Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Dielectric investigations of the N-SmB transition in a porous glass

J. Werner[a]; K. Otto[b]; D. Enke[b]; G. Pelzl[a]; F. Janowski[a]; H. Kresse[a]
[a] Fachbereich Chemie, Institut für Physikalische Chemie, Martin-Luther-Universität Halle-Wittenberg, Mühlpforte 1, 06108 Halle/Saale, Germany, [b] Fachbereich Chemie, Institut für Technische Chemie und Makromolekulare Chemie, Martin-Luther-Universität Halle-Wittenberg, Schlossberg 2, 06108 Halle/Saale, Germany,

To cite this Article Werner, J. , Otto, K. , Enke, D. , Pelzl, G. , Janowski, F. and Kresse, H.(2000) 'Dielectric investigations of the N-SmB transition in a porous glass', Liquid Crystals, 27: 10, 1295 — 1300
To link to this Article: DOI: 10.1080/026782900423331
URL: http://dx.doi.org/10.1080/026782900423331

LIQUID CRYSTALS, 2000, VOL. 27, NO. 10, 1295–1300

Dielectric investigations of the N–SmB transition in a porous glass

J. WERNER, K. OTTO†, D. ENKE†, G. PELZL, F. JANOWSKI†
and H. KRESSE*
Fachbereich Chemie, Institut für Physikalische Chemie,
Martin-Luther-Universität Halle-Wittenberg, Mühlpforte 1, 06108 Halle/Saale,
Germany
†Fachbereich Chemie, Institut für Technische Chemie und Makromolekulare Chemie,
Martin-Luther-Universität Halle-Wittenberg, Schloßberg 2, 06108 Halle/Saale,
Germany

(*Received 3 February 2000; accepted 25 April 2000*)

Dielectric measurements in the frequency range 0.01 Hz to 10 MHz on a liquid crystal material with SmB/N dimorphism confined to randomly oriented and interconnected mesoporous (pore diameter 2–10 nm) and macroporous glasses (pore diameter 86 nm) were carried out. In the macroporous glasses the liquid crystal behaves similarly to the bulk phase, but the phase transition temperature SmB–N is suppressed. In the mesoporous glass the transition SmB–N is completely suppressed.

1. Introduction

Dielectric measurements can give information about the mutual arrangement and dynamics of polar molecules. The measured quantities, dielectric increment and relaxation time, are related to the structure of the molecule investigated and the phase. If one considers only the reorientation of rod-like molecules about the short axes, the information obtained is restricted to the short range. In different liquid crystalline phases, the influence of the surroundings can formally be described by the nematic potential [1]. On the one hand, this potential is responsible for the formation of the nematic phase with its degree of order and, on the other hand, for the hindrance of reorientation at the phase transition from the isotropic into the nematic (N) state [2]. The relation between relaxation time and degree of order seems to hold also for the transition nematic–smectic B [3].

Another problem is related to the question of how many molecules are necessary to form a phase. In the case of liquid crystals, the molecules can be enclosed in porous glasses with different pore size. In this way the gradual change of the transition temperatures and relaxation times can be measured in confined systems and compared with those of the bulk [4–12].

2. Experimental

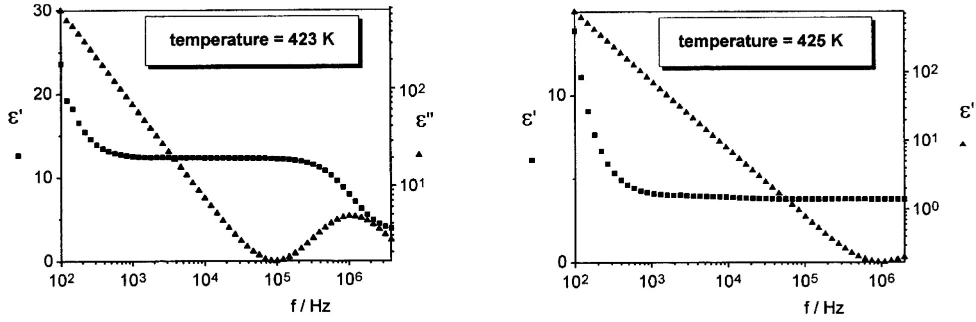
The porous glasses used in our studies were made by a standard procedure [13]. Porous glasses can be prepared by phase separation in alkali borosilicate glasses followed by a combined acidic and/or alkaline leaching [14, 15]. The first treatment step results in phase separation into pure silica and an alkali-rich borate phase with certain amounts of silica dissolved in it [16, 17]. After the acidic leaching process, due to the very low solubility of silica in acidic media, SiO_2 aggregates remain as finely dispersed silica gel in the cavities of the main silica framework of the macroporous glasses, and this affects the pore structure of the resulting porous glass system. The additional treatment with an alkaline solution removes the finely dispersed silica gel [18].

In our case an initial sodium borosilicate glass (70 wt % SiO_2 23 wt % B_2O_3, 7 wt % Na_2O) in the form of thin glass plates ($20 \times 15 \times 0.1\,mm^3$) was phase separated by thermal treatment for several hours. The formation of the mesoporous silica gel phases inside the macroporous 'frame' glasses was initiated under various acidic leaching conditions of the initial phase separated glass, resulting in mesoporous 'two-phase systems'. Nitrogen physisorption measurements were performed to characterize the texture properties of these mesoporous glass samples. Pore diameters of 2–4 and 6–10 nm were found. To reveal the properties of the

---

*Author for correspondence;
e-mail: kresse@chemie.uni-halle.de

Liquid Crystals ISSN 0267-8292 print/ISSN 1366-5855 online © 2000 Taylor & Francis Ltd
http://www.tandf.co.uk/journals



(*a*) (*b*)

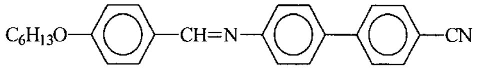
Figure 1. Dielectric constants (ε') and losses (ε'') (*a*) parallel (423 K) and (*b*) perpendicular (425 K) with respect to the nematic director.

frame glasses, an alkaline leaching has to be carried outto remove the finely dispersed silica gel from the macropores of the porous glass. This is proved by results of mercury intrusion experiments which give a pore diameter of 86 nm. The data from the N_2-sorption and mercury intrusion measurements showed a narrow pore size distribution of the meso- and macro-porous samples prepared. The confined topology can be described as a network of a three-dimensionally connected pore system. The mean pore diameters were 2–4, 6–10 and 86 nm. The volume fraction of pores was of the order of magnitude 10–20% for the mesoporous glasses and about 40% for the macroporous glasses.

Plates were cleaned by H_2O_2 solution and thereafter carefully dried. To eliminate the SiOH groups from the glass surfaces, we treated the glass plates with hexamethyldisilazane (HMDS).

3. Dielectric investigations of the bulk

Dielectric investigations were carried out in a glass capacitor coated with gold electrodes ($d = 0.02$ cm); the cell was first calibrated with cyclohexane. Capacity and resistance were measured in the frequency range 0.01 Hz to 10 MHz with a Solartron-Schlumberger SI1260 impedance analyser in combination with a current/voltage converter (Chelsea Dielectric interface). Dielectric measurements were performed up to a maximum temperature of 430 K to avoid thermal decomposition. The temperature was controlled by a PID-Controller Eurotherm 900. The liquid crystal was oriented by a magnetic field of 0.6 T. As the sample, the strongly polar compound **1** (shown below) was chosen; its phase transition temperatures are given in K.



Cr 365 SmB 385 N 558.5 I [19]

Dielectric constants at different frequencies are presented in figure 1.

Only one intense absorption in the parallel direction could be detected, confirming the reorientation about the molecular short axes discussed above. The data were analysed using absorption terms according to the Cole–Cole equation and a conductivity term

$$\varepsilon^* = \varepsilon_{i+1} + \frac{\varepsilon_0 - \varepsilon_1}{1 + (i\omega\tau_0)^{1-\alpha_0}} + \dots + \frac{\varepsilon_i - \varepsilon_{i+1}}{1 + (i\omega\tau_i)^{1-\alpha_i}} + \frac{iA}{f} \qquad (1)$$

were ε_0 and ε_1 are the low and high frequency dielectric constants of the first relaxation process, τ_0 is the relaxation time and α_0 is the distribution parameter of the respective process. The quantities $\omega = 2\pi f$ (f = frequency) characterize the measuring electric field and A, the specific conductivity $\sigma = A \times 2\pi\varepsilon^0$ ($\varepsilon^0 = 8.85 \times 10^{-12}$ F m). Both components of the complex dielectric function were fitted to equation (1) as the real and imaginary part. For sample **1** in the bulk, the relaxation times given below (figure 2) were obtained. A step in the relaxation

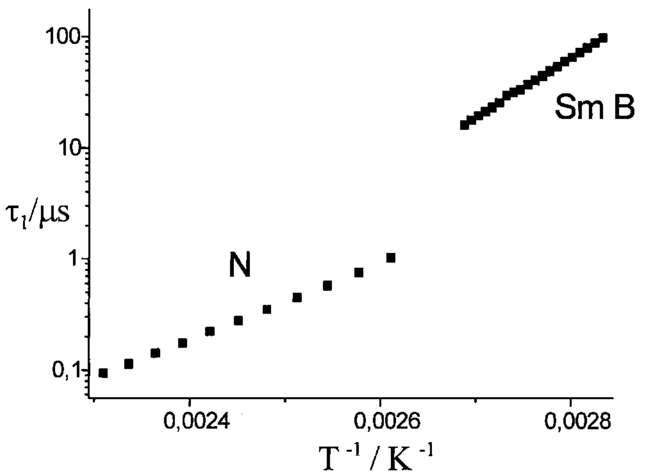


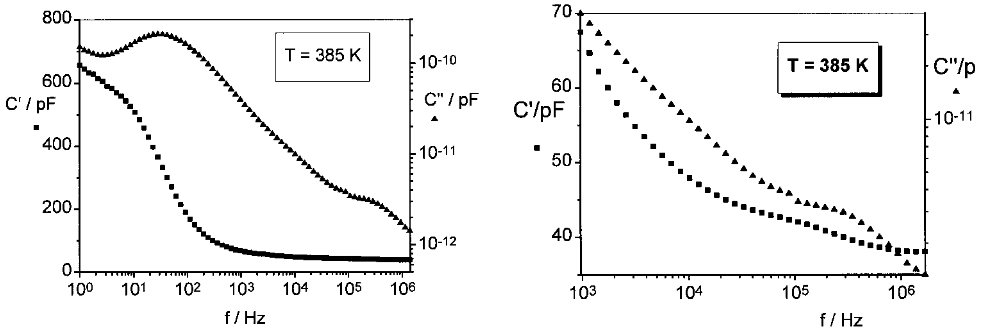
Figure 2. Arrhenius diagram of relaxation times for reorientation about the molecular short axes in the bulk.

time at the N–SmB transition by a factor 7.5 can be seen. The distribution parameter α_0 was zero within the experimental error of 0.02.

