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Dielectric Spectroscopy of Ferronematics Based on 6CHBT Liquid Crystal

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In our study, the dielectric behaviour of the rod-like liquid crystal (6CHBT) doped with magnetic nanoparticles of spherical shape was investigated by means of dielectric spectroscopy in the frequency range from 20 Hz to 2 MHz. A low frequency dielectric dispersion in the nematic and isotropic phases of the pure liquid crystal (LC) has been assigned to the space charge polarization. After doping the host LC with the magnetic nano particles, a nearly Debye-like relaxation process was observed with the temperature dependence obeying the Arrhenius law. Considering a possible electric double layer formation on the particle surfaces, the detected relaxation process in the doped LC can be associated with the electric double layer polarization. The experimental results point out that in the measured frequency range the space charge and interfacial effects constitute the main dielectric response. Any anchoring effects were not observed and are therefore expected to appear in higher frequencies.

Keywords ferronematics; magnetic nanoparticles; dielectric spectroscopy; dielectric relaxation

Introduction

The great idea to increase the magnetic susceptibility of liquid crystals (LCs) by doping them with fine magnetic particles originates from F. Brochard and P. G. de Gennes' theory [1]. Since then, experimental efforts are being made to achieve magnetic field induced liquid crystal phase transitions [2]. Investigating such composites, the dielectric properties provide an important insight into the structural, stability and anchoring characteristics. Especially, the dielectric spectroscopy is a very useful method focusing on relaxation processes present in complex systems [3]. In general, the doping of nematic LCs with a small amount of nanoparticles strongly affects the dielectric properties of the system. It was found, that the

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adding of the ferroelectric particles results in a shift of the absorption bands corresponding to the LC molecules rotation to lower frequencies, pointing out the strong interactions between the LC molecules and particles [4]. Recently, the lowering of ionic concentration in nematic LCs doped with anatase titania nanoparticles was reported as a consequence of the dopant effect on the ion transport [5]. A discussion on interfacial dielectric relaxations in nematic LCs doped with metal nanoparticles and the related dependence on the concentration of the doped nanoparticles and their electric and dielectric properties can be found in [6]. Similar dielectric phenomena can be observed in composites based on LCs doped with different magnetic nanoparticles. Moreover, when stabilizing the nanoparticles by additional surfactants like oleic acid molecules, one can expect the formation of electric double layer (EDL) around the particles in consequence of the space charge presence in the host LC. Then the corresponding EDL polarization may contribute to the dielectric spectrum.

In this paper we report on the experimental study focused on the low frequency dielectric spectroscopy of a ferronematic sample consisted of 6CHBT LC and a low concentration of magnetite nanoparticles covered with oleic acid molecules. The temperature dependent complex dielectric permittivity spectra of both, the pure and doped LC are analyzed in order to partially reveal the structural properties and particle – LC interaction.

Materials and Methods

The synthesis of the spherical magnetic nanoparticles was based on coprecipitation of Fe^{2+} and Fe^{3+} salts by NH_4OH. To obtain a Fe_3O_4 precipitate, $FeSO_4{\cdot}7H_2O$ and $FeCl_3{\cdot}6H_2O$ were dissolved in deionized water by vigorous stirring (the molar ratio Fe^{3+} : Fe^{2+} was 2:1). The solution was heated to 80°C and 25% NH_4OH was added. The precipitate was isolated from the solution by magnetic decantation and washing with water. To prepare a magnetic paste, the precipitated particles were coated with monolayer of oleic acid at 85°C and the water from the sample was removed by drying in a drying oven at 80°C for 3 hours. The mean diameter of the magnetic nanoparticles was 4.8 nm (obtained by TEM).

The studied ferronematic sample was based on the thermotropic nematic 4-(trans-4′-*n*-hexylcyclohexyl)-isothiocyanatobenzene (6CHBT). 6CHBT is a low-melting enantiotropic liquid crystal with high chemical stability [7]. The temperature of the nematic-to-isotropic transition (clearing point) of the studied nematic is $T_{NI} = 42.8$°C. The nematic samples were doped with a magnetic suspension consisting of the nearly spherical Fe_3O_4 magnetic nanoparticles coated with oleic acid in the organic solvent heptane. Aggregates were removed from the suspension by centrifugation. The doping was simply done by adding this suspension under the continuous stirring to the liquid crystal in the isotropic phase. Then, the mixture was heated until the heptane was completely evaporated. In this study, the volume concentration of the magnetic nanoparticles in the ferronematic sample was 0.05 %.

