Dielectric and thermal properties of organic ferroelectric (R)-3-quinuclidinol in porous glass

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Abstract. The results of studies of the dielectric constant $\varepsilon'$ and the DTA signal of a new organic ferroelectric (R)-3-quinuclidinol (C$_7$H$_{13}$NO), embedded in porous glasses with an average pore size of 100 nm, are presented. The phase transition was found to shift to low temperatures by 3 K upon heating and 6 K upon cooling, in comparison with bulk (R)-3-quinuclidinol. A decrease in the phase transition temperature in composites with (R)-3-quinuclidinol nanoparticles is consistent with theoretical models of the influence of size effects on the structural phase transition.

1. Introduction

Ferroelectrics are multifunctional materials with a wide range of applications. Their temperature-dependent spontaneous polarization and dielectric constant can change under the influence of an electric field or mechanical stresses, which makes them attractive for the creation of various electronic devices. Currently, there is an active search for ferroelectric materials with high functional parameters, which are environmentally friendly, and at the same time cheap and lightweight. In recent years, several organic ferroelectrics, belonging to the C$_6$H$_{16}$NA family of salts, have been discovered, where A stands for Cl, Br, and I [1]. Such ferroelectrics include diisopropylammonium chloride (DIPAC) $P_s \approx 8.2 \ \mu$C $\times$ cm$^{-2}$, $T_c = 440$ K [2]; diisopropylammonium bromide (DIPAB) $P_s \approx 23 \ \mu$C $\times$ cm$^{-2}$, $T_c = 426$ K [3]; diisopropylammonium iodide (DIPAI) $P_s \approx 5.17 \ \mu$C $\times$ cm$^{-2}$, $T_c = 378$ K [4].

In [5], the discovery of ferroelectric properties in one-component homochiral organic crystals of (R)- and (S)-3-quinuclidinol (C$_7$H$_{13}$NO) was reported. These crystals exist in 2 mirror-isomeric (enantiomorphic) forms. Homochiral (R)- and (S)-3-quinuclidinol crystallize at room temperature in the enantiomorphic polar point group 6 (C6), which shows a mirror image in vibrational spectra. The Curie temperature during heating $T_{c1} \approx 400$ K and during cooling $T_{c2} \approx 360$ K. The dielectric constant during the phase transition has a sharp stepwise anomaly, varying from about 5 to 17. Spontaneous polarization at a temperature of 300 K is $\sim 7 \ \mu$C/cm$^2$, the coercive field 15 kV/cm. It was also found that their racemic mixture (Rac)-3-quinuclidinol crystallizes in the centrosymmetric point group 2/m (C2h) and is not ferroelectric. This discovery shows the significant role of homochirality for the occurrence of a ferroelectric state in organic ferroelectrics.

In connection with the prospects for the practical use of new organic ferroelectrics, studies of the effect of size reduction on their properties are of considerable interest. Phase transitions in
nanocomposites, based on DIPAC in an opal matrix and DIPAB in porous Al2O3 films, were studied in [6–9]. Temperature shifts and a change in the sequence of ferroelectric phase transitions were detected. As shown in [11], for (R)-3-quinuclidinol (150 nm) films on a substrate, the phase transition temperatures decrease to $T_{c1} \approx 338$ K upon heating and $T_{c2} \approx 324$ K upon cooling.

This paper presents the results of studies of the dielectric properties and the DTA signal of (R)-3-quinuclidinol, embedded in porous glass with an average pore size of 100 nm, in comparison with the properties of bulk (R)-3-quinuclidinol.

2. Samples and experimental procedure
To obtain nanocomposites, we used (R)-3-quinuclidinol manufactured by Acros Organics and porous glass with an average pore size of 100 nm and a porosity of 48.8%. The introduction of a ferroelectric into the pores was carried out from a heated saturated solution of (R)-3-quinuclidinol in methanol. Then the solution with the sample was slowly cooled, as a result, nanocrystals were formed in the pores. After repeating the described procedure three times, the degree of filling of the pores, determined from the change in the mass of the sample, using the AND BM-252G balance, was at least 50%.

To measure the complex dielectric constant, an E7–25 digital immittance meter with a frequency range of $20 – 10^6$ Hz and an operating voltage of 0.7 V was used. In-Ga paste was applied as electrodes. We determined the temperature, using a TC-6621 electronic thermometer with a chromel-alumel thermocouple. The accuracy of temperature determination was 0.1 K. The studies were carried out in the heating and cooling mode at a rate of 0.5 to 4 K per minute in a temperature range of 300-455 K.

A Linseis STA PT 1600 synchronous thermal analyzer was used to record the DTA signal. The temperature was determined with an accuracy of 0.1 K. The measurements were taken in the heating -cooling mode at a rate of 0.5 to 4 K/min in the same temperature range.

3. Experimental results and discussion
The results of studying the DTA signal and dielectric permittivity $\varepsilon'$ at different frequencies for a sample of bulk (R)-3-quinuclidinol are shown in Fig. 1 a. Upon heating, the DTA and $\varepsilon'(T)$ dependences exhibit one anomaly at $T_{c1} = 390$ K, which corresponds to a phase transition from the ferroelectric to the nonpolar phase. With increasing frequency, the values of $\varepsilon'$ decrease (Fig. 1 a).

The transition temperature $T_{c2}$ depends on the temperature to which the sample is heated and at what rate the cooling proceeds. When heated to 435 K and a cooling rate of 1 K/min, $T_{c2}$ is 364 K. The dependences of the transition temperature for (R)-3-quinuclidinol on the maximum heating temperature and cooling rate are shown in Figures 2 a, b.

For (R)-3-quinuclidinol/porous glass (100 nm) nanocomposites, the results of studying the temperature dependences of the dielectric constant and the DTA signal are shown in Fig. 3. For (R)-3-quinuclidinol in porous glass, there is a slight decrease in the phase transition temperatures from 390 K to 387 upon heating, and from 364 to 358 upon cooling, in comparison with the bulk sample.

When interpreting the shift of the phase transition with respect to temperature for nanoparticles under nanoconfinement conditions, as a rule, the models, developed for isolated particles, based on the phenomenological Landau theory, are used [10, 11]. These models predict that the temperature of the structural phase transition should decrease with decreasing particle size, if the order parameter at the particle boundaries is less than one in the bulk. Secondly, for particles in matrices, the phase transition temperature can be shifted due to the interaction with pore walls and dipole – dipole interaction between particles in neighboring pores [12, 13]. Moreover, depending on the geometry of the pore network and the shape of the particles, such interaction can lead to both an increase and a decrease in the transition temperature. Thirdly, the Curie temperature can be influenced by mechanical stresses, arising from different coefficients of thermal expansion of the ferroelectric and matrix.
Figure 1. The DTA signal in comparison with the \( \varepsilon'(T) \) dependence at a frequency of \( f = 10^3 \) Hz upon heating the sample to a temperature of 435 K and a cooling rate of 1 K/min \((a)\). Dependences of \( \varepsilon'(T) \) for a bulk sample on temperature under the same thermal conditions \((1 - f = 10^3 \) Hz, \( 2 - f = 10^4 \) Hz, \( 3 - f = 10^5 \) Hz) \((b)\).

The decrease in the ferroelectric phase transition of (R)-3-quinuclidinol in porous glasses with a pore size of 100 nm, found in this work, may be associated with the influence of size effects. In addition, particles of (R)-3-quinuclidinol may experience compressive mechanical stresses from the porous glass, since the linear coefficient of thermal expansion \( \alpha \) for SiO\(_2\) is \( \sim 6 \times 10^{-6} \) K\(^{-1}\), whereas for (R)-3-quinuclidinol \( \alpha > 100 \) \( 10^{-6} \) K\(^{-1}\) [5]. However, for a quantitative assessment of the change in the Curie temperature with increasing pressure, there is no information in the scientific publications of the effect of hydrostatic pressure on the temperature of the ferroelectric phase transition in (R)-3-quinuclidinol.

Figure 2. Dependence of \( T_{c2} \) for a bulk sample on the temperature of maximum heating at a cooling rate of 1 K/min \((a)\). Dependence of \( T_{c2} \) on the cooling rate for a bulk sample at a heating temperature up to 408 K \((b)\).

A series of experiments with changes in parameters such as the rate of temperature change and the maximum heating temperature of the sample showed that the phase transition temperature during heating remains constant, which guarantees a stable temperature during measurements. However, a shift in the phase transition temperature is noted upon cooling. Figure 2a shows the dependence of the phase transition temperature \( T_{c2} \) for a bulk sample on the temperature of maximum heating at a cooling rate of 1 K/min. As can be seen, an increase in the temperature of maximum heating of the sample leads to a decrease in the temperature of phase transition upon cooling. This behavior leads to an increase in hysteresis and may be due to the slow kinetics of (R)-3-quinuclidinol in cooling mode. The kinetics of phase transformations essentially depends on the ratio of many parameters, for
example, surface tension, heat supply, heat transfer, and "inertia" of the system. One of the possible explanations is that the change in the temperature of the system during cooling lags behind the increase in the number of particles of the new phase. Upon cooling, the nonpolar phase remains in a supercooled state up to a temperature corresponding to the equilibrium ferroelectric transition. The presented dependence of the phase transition temperature on the cooling rate of the sample (Fig. 2b) also confirms the slow kinetics of the phase transition in bulk (R)-3-quinuclidinol upon cooling.

![Graph](image)

**Figure 3.** The DTA signal in comparison with the $\varepsilon'(T)$ dependence at a frequency of $f = 10^3$ Hz for the (R)-3-quinuclidinol/porous glass nanocomposite, measured under the same conditions as for a bulk sample.

On the other hand, the effect of the nanoconfine does not have such a significant effect on the change in the phase transition temperature. Under fixed conditions (rate of change of temperature and temperature of maximum heating), the shift of the phase transition temperature both during heating and during cooling occurs towards low temperatures and is $3.0 \pm 0.5$ and $6.0 \pm 0.5$ K, respectively.

### 4. Conclusion

Thus, the studies of (R)-3-quinuclidinol, embedded in porous glass, carried out in this work revealed a decrease in the Curie temperature from 390 K to 387 upon heating, and from 364 to 358 upon cooling in comparison with a bulk sample. A decrease in the phase transition temperature can be interpreted on the basis of known theoretical models for ferroelectric small particles.

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