perhydrotriphylene PHTP based inclusion compound. Although the PHTP host lattice and most of the pure guest crystal structures themselves are centrosymmetric, the inclusion crystals appeared to be polar for most of the tested polar guest molecules (e.g. NPP, 4-iodo-4'-nitrophenyl (INBP)) [12].

A first important result from SPEM imaging on PHTP-NPP inclusion crystals was the observation of macrodomains featuring opposite polarizations [7,12]. Recent SPEM experiments of the crystal core region, utilizing an improved spatial resolution (~10 μm), showed an hourglass shaped domain structure, which was predicted by a growth model based on Markov’s theory of stochastic processes. Figure 8 gives an example of a successively thinned PHTP-NPP crystal, yielding the lateral polar domain structure at three different depths. In particular, the third scan (Figure 8(c)), which refers to a layer 100 μm beneath the original surface, shows conical structures pointing to the suggested seed region. Whereas the domain structure is rather complicated in the center of the
crystal, the polarization becomes almost homogeneous near the capping faces of the crystal (Figures 8(a) to (c)).

In order to scan a capping face we have replaced one of the metal sample electrodes by a transparent (indium tin oxide (ITO) coated glass) electrode. The result of a scan with the laser beam parallel to the crystal's needle axis is presented in Figure 9 and confirms the suggested unipolar state at the end of the growth process.

6 DYNAMICS OF pNA GUESTS IN ALPO4-5

6.1 DIELECTRIC RELAXATIONS

Dielectric experiments on AlPO4-5/PNA powder samples were performed isothermally at temperatures increasing and decreasing stepwise (ΔT = 2.5 K). After a first heating run to 195°C, during which residual absorbed water was removed, the samples were slowly cooled to -150°C. Subsequent repeated heating and cooling showed a highly reproducible relaxation behavior that hardly depends on the direction of the temperature variation. Typical spectra are given in Figure 10. Three well-separated relaxations show up:

1. the fastest and weakest (β relaxation) becomes visible only at T > 50°C, its peak maximum shifts only a little with temperature,
2. a strong asymmetric α relaxation, and
3. a slow process (II), the peak frequency of which is > 4 decades lower than \( f_\alpha \) and which depends slightly on the thermal history of the sample.

For a quantitative analysis we fitted the two strong relaxation processes in the loss spectra with Havriliak-Negami (HN) functions according to Equation (1)

\[
\varepsilon''(\omega) = -\sum_{k=1}^{2} \frac{\Delta \varepsilon_k}{\left(1 + (i\omega \tau_k)^{\alpha_k}\right)^{\beta_k}}
\]

where \( \Delta \varepsilon_k \) and \( \tau_k \) denote the relaxation strength and the mean relaxation time of the kth process, and \( \beta_k \) indicates the imaginary part. The two peak shape parameters \( \alpha_k \) and \( \beta_k \), which determine the slope of the low frequency tail \( n = a \) and the high frequency tail \( n = -ab \), are related to the underlying distribution in relaxation times. The peak relaxation frequencies of both relaxation processes vs. the inverse temperature are presented in Figure 11.

The most striking result is the behavior of \( f_\alpha \) (or \( \tau_\alpha = \left(2\pi f_\alpha^{-1}\right) \)), the temperature dependence of which at high (75°C < T < 160°C) temperatures can be described quite well by a VFT Equation (2) with the parameters \( \log(T_0) = -5.8 \), \( E_V = 3.4 \text{ kJ/mol} \) and \( T_V = 296 \text{ K} \).

\[
\tau(T) = \tau_0 \exp \left[ \frac{E_V}{R(T - T_V)} \right]
\]

Such a VFT-behavior is typical for a dynamic glass transition and indicates cooperative rearrangements of the participating (PNA) molecules on a temperature dependent cooperativity length scale \( \xi(T) \). At T \( \sim \) 72°C the relaxation time \( \tau_\alpha \) departs markedly from the VFT law, indicating a change in the cooperative dynamics; this usually defines
interchannel dipole-dipole interactions are considered. The existence of 
rate which followed an Arrhenius law. Since in AlPO4-5 each individual 
molecules adsorbed in the straight channels of AlPO4-5 might even un-
change in its temperature dependence from VFT to Arrhenius behavior,
has been discussed in detail in [6], in terms of the cooperativity length
neighboring molecules
rather than one-dimensional interactions of the PNA molecular ensem-
eters for the
process were obtained by fitting the high temperature data (solid line) and the low temperature data (dashed line) with the VFT and the Arrhenius-equation separately.
the glass transition temperature $T_g$. Further lowering of the tempera-
clearly reveals an Arrhenius-like behavior of $\tau_a$ which can be an-
alyzed conveniently, since the relaxation rate at $T_g$ is unusually high
($f_{T_g} = 24$ Hz). The Arrhenius parameters of the $\alpha$ relaxation as well as those of process II are given in Figure 11.

The observation of liquid-like dynamics in one-dimensional molecu-
chains of PNA is far from self-evident. Recently, Huwe et al. [13, 14]
studied the relaxation behavior of ethylene glycol (EG) confined to zeo-
lite host systems with different pore sizes. These authors found that co-
operative (liquid-like) dynamics already exists in ensembles of as small
as 6 EG molecules as manifested by a VFT behavior of the relaxation
time. By contrast, zeolitic hosts with smaller pores or cages, result-
ing in arrangements of EG molecules with a lower average number of
neighborings molecules ($<6$), showed a drastically increased relaxation
rate which followed an Arrhenius law. Since in AlPO4-5 each individual
PNA molecule can have only two directly interacting neighbors, other
long-range PNA-PNA interactions along and across the zeolite channels
must be taken into account to explain the cooperative dynamics.

Leike and Marlow [15] have shown by model calculations that PNA
molecules adsorbed in the straight channels of AlPO4-5 might even un-
dergo a first order phase transition when both intra- and (long-range)
interchannel dipole-dipole interactions are considered. The existence of
a VFT type behavior, therefore, supports the idea that both intrachan-
(H bonding, van der Waals and electrostatic forces) and interchan-
(delectric interactions) evolve to 3-dimensional rather than one-dimensional interactions of the PNA molecular ensemble.

The second peculiarity of the dielectric $\alpha$ process, the pronounced
change in its temperature dependence from VFT to Arrhenius behavior,
has been discussed in detail in [6], in terms of the cooperativity length
$\xi$ of the $\alpha$ process. In this view, the change from VFT to Arrhenius
behavior marks the temperature below which $\xi$ probes the size of PNA
molecular ensembles.

6.2 PYROELECTRIC SPECTROSCOPY AND COMPARISON WITH DIELECTRIC RESULTS

The manifestation of a molecular relaxation process in the pyroelec-
response became already clear by temperature dependent pyroelec-
measurements on AlPO4-5/PNA, which revealed a maximum at $\sim$
85°C and $f = 1$ kHz, see Figures 6 and 7. Systematic pyroelectric mea-
ments using different frequencies, i.e. pyroelectric spectroscopy
experiments, were performed using a similar temperature schedule as
for the dielectric experiments. Again, the samples first were dried at
185°C and then measured during slow cooling to 25°C. A typical result
is given in Figure 12, which shows the absolute value of the pyroelec-
tic current as function of temperature and frequency. All curves clearly
reveal a peak at high frequencies that shifts toward lower temperatures
at lower frequencies. The similar behavior of the high-frequency curves
at low temperatures ($T<60^\circ$C) as well as the additional local maximum
$T \sim 55^\circ$C for the low-frequency curves can be attributed to the pyro-
electric $\rightarrow$ paraelectric transition of the AlPO4-5 lattice itself [10].

![Figure 11](image)

**Figure 11.** Arrenhius plots of the peak relaxation frequency $f_\alpha$ for AlPO4-5/PNA as function of 1/temperature. The relaxation peak data of process II at low temperatures ($\alpha$) were extrapolated by a constrained HN-fit, assuming temperature independent values for $\Delta c_2$ and $\alpha_2$ in Equation (1). The two fit curves of the (upper) $\alpha$ process were obtained by fitting the high temperature data (solid line) and the low temperature data (dashed line) with the VFT and the Arrhenius-equation separately.

![Figure 12](image)

**Figure 12.** (Top) Pyroelectric current of an AlPO4-5/PNA single crystal as function of temperature and frequency; (bottom) dielectric loss of an AlPO4-5/PNA powder sample.

For comparison, the pyroelectric relaxation data are presented to-
gether with the dielectric relaxation loss maxima in Figure 13. On first
sight, there is a fair agreement between the pyroelectric and dielectric
relaxation peak frequencies, which clearly implies a common molecular
relaxation mechanism. Nevertheless, the pyroelectric relaxation seems
to be significantly slower than the dielectric $\alpha$ process. This prompted
us to re-analyze the dielectric loss data by using two symmetric HN
functions for the $\alpha$ peak instead of one symmetric HN function. A good
reason was the particular asymmetric shape of the $\alpha$ process ($\tau_\alpha < \tau$),
which is very unlikely for cooperative $\alpha$ relaxations. As a result, the
dielectric $\alpha$ process could be decomposed in two well separated relax-
action processes, one close to the overall peak maxima, the other more
than one decade slower than the fast relaxation mode.

Given the fact that two dielectric and one prominent pyroelectric re-
xaction modes were encountered, one should visualize the possible co-
operative relaxation modes for an H-bonded PNA chain segment. Two
rather too high than too low. However, the discrepancies are still within the experimental uncertainties, e.g. caused by pronounced orientation and depolarization effects due to the very different sample geometries in the dielectric and pyroelectric experiments.

7 CONCLUSIONS
Scanning pyroelectric microscopy has proven to be a powerful tool for the spatially resolved pyroelectric characterization of host/guest materials. Two types of host/guest materials were investigated,

1. the zeolite AlPO4-5/PNA, and
2. an organic channel-type PHTP-NPP inclusion crystal, both reveal 180° macro-domains of the polarization.

Besides simple polarization reversals, a few examples for more complicated domain shapes were discussed in terms of models for the crystal growth and/or the filling process (AlPO4-5/PNA).

In addition to the static polarization domain structure, the molecular dynamics of PNA molecules confined in the nano-channels of AlPO4-5 was elucidated by broadband dielectric relaxation spectroscopy and pyroelectric spectroscopy, based on SFEM. These complementary techniques revealed independently the ‘liquid-like’ cooperative dynamics of PNA chain fragments, which is indicated by the VFT temperature dependence of the corresponding relaxation. In particular, two coupled dielectric relaxation modes and one pyroelectric relaxation process were found, the existence of which is in fair agreement with a proposed cooperative relaxation mechanism for molecular chains of hydrogen-bonded PNA guest molecules.

REFERENCES


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