After the final fabrication procedure, the suspension was left in a vessel for a day to allow potential segregation. For the dielectric spectroscopy experiment, the top layer of the sample was used. It was heated above the clearing point and drawn into a commercial liquid crystal cell by capillary action. In the LC cell, two electrodes in the form of conducting ITO layers with the active electrode area $A = 25$ mm^2 were separated in distance $d = 5.1$ μm. The measurements were performed on the LCR meter (Agilent E4980A) in the frequency range from 20 Hz up to 2 MHz with the applied test voltage of 100 mV. As a consequence of the capacitor having planar orientation, the permittivity $\varepsilon_\perp$measured in the direction

perpendicular to the director was obtained. The experimental setup was also equipped with a temperature controller (Linkam Scientific Instruments). During the measurements, the sample temperature was varied from 59°C to 26°C in 3°C intervals, with the stabilization within 0.1°C. In order to avoid any external electromagnetic interference up to 18 GHz, the experiment was conducted in an electromagnetically shielded, anechoic chamber. The uncertainty of the acquired data is less than 0.3 %.

Results and Discussion

Frequency-dependent complex dielectric permittivity $\varepsilon(\omega, T)$ is given by

$$\varepsilon^*(\omega, T) = \varepsilon'(\omega, T) - i\varepsilon''(\omega, T) \tag{1}$$

where $\varepsilon'(\omega, T)$ and $\varepsilon''(\omega, T)$ are the real and imaginary parts of the dielectric permittivity, respectively, ω is the angular frequency, and T is the temperature of the medium [8]. The dielectric spectra of the pure 6CHBT in nematic and isotropic phase are shown in Fig. 1(a, b) which were taken consecutively during slow cooling from the isotropic phase at 60°C down to room temperature (nematic phase). In these pictures one can clearly see the I-N phase transition demonstrated by the change in the permittivity level. The LC sample shows a low frequency dielectric dispersion, which is associated with a space charge polarization usually appearing in extremely low frequency region [9]. In the higher frequency range, the spurious contribution from the ITO layer dominates the dielectric spectrum [10]. The understanding of the dielectric behavior of the pure 6CHBT allows the comparison of the spectra obtained on the doped sample, which are depicted in Fig. 2 (a, b).

In Fig. 2(a) one can notice that the spurious ITO signal is no more striking in comparison to the pronounced low frequency real permittivity dispersion. This dispersion, related to a relaxation process, is considerably dependent on the sample temperature in both LC phases. From Fig. 2(b) it can be noticed that the relaxation time of that process decreases with increasing temperature while the shape of the loss spectra looks like a Debye-like dielectric relaxation mode [8].

In order to get a better view of those maxima, we have presented the experimental data in the form of dielectric modulus, what is the reciprocal permittivity [11]. Its imaginary part was calculated according to the following formula

$$M'' = \frac{\varepsilon''}{\varepsilon'^2 + \varepsilon''^2} \tag{2}$$

Figure 3 represents the temperature dependent imaginary part of the dielectric modulus of the doped LC sample. In this representation, the ITO relaxation maximum rose significantly, so the data in the graph have been removed above 0.6 MHz. In this form of data presentation the low frequency relaxation maxima clearly form symmetrical peaks, pointing out the Debye-like relaxation behavior. Moreover, when the acquired data are depicted in a Cole-Cole plot (Fig. 4), one can see the tendency to create semicircles with the center on the x axis, intersecting so the real permittivity in the low and high frequency limit. The intersections yield the static (relaxed) ε_s and infinity (unrelaxed) ε_∞ permittivity values, respectively. To verify the Debye-like relaxation behavior, we applied the Debye fitting function on the Cole-Cole data presentation (3). The fit has been conducted on the curve representing the

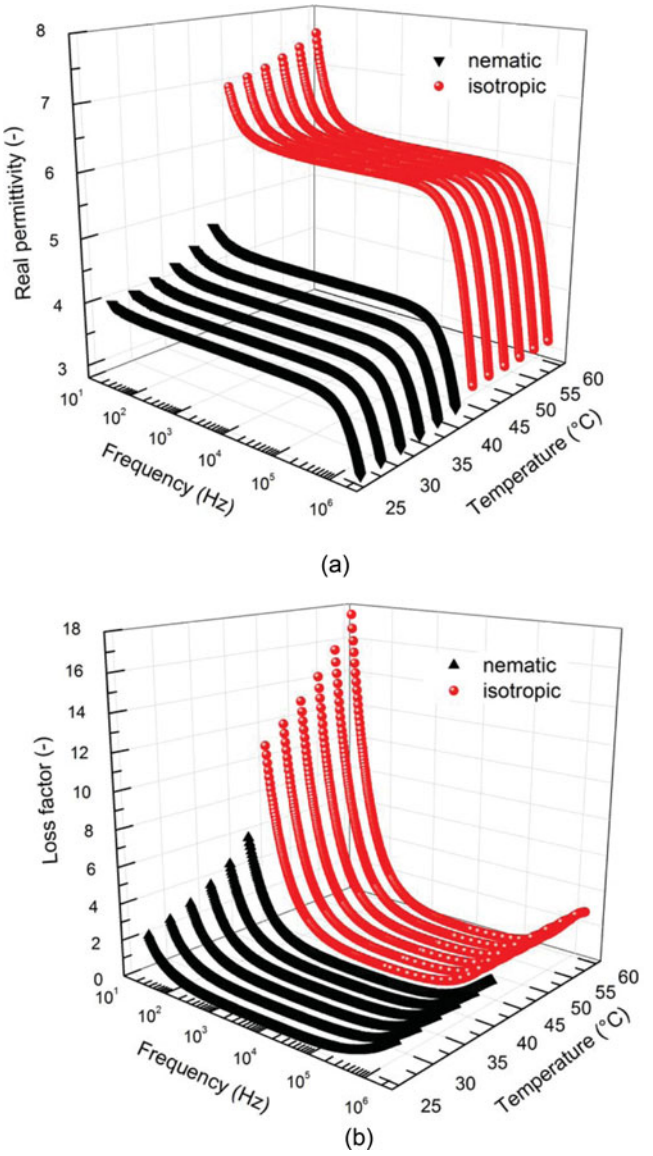

Figure 1. (a) Real permittivity spectra of 6CHBT measured at several temperatures in isotropic and nematic phase. (b) Dielectric loss spectra of 6CHBT measured at several temperatures in isotropic and nematic phase.

data taken at the highest isotropic temperature state

$$\left(\varepsilon' - \frac{\varepsilon_s - \varepsilon_\infty}{2}\right)^2 + \varepsilon''^2 = \left(\frac{\varepsilon_s - \varepsilon_\infty}{2}\right)^2 \tag{3}$$

In Fig. 5, the small deviation in the experimental data from the Debye-like fitting curve is observed especially in the low frequency region. This deviation is caused by the dielectric