4. Dielectric investigations of porous glass filled with compound 1

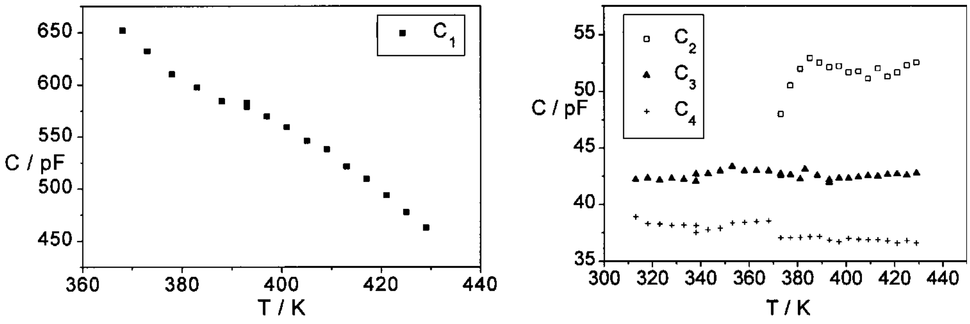
For the sample preparation, the porous glass was evacuated to 10^{-5} mbar at 600 K for 4 h. With this procedure, we tried to remove the absorbed water and other volatile impurities. After that, the pores were filled under vacuum by capillary wetting during 2 h at a temperature of about 400 K. The sample at the surface was removed. Mass measurements before and after this process indicate that filling of the pore network was achieved. For dielectric measurements the filled glass slice was mounted between the gold plated brass electrodes of the capacitor.

In porous glasses, the liquid crystal could not be oriented and the cell could not be calibrated. Therefore, only the capacities C' and the losses $C''=(2\pi fR)^{-1}$ (R= resistance) were measured and fitted to equation (1). Experimental data for a sample with a pore diameter between 6 and 10 nm (P6-10), filled with 10% by weight of **1** are presented in figure 3. For a good description of the data three dielectric dispersion ranges and an additional one for the double layer were needed. The high frequency absorption ($f_R=10^6$ Hz) is related to reorientation about the molecular short axes, and the low frequency and very intense dispersion at 100 Hz to the Maxwell–Wagner relaxation. A less intense process at about 10 kHz is probably connected with a polar impurity. This process could also be seen in the dielectric data for the bulk for the perpendicular direction. The process at 10 kHz could not be clearly separated below 330 K. The calculated capacities are shown in figure 4. In order to describe the increase of C' and C'' below 10 Hz due to the double layer, an additional dielectric absorption range from C_0 to C_1 was introduced. These data are without meaning for our present considerations. The relaxation times of the Maxwell–Wagner relation τ_1, of the dispersion at middle frequencies τ_2 and of the orientation about the molecular short axes τ_3 are shown in figure 5. It should be noted that the given data are from two different experimental runs. The instability of the τ_2 values at lower temperatures can also be seen



(*a*) (*b*)

Figure 3. (*a*) Loss (C'') and capacity (C') of sample P6-10: $\alpha_1=0.21$, $\alpha_2=0.15$ and $\alpha_3=0.05$. (*b*) The same at higher frequencies with different scale.



(*a*) (*b*)

Figure 4. (*a*) Static capacity C_1 of P6-10; (*b*) further limits of capacity of P6-10.

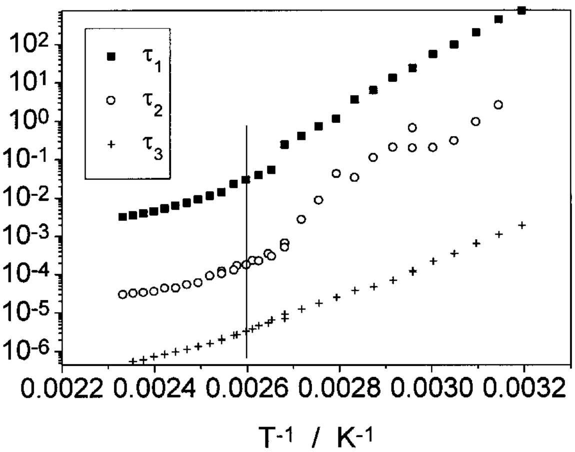


Figure 5. Relaxation times of the three mechanisms. τ_1: Maxwell–Wagner relaxation, τ_2: middle frequency mechanism, τ_3: reorientation about the short axes. The phase transition temperature N–SmB in the bulk is indicated.

here. It is important that the molecular mechanism τ_3 did not show any step in the investigated temperature range. These results point to a suppression of the SmB phase in the confined geometry. This is supported by calorimetric measurements where a SmB–N transition peak could not be detected in its mesoporous glasses.

Dielectric absorption and dispersion data for a sample with a diameter of the porous glass of 2–4 nm (P2-4) with 6% by weight of the liquid crystal are shown in figure 6.

In this case the middle frequency absorption could not be separated. Therefore, the points were fitted to only three Cole–Cole mechanisms—double layer, Maxwell–Wagner relaxation (MW) and reorientation about the short axes (sa). The distribution parameters are $\alpha_1(\mathrm{MW}) = 0.21$ and $\alpha_2(\mathrm{sa}) = 0.3$. Also in this case, no step in the relaxation time of the molecular mechanism τ_2 (figure 7) is detected down to 308 K indicating the suppression of the SmB phase.

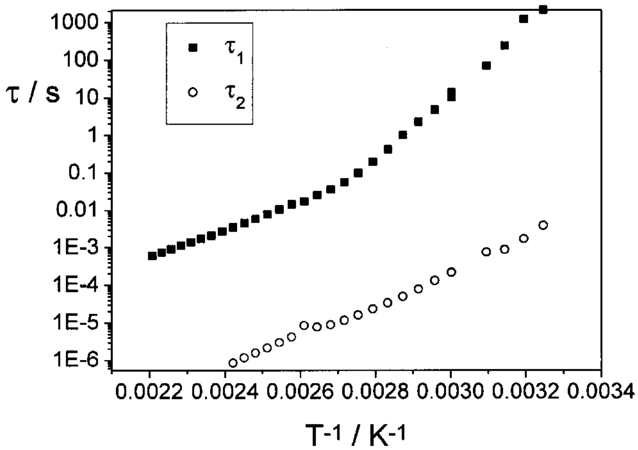


Figure 7. Relaxation times of P2-4. τ_1: MW relaxation, τ_2: reorientation about molecular short axes.

Finally a porous glass with a pore diameter of 86 nm was filled with 45% by weight of the liquid crystal **1** (P86). Due to the higher content of liquid crystal, the absorption intensity at higher frequencies can be well separated (see figure 8). A distribution parameter for the

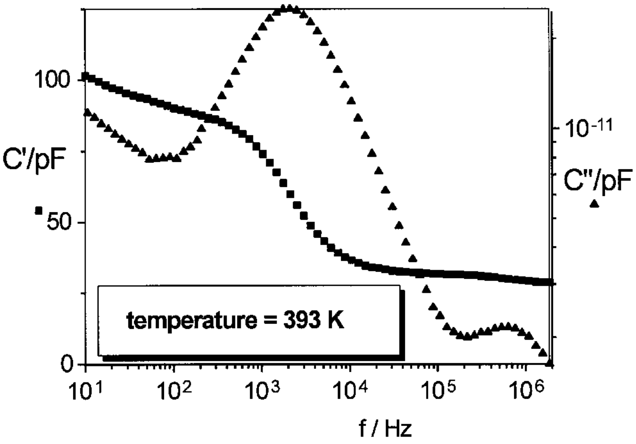
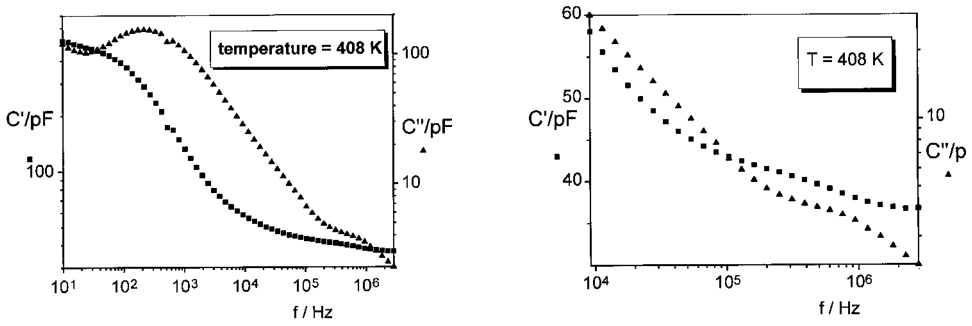


Figure 8. Absorption and dispersion data for P86.



(*a*) (*b*)

Figure 6. (*a*) Absorption and dispersion data for P2-4; (*b*) selected frequency range.

molecular mechanism of $\alpha_2 = 0.00$ was obtained from the fitting procedure. The increase of C' and C'' at low frequencies was simulated by a relaxation range between C_0 and C_1. The fitted capacities, C_1, C_2, and C_3 are practically stable with temperature. The respective relaxation times of the Maxwell–Wagner relaxation τ_1 and of the molecular process τ_2 are shown in figure 9. In both cases, a clear step in the relaxation can be detected. The molecular process (τ_2) increases its relaxation time by a factor 5 at the phase transition. The phase transition temperature is at about 372 K, that is 13 K below the phase transition N–SmB in the bulk. The strong change of the relaxation time at this phase transition supports the idea that we are again dealing in P86 with a N–SmB transition. This is also in agreement with results from calorimetric measurements. Furthermore we assume that in the mesoporous glasses, the nematic state is present over the whole measured temperature range, but for this we have no experimental evidence.

The relaxation times of different porous glasses are compared in figure 10. The respective activation energies are presented in the table. From both of these, at least two tendencies can be recognized: the transition from the bulk to a confinement of 86 nm results in lower relaxation times in general and decreasing activation energies in the isotropic phase. This may be connected with the incomplete nematic order due to the confinement. The increase in relaxation time in the mesoporous glass may be related to a stronger influence of the absorbed layer of liquid crystal, which according to Shina and Aliev [20] gives a higher relaxation time.

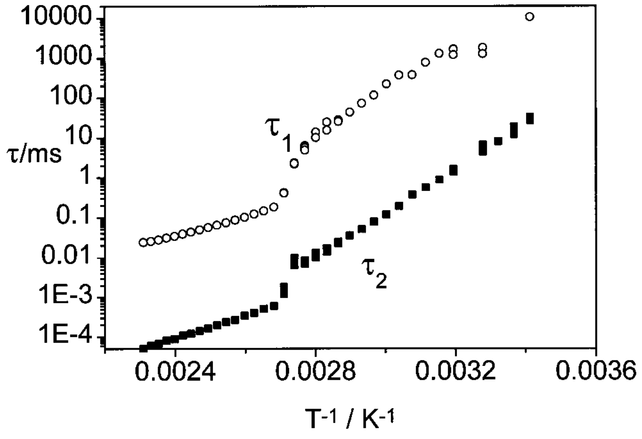


Figure 9. Relaxation times of the MW relaxation (τ_1) and of the molecular process (τ_2).

Table. Activation energies of the reorientation about the short axes.

Sample	E_A/kJ mol^{-1} (N)	E_A/kJ mol^{-1} (SmB)
bulk	65.0 ± 1.0	102.0 ± 1.0
P86	54.4 ± 1.0	106.8 ± 2.0
P6-10	80.6 ± 2.0	—
P2-4	81.2 ± 2.0	—

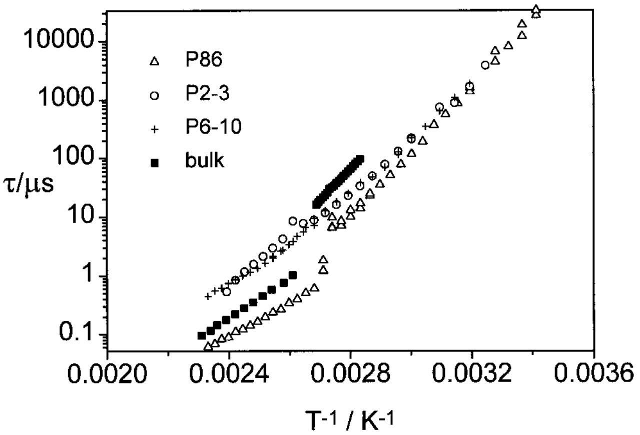


Figure 10. Comparison between the reorientation times of the molecular process for different samples.

In conclusion we can say that confinement of about 100 nm results in a decrease in the phase transition temperature N–SmB, whereas a decrease of the pore diameter by a further decade gives complete elimination of the smectic B phase in the temperature range investigated.

The authors are indebted to the DFG for financial support.

References

[1] Maier, W., and Saupe, A., 1958, *Naturforsch.*, **13a,** 564.
[2] Kresse, H., Weigeleben, A., and Gajewska, B., 1985, *Z. phys. Chem.*, **266,** 193.
[3] Gajewska, B., Kresse, H., and Weissflog, W., 1892, *Cryst. Res. Technol.*, **17,** 897.
[4] Sheng, P., 1976, *Phys. Rev. Lett.*, **37,** 16.
[5] Kralj, S., Lahajnar, G., Zidansek, A., Vrbancic-Kopac, N., Vilfan, M., Blinc, R., and Kosec, M., 1993, *Phys. Rev.*, **48,** 340.
[6] Aliev, F. M., and Kelly, J., 1994, *Ferroelectrics*, **151,** 263.
[7] Iannacchione, G. S., Qian, S., Crawford, G. P., Keast, S. S., Neubert, M. E., Doane, J. W., Finotello, D., Steele, L. M., Sokol, P. E., and Zumber, S., 1995, *Mol. Cryst. liq. Cryst.*, **262,** 13.
[8] Iannocchione, G. S., Crawford, G. P., Zumer, S., Doane, J. W., and Finotello, D., 1993, *Phys. Rev. Lett.*, **71,** 2595.
[9] Tripathi, S., Lu, M.-X., Terentyev, E. M., Petschek, R. G., and Rosenblatt, Ch., 1991, *Phys. Rev. Lett.*, **67,** 3400.
[10] Cramer, Ch., Cramer, Th., Kremer, F., and Stannarius, R., 1997, *J. chem. Phys.*, **106,** 3730.
[11] Aliev, F. M., 1992, *Mol. Cryst. liq. Cryst.*, **222,** 147.
[12] Aliev, F. M., 1994, *Mol. Cryst. liq. Cryst.*, **243,** 91.
[13] Otto, K., 1999, PhD thesis, University Halle, Germany.

[14] US-Pat. 2 106 744 (1934), 2 215 039 (1940), 2 221 709 (1940).

[15] Janowski, F., and Heyer, W., 1982, *Poröse Gläser—Herstellung, Anwendung und Eigenschaften* (Leipzig: Deutscher Verlag für Grundstoffindustrie).

[16] Zhdanov, S. P., 1958, *The Structure of Glass* (New York: Consultants Bureau).

[17] Tanaka, H., Yazawa, T., Eguchi, K., Nagasawa, H., Matsuda, N., and Einishi, T., 1984, *J. non-cryst. Solids*, **65,** 301.

[18] Haller, W., 1965, *J. chem. Phys.*, **42,** 686.

[19] Demus, D., Pelzl, G., Weigeleben, D., and Weissflog, W., 1980, *Mol. Cryst. liq. Cryst. Lett.*, **56,** 289.

[20] Shina, G. P., and Aliev, F. M., 1998, *Phys. Rev. E.*, **58,** 1.