Pyroelectric Effects on Molecular Sieve Crystals Loaded with Dipole Molecules

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The pyroelectric effects of dipolar guest molecules in molecular sieve crystals have been studied for the first time. The measurements have been done on assemblages of aligned crystals as well as on individual single crystals of the aluminophosphate molecular sieve $\text{AlPO}_4\text{-5}$ loaded with *p*-nitroaniline (PNA). The PNA molecules form unidirectionally aligned dipole chains in parallel molecular sieve channels. We found that the PNA dipoles are oppositely directed in the two halves of a single crystal, forming two macroscopic regions of opposite polarization. It is concluded that the preferred direction of the dipole chains in the channel is a result of the adsorption process of the molecules into the channels.

1. Introduction

The ordering of guest molecules by the channels of molecular sieves attracts increasing interest because of the resulting optical effects.¹⁻⁹ The anisotropy in the adsorption of visible⁶ and infrared⁵ light, in Raman scattering,⁸ and in fluorescence shows that the guest molecules are very well aligned. It is found that *p*-nitroaniline (PNA) molecules in the channel of the molecular sieve $\text{AlPO}_4\text{-5}$ form solidlike dipole chains, in which the orientation of the molecular length axis differs from the channel axis by less than 9° (ref 8). This good alignment is a result of the interplay of the restricted space in the channels and the electrostatic forces in the dipole chain.

In addition to the alignment of the molecules, the occurrence of nonlinear optical effects of second order on dye-loaded molecular sieves proves that the molecules must have a preferred direction in all channels. Otherwise, the effects of differently oriented molecules would cancel each other, and nonlinear optical effects of second order (e.g., second harmonic generation^{1,2,7}) would not be observed. There is no doubt about the existence of the preferred direction of the molecules inside the channels, but nevertheless, the question *why* it exists is still not answered. According to our knowledge, there are two hypotheses to explain the molecular ordering: The first one¹ makes use of the electrostatic fields that likely exist in a number of acentric molecular sieves. These electric fields may align the molecules into the field direction. The second hypothesis² is based on adsorption effects. For an asymmetrically para-substituted benzene, for example, there should exist a different probability for the molecule to enter the molecular sieve channel with one of the two substituents at the benzene ring in front. Then the first adsorbed dipole molecule determines the direction of the chain of molecules. Obviously, these two hypotheses have striking consequences on the resulting distribution of the dipole orientation. According to the first hypothesis, the dipoles have to be oriented in the same direction in the whole crystal ($\rightarrow\rightarrow\rightarrow\rightarrow\rightarrow$), whereas the second hypothesis forecasts a polarization reversal in the middle of the crystal since the molecules can enter from both sides ($\rightarrow\rightarrow\rightarrow\leftarrow\leftarrow\leftarrow$).

In the present paper we intend to decide which of these hypotheses can be right by investigating the permanent polarization of the crystals. To this aim we studied the pyroelectricity of a permanent polarization as the probe for the orientation of the dipoles in the crystal.

Every permanent polarization will change when the temperature is changed. Therefore, molecular sieve crystals loaded with dipolar molecules must show pyroelectric effects. In our experiments the temperature of the sample is varied by laser-stimulated heating. This technique is extensively used in the investigation of poled polymer films.¹⁰ By comparing the measured results with models describing the conduction of heat in the sample, one can find the polarization distribution in the sample.^{12,13} However, no standard model fits the thermal properties of our samples. Nevertheless, some conclusions can be drawn right away from the measurement results. For example, if there were oppositely directed dipole chains in the two halves of the rod-shaped $\text{AlPO}_4\text{-5}$ crystal, the pyroelectric currents would have to be strongly dependent on the position where the crystal is heated. In this paper we therefore focus on the qualitative results concerning the dipole distribution. In a forthcoming paper theoretical models of the thermal processes in the sample will be discussed, which allow a full quantitative analysis of the measured data.

2. Experimental Section

Method. Measurements of the pyroelectric coefficient require a well-defined temperature variation in the sample as well as the measurement of the resulting surface charge density. The variety of different pyroelectric techniques is often distinguished in either quasistatic or dynamic temperature changes by means of heat pulses or periodically modulated heat fluxes.^{11,12} Then the resulting change of surface charge density can be measured as a change of the surface potential or as a discharge current. The current measurement has some advantages; e.g., it ensures that the sample is kept under zero-field conditions.

In our measurements we applied the so-called continuous wave technique using a sinusoidally modulated heat flux. For a one-dimensional heat transport model the dissipation of heat from a heat source can be described by the thermal diffusion length

$$\mu = \sqrt{2K/\omega} \quad (1)$$

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Figure 1. Experimental setup.

where K and ω denote the thermal diffusivity of the sample and the circular frequency, respectively. The meaning of μ is that a thermal wave after the distance μ will be attenuated to $1/e$ of its initial amplitude. In other words, the modulation frequency controls the propagation length of the thermal wave and, therefore, the volume in which the thermal excitation changes the temperature.

A pyroelectric spectrum (dependence of the pyroelectric current on the modulation frequency of the heat flow) contains information about inherent material properties (distribution of the pyroelectric activity $p(x)$, thermal constants) as well as about the sample geometry which affects the particular heat conduction problem. The low-frequency region describes integral properties of the sample, whereas the high-frequency values involve only those parts of the sample which are near to the heat source. In principle, one can reconstruct the pyroelectric distribution $p(x)$ by deconvolution of the pyroelectric spectra.¹³

Experimental Setup. The experimental setup is shown in Figure 1. For modulated heating of the samples the beam of a He-Ne laser (25 mW, attenuated to 7...16 mW) is used. The beam passes an acousto-optical modulator (AOM), and its modulated output component reaches the sample. To keep the sample under short circuit condition, we fed the sample response to a current amplifier (Keithley Model 428, gain 10^7 V/A). A lock-in-amplifier (SR 850) provides the sinusoidal reference voltage for driving the AOM and for the phase-sensitive analysis of the pyroelectric response. In our experiments we used modulation frequencies from 0.1 Hz to 100 kHz. Pyroelectric spectra were measured with a current sensitivity practically better than 10^{-14} A. The entire data acquisition was under computer control.

For the particular requirements of measuring molecular sieve single crystals, we have modified this standard setup by optical components for focusing and scanning the laser spot across the sample surface. It was possible to scan with the focus (diameter about 40, 100, or 500 μm) over the sample (resolution 1 μm). Measurements were generally done at room temperature (25 $^{\circ}\text{C}$). Only the results given in Figure 3d refer to 20 $^{\circ}\text{C}$.

Samples. The $\text{AlPO}_4\text{-5}$ crystals used were synthesised hydrothermally by Finger and Kornatowski¹⁴ and stem from only one batch. The $\text{AlPO}_4\text{-5}$ molecular sieve has a one-dimensional pore system of 7.3 $\text{\AA}$ wide parallel channels extending in the length direction of the crystals. The crystals themselves are supposed to be pyroelectric (intrinsic pyroelectricity). From our experiments it turns out that the pyroelectric effect of the adsorbed molecules dominates the total pyroelectric signal. A gas phase adsorption process was used to load the crystals with the PNA molecules (150 $^{\circ}\text{C}$, 6 h). After loading, the crystals showed a homogeneous yellow color with light yellow endings. The color depends on the polarization direction of light indicating an ordered incorporation into the molecular sieve

Figure 2. Microscopic picture of the single crystal samples: (a) HSC and (b) WSC.

channels.⁶ The mean loading with PNA molecules amounts to about 11% (w/w).

Four kinds of samples have been investigated; we name them as follows:

- HCA, half-crystal assemblage;
- WCA, whole-crystal assemblage;
- HSC, half single crystal; and
- WSC, whole single crystal.

The HCA and the WCA are vertically aligned assemblages of PNA-loaded molecular sieve crystals imbedded in an epoxy resin film with a thickness of about 100 and 200 μm , respectively. These aligned arrangements of crystals may be assembled by the application of electric fields¹⁵ or using electrostatic pincers consisting of a thin metallic wire. The HCA were obtained by abrading the epoxy resin film containing the vertically oriented PNA-loaded crystals until one-half of each crystal was lost. The epoxy resin films were attached to a Cu plate (1 mm thickness). For providing the second electrical contact of the epoxy layer, a thin Au film was sputtered onto the epoxy resin film opposite to the Cu plate. The Au electrode was colored black with a very thin color film (about 1 μm) to ensure a high absorption of laser radiation and to avoid absorption in the sample volume. From the viewpoint of heat conduction these samples may approximately be regarded as a (one-dimensional) layer structure.

The HSC and the WSC are single crystals or fragments of them between two Cu wires (see Figure 2). The wire and the crystal are imbedded in epoxy resin. Before assembling the HSC sample a single crystal was broken in two parts. We took the smaller fragment for our investigations. The crystal's length axis was placed perpendicularly to the laser beam. The absorption of the light by PNA in the crystal was used to heat the samples. Therefore, there are sources of heat in the crystal volume. The heat flows mainly from the crystal to the Cu wires.

Figure 3. Pyroelectric current as a function of the heat flow modulation frequency for different samples: (a) half-crystal assemblage, (b) whole-crystal assemblage, (c) half single crystal, (d) whole single crystal with the laser focus on the left (circles) or on the right half (squares), respectively. The full symbols refer to real parts, and the open symbols refer to the imaginary parts of the current.

Approximately, the heat conduction can be regarded as quasi-one-dimensional perpendicular to the laser beam.

It was not our aim to have electrically conducting contacts between the crystals and the copper wires. The polarization induced by the pyroelectric effect induces compensation charges in the electrodes. The change of these compensation charges is the measured current.

3. Results

The pyroelectric spectra are shown in Figure 3. In detail we point out the following observations:

(a) Half-Crystal Assemblage (HCA). Here a signal for frequencies lower than 1 kHz has been observed. For $f = 1$ Hz it still differs from zero. The real part of the current has its maximum at about 30 Hz (± 10 Hz, dependent on the position of the beam on the sample). For $f < 1$ Hz the signal becomes very small.

(b) Whole-Crystal Assemblage (WCA). The pyroelectric spectrum is similar to that of the HCA; however, the maximum frequencies are shifted toward higher frequencies. The real part has now the maximum at about 100 Hz. The signal nearly vanishes for $f < 10$ Hz.

For a WCA prepared with nonloaded crystals no pyroelectric current differing from noise has been found.

(c) Half Single Crystal (HSC). A pyroelectric signal has been measured for both focused and homogeneous irradiation. Approximately, the signal only depends on the amount of laser power that is reaching the crystal. This is also visible in Figure 4a, showing a scan over the crystal in length direction. Here, the maximum response corresponds to irradiation of the crystal middle.

The absolute value of the pyroelectric current grows monotonously with rising frequency. However, the phase of the

signal changes strongly. Between 1 and 7 kHz the signal changes its sign. This behavior strongly depends on temperature.¹⁶ At temperatures below 0 °C the change in sign completely disappears.

(d) Whole Single Crystal (WSC). The signal strongly depends on the size of the heating laser spot. Homogeneous illumination of the entire crystal results in a low pyroelectric response whose intensity is at most one-fifth of the signal of the HSC with the same optical excitation. Furthermore, the signal strongly depends on the position of the laser focus on the crystal. Figure 3d shows the spectra obtained near the different ends of the crystal. Obviously, the two signals possess different signs. Scanning with the laser focus over the crystal, one finds that the signal is very small somewhere in the middle of the crystal and reaches the extreme values near the crystal ends (see Figure 4b). However, in the two extreme positions it is just in opposite quadrants of the complex plane.

The two crystal halves do not fully behave symmetrically. This asymmetry differs for different samples of the WSC type.

For estimating the absolute magnitude of the pyroelectric effect, we compared the response of the WSC with the response of a well-characterized PVDF film. The PVDF result was used to determine the modulation amplitude of the laser intensity (1.5 mW). For this modulation amplitude we found a pyroelectric response of 0.6 pA for the WSC at high frequencies at the position of maximum response. Approximately 94% of the laser light is absorbed by the used crystal for the used polarization parallel to the crystal's long axis (K. Hoffmann, microfocus absorption measurement, unpublished). Using an estimate of the crystal specific heat ($c_p = 3 \text{ J m}^{-3} \text{ K}^{-1}$), one finds for the pyroelectric coefficient an experimental value of $|p| \approx 1.5 \text{ } \mu\text{C m}^{-2} \text{ K}^{-1}$ (see e.g. ref 10, discussion below).

From the direction of the currents we deduced that both ends

Figure 4. Real part of the pyroelectric current as a function of the x -position on the sample and of the logarithmic frequency: (a) HSC ($f = 0.3\text{--}30$ kHz), (b) WSC ($f = 2\text{--}10$ kHz). For more clarity the frequency scans in (b) were smoothed, and the frequency axis is drawn in the reversed direction.

Figure 5. Schematic representation of the single crystal samples. The arrows denote the distribution of dipoles in the crystal. Our measurements suggest that the arrows point from the NH_2 to the NO_2 group (see text).

of whole single crystals must become more negatively charged while raising the temperature.

4. Discussion

The experimental results yield three independent arguments, indicating that there are opposite dipole directions in the two parts of the PNA-loaded $\text{AlPO}_4\text{-5}$ crystals.

1. The pyroelectric signals have opposite signs at the two crystal ends of the WSC. An opposite polarization direction would explain this in a natural way. Consequently, the HSC shows no dependence in sign on the position. Simply the

amplitude of the signal is varied depending on the amount of light reaching the crystal. The differences in the intensities of the signal of the left and of the right parts in the WSC can be explained by the intrinsic pyroeffect of the molecular sieve framework, by differences in the PNA concentration in the two parts or by asymmetries in the macroscopic sample arrangement (different gaps between crystal and electrode).

2. Under homogeneous irradiation the HSC shows a much higher signal than the WSC. This can be understood if the pyroelectric effects of the two crystal halves partly cancel each other. If both crystal parts had nearly the same polarization (including their direction), the pyroelectric signal of the WSC would have to be about the same as for the half crystal (compensation of the effects of more dipoles and larger electrode distance).

3. Comparing the ensemble samples, one finds that the HCA shows pyroeffects at low frequencies down to 1 Hz and the WCA does not. For these slowly varying temperatures the thermal diffusion length μ is much larger than the relevant lengths in the sample. In other words, the crystals are nearly homogeneously heated. Half crystals produce pyroelectric currents then, whereas the whole crystals do not. This finding is based again on the cancellation of the pyroeffects. The pyroelectric effect of the molecular sieve framework is not visible here since both crystal directions occur in the assemblage with the same probability. If there was only one dipole direction in the crystals, there would be no difference whether the crystals were abraded or not.

Summarizing, we have found just that dipole distribution in the PNA-loaded crystals which is a main consequence of an ordering mechanism for the PNA molecules connected with the entering of the molecules into the channels. Therefore, this finding is a strong hint for the sorptive ordering mechanism.

Normally, a permanent polarization becomes smaller when the temperature is risen (negative temperature coefficient). Using that, one can conclude from the current direction measured that the PNA-loaded WSC's are positive at the endings and negative in the middle due to the permanent polarization. Since the nitro group is the negative pole of the PNA molecule, we conclude that the molecules must enter the channel with this group in front.

The estimated value for the pyroelectric coefficient ($|p| \approx 1.5 \mu\text{C m}^{-2} \text{K}^{-1}$) is about 2 orders of magnitude lower than in good pyroelectrics such as lithium tantalate ($|p| = 160 \mu\text{C m}^{-2} \text{K}^{-1}$). Although the polarization P in our crystals must be rather high ($P = 2 \mu\text{C/cm}^2$ for 11% loading with PNA), the flexibility of the dipoles is relatively low, resulting in low-temperature changes of the polarization. Our value for p is a rough estimate since we neglected all temperature losses from the heated pyroelectric region and scattering losses of the heating laser radiation. Therefore, the estimate can be taken as a lower limit.

Let us compare our experimental result with an estimate for the pyroelectric coefficient on the basis of one very likely mechanism assumed for the temperature dependence of the polarization. The dipoles are very well aligned, but they can deviate by small fluctuation angles ϕ from the pore's length axis. From Raman investigations⁸ it is known that the mean deviation is about 9° at 300 K. Using this value and assuming a parabolic potential minimum for the molecules, one finds for the temperature coefficient of the polarization $p/P = -\langle\phi\rangle^2/2T = -4 \times 10^{-5} \text{ K}^{-1}$. This results in a pyroelectric coefficient of $p = -0.8 \mu\text{C m}^{-2} \text{K}^{-1}$, which is about one-half of the value estimated from the measurements. However, the theoretical value describes only one possible component of the measured pyroelectricity. From the other possible origins for the pyroelectric current we especially point out changes of the physical PNA state in the channels,¹⁷ dielectric changes, and effects of compensation charges.

In the last part of this discussion we would like to address two surprising phenomena indicated by our measurements and still under consideration. The first one is connected with the high-frequency behavior of the pyroelectric response in the single crystal samples. This points to an unusually high thermal conductivity which can be derived from the following considerations. Let us regard a model consisting of one homogeneously polarized layer (thickness L_1) and an adjacent semi-infinite nonpolarized region acting as a heat sink. If this arrangement is heated within the pyroelectric active part, one can observe an increase of the pyroelectric response with frequency at low frequencies until the pyroelectric response approaches a plateau value at the frequency ω_{PL} . The latter situation is reached when the dimensions of the pyroelectric active part (length l) exceeds the thermal diffusion length $\mu = (2K/\omega)^{1/2}$ (eq 1). To estimate the plateau frequency ω_{PL} we set $l \approx \mu$. Using $\omega_{PL}/2\pi > 100$ kHz and $l = 20$ μm (estimate from L_1 and the spot diameter), we find a thermal diffusivity value of $K \approx 1.3 \times 10^{-4}$ m^2/s according to eq 1, which is close to the K value of copper.

This estimate could be wrong by 1 order of magnitude. But even then the thermal conductivity of the loaded crystals in the direction of the channels would be remarkably high. This might be a hint for an exceptionally high thermal conductivity in one-dimensional solids as they are formed by PNA in zeolite channels.⁸ The phonon-phonon scattering in such chains is likely to be less probable because of the restricted possibilities of fulfilling the conservation law of quasimomentum in one dimension.

The second surprising phenomenon is the change of the sign of the pyroelectric signal of the HSC in the range between 1 and 7 kHz in the frequency scan (cf. Figure 3c). If there was a uniform pyroelectric coefficient over the crystal, one would expect a monotonously growing signal intensity with slight phase changes. This is because the crystal changes its temperature increasingly quicker. However, the direction of the current should remain the same. One way of explaining the observed change of the sign is to assume alternating polarizations in the sample caused by compensation charges at the ends of the crystal. Then, however, it is difficult to understand why we found no qualitative changes in scanning the laser focus over the crystal. In an alternative explanation one assumes a uniform pyroelectric coefficient and a simple layer model for the thermal processes. Such a model will result in a behavior

$$I_p = \text{const} (1 + i)\sqrt{\omega} \quad (2)$$

for low frequencies. This behavior describes the rise of the modulated temperature changes in a relatively small pyroelectric region of the sample. In our case this happens as long as the crystal has a nearly homogeneous modulated temperature, and the temperature oscillations are attenuated in the surroundings only. If one assumes that our frequency dependence (Figure 3c) is modified by a frequency-dependent factor $a(\omega)$ only, one finds that this factor is about

$$a(\omega) = a_1 + \frac{a_2}{\omega - i/\tau} \quad (3)$$

This can be visualized by plotting this factor in the complex plane as it is done in Figure 6. (This presentation is similar to a Cole-Cole plot). If one attributes this behavior to the pyroeffect itself, the pyroelectric coefficient must show an (exponential) relaxation in the time domain. The long relaxation times could be a result of cooperative phenomena in the dipole chain inside the pore. However, there might be also other

Figure 6. Pyroelectric current divided by $(1 + i)\sqrt{\omega}$ plotted in the complex plane for different frequencies. This figure is another representation of the results shown in Figure 3c for the half crystal. The frequencies range from 120 Hz to 55 kHz with a constant factor of about 1.5 between them. Each point represents the average of eight adjacent data points of Figure 3c. The top of the curve is at about 1.8 kHz. The unit of the axes is $0.01(2\pi \text{ Hz})^{-1/2}$ pA.

possibilities of explaining the frequency dependence. Corresponding investigations are in progress.

5. Summary

Dipolar molecules adsorbed in the pores of molecular sieve crystals form dipole chains which show pyroelectricity. $\text{AlPO}_4\text{-5}$ crystals loaded with PNA have two domains with opposite pyroelectric coefficients. The preferred direction of dipolar guest molecules in the pores is very likely to be due to sorptive ordering, i.e., by the different probabilities for the substituents in PNA to enter the channels.

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