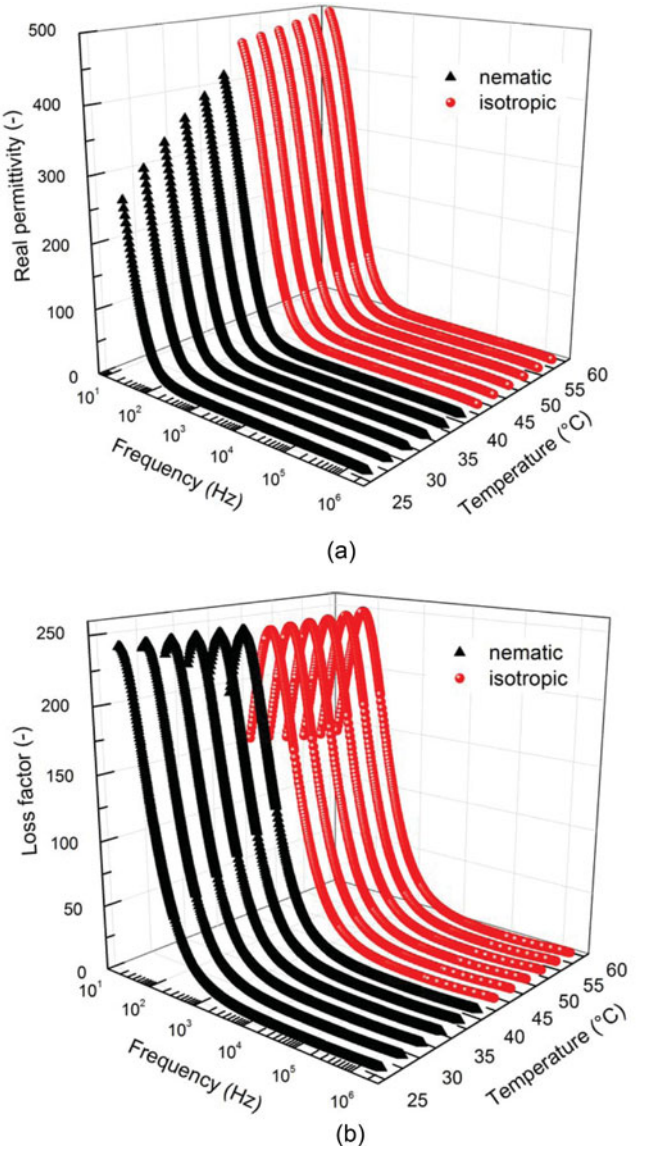

Figure 2. (a) Real permittivity spectra of 6CHBT doped with 0.05 % (vol.) of magnetite nanoparticles, measured at several temperatures in isotropic and nematic phase. (b) Dielectric loss spectra of 6CHBT doped with 0.05 % (vol.) of magnetite nanoparticles, measured at several temperatures in isotropic and nematic phase.

losses due to the space charge relaxation in the LC and a small contribution from the DC conductivity (Fig. 1b).

In the case of the studied ferronematic sample, the nearly Debye-like dielectric relaxation appearing in the frequency range from which the molecule rotation polarization and any anchoring effects are sufficiently distant (GHz) can be attributed to an interfacial polarization. Owing to the high conductivity of the magnetite particles (around 25

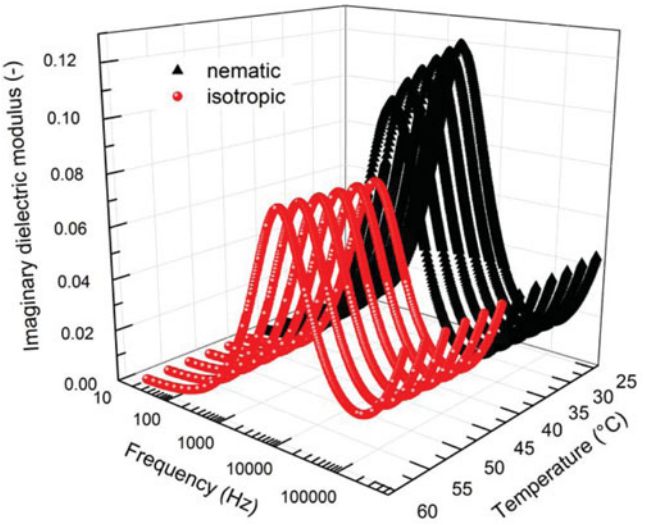

Figure 3. Frequency and temperature dependent imaginary part of dielectric modulus of 6CHBT doped with 0.05 % (vol.) of magnetite nanoparticles.

kS/m), the appearance of Maxwell-Wagner polarization may be also expected at higher frequencies. However, beside that interfacial-polarization, there can be another polarization phenomenon taking place at the particle-LC interface. As the particles are covered by the oleic acid molecules, the adsorbed OH^- heads charge the particle surface negatively. Then, the particles can electrostatically attract the positive space charge, what leads to the formation of the electric double layer (EDL) on the particles. In the external electric field, these

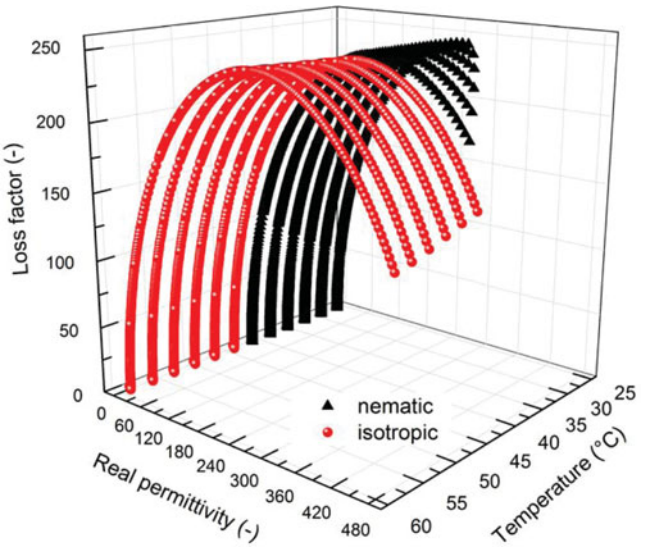

Figure 4. Cole-Cole plot of complex permittivity of the 6CHBT doped with 0.05 % (vol.) of magnetite nanoparticles.

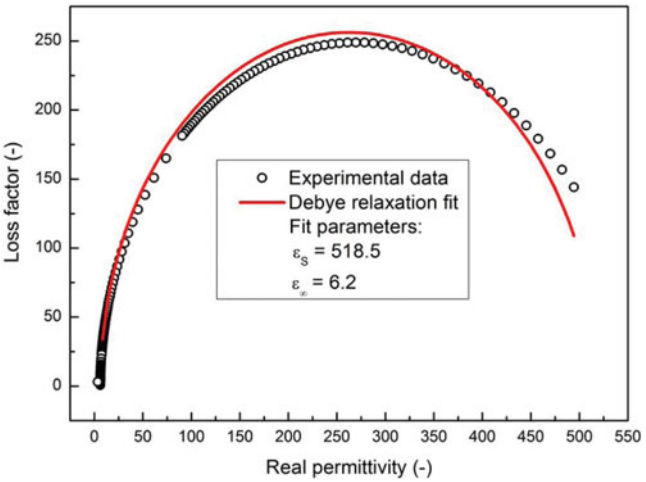

Figure 5. Cole-Cole plot of the complex permittivity of 6CHBT doped with 0.05 % (vol.) of magnetite nanoparticles measured at 56°C. The line corresponds to the Debye relaxation fit.

counter charges may move along the particle surfaces, creating so electric dipoles on the particles. This polarization and the related relaxation were explained by the Schwarz theory of EDL polarization [12]. We propose therefore, that the low frequency relaxation process in the ferronematic sample is associated with the EDL polarization. The corresponding relaxation time is given according to the above mention theory as follows:

$$\tau = \frac{R^2}{2ukT} = \frac{R^2}{2u_0kT}\exp\left(\frac{E_A}{kT}\right) \tag{4}$$

where R is the radius of the colloidal particle, k is Boltzmann constant, T is the absolute temperature, u is the mechanical mobility of the ions on the particle's surface dependent on the activation energy E_A and the mobility in free solution u_0. As in the studied system it is difficult to determine the mechanical mobility, the relaxation times of the EDL relaxation were obtained from the Havriliak-Negami relaxation (5) and conductivity fitting parameters.

$$\varepsilon^*_{(\omega)} = \varepsilon_\infty + \frac{\Delta\varepsilon}{\left[1 + (i\omega\tau)^\alpha\right]^\beta} \tag{5}$$

In the equation (5) the $\Delta\varepsilon$ (dielectric increment) means the difference $\varepsilon_s - \varepsilon_\infty$, α and β are Havriliak-Negami empirical exponents [8] (for the studied sample β equals 1 for all the spectra and α deviates from 0.972 to 0.964). By fitting all the temperature dependent dielectric spectra in Fig. 2(a) and (b), it was possible to get the relaxation times, which are depicted in Arrhenius plot in Fig. 6. From that figure it is clearly seen, that the logarithm of the relaxation time linearly decreases with increasing temperature in both, nematic and isotropic phases. The relaxation time thus exponentially decreases with temperature in accordance to the famous Arrhenius law [8, 13]

$$\ln\tau\,(T) = \ln\tau_0 + \frac{E_A}{\mathrm{R}T} \tag{6}$$

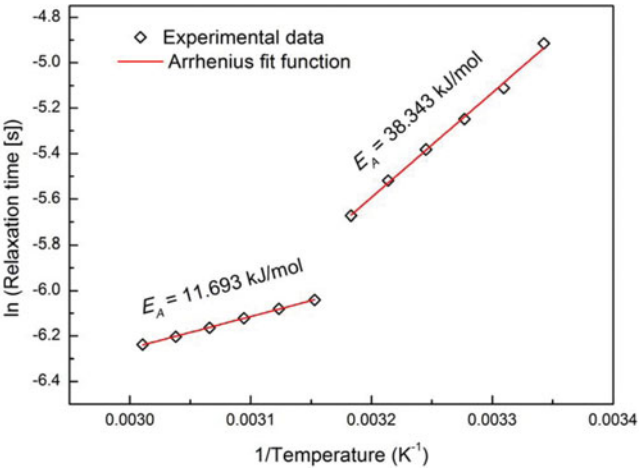

Figure 6. Arrhenius plot of the temperature dependent EDL relaxation time in 6CHBT doped with 5 % (vol.) of magnetite nanoparticles in isotropic and nematic phase.

where τ_0 is a pre-exponential factor, R is the universal gas constant, T is the absolute temperature and E_A is the activation energy. The calculated energy in the isotropic phase (11.693 kJ/mol) is expectedly lower than that in the nematic phase (38.343 kJ/mol).

Conclusion

The dielectric spectroscopy study of the magnetite nanoparticles doped 6CHBT has been compared with that of the pure 6CHBT. The low frequency dielectric dispersion in the pure 6CHBT has been attributed to the space charge polarization. In the higher frequency range (from 100 kHz) the spurious ITO relaxation dominates the dielectric spectrum. The magnetite nanoparticles doped 6CHBT shows a Debye-like dielectric relaxation with the notable temperature dependence. Since the nanoparticles are negatively charged by polar heads of the oleic acid, the observed relaxation process has been associated with the electric double layer (EDL) polarization taking place on the particle surfaces. The related relaxation time decreases with increasing temperature according to Schwarz theory of EDL polarization and obeys Arrhenius law. Though the high frequency ITO peak disturbs the real sample response, the relaxation due to the reorientation around the long LC axis should appear at GHz frequencies, what is beyond the available frequency range.

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References

[1] Brochard, F., & de Gennes, P. G. (1970). *J. Phys.*, *31*, 691–708.

[2] Ostapenko, T., Wiant, D. B., Sprunt, S. N., Jákli, A., & Gleeson, J. T. (2008). *Phys. Rev. Lett.*, *101*, 247801.
[3] Kremer, F. (2002). *J. Non-Cryst. Solids*, *305*, 1–9.
[4] Ouskova, O. B. (2003). *Liq. Cryst.*, *30*, 1235–1239.
[5] Tang, C.-Y., Huang, S.-M., & Lee, W. (2011). *J. Phys. Appl. Phys.*, *44*, 355102.
[6] Kobayashi, S., Miyama, T., Nishida, N., Sakai, Y., Shiraki, H., Shiraishi, Y., & Toshima, N. (2006). *J. Disp. Technol.*, *2*, 121–129.
[7] Dabrowski, R., Dziaduszek, J., and Szczucinski, T. (1984). *Mol. Cryst. Liq. Cryst. Lett.*, *102*, 155.
[8] Feldman, Y., Puzenko, A., & Ryabov, Y. (2005). in *Fractals Diffus. Relax. Disord. Complex Syst.* (eds. Coffey, W. T. & Kalmykov, Y. P.) 1–125 (John Wiley & Sons, Inc.,). at <http://onlinelibrary.wiley.com/doi/10.1002/0471790265.ch1/summary>
[9] Sawada, A., Tarumi, K., & Naemura, S. (1999). *Jpn. J. Appl. Phys.*, *38*, 1418.
[10] Marik, M., Mukherjee, A., Jana, D., Yoshizawa, A., & Chaudhuri, B. K. (2013). *Phys. Rev. E Stat. Nonlin. Soft Matter Phys.*, *88*, 012502.
[11] Wübbenhorst, M., & van Turnhout, J. (2002). *J. Non-Cryst. Solids 305*, 40–49.
[12] Schwarz, G. (1962). *J. Phys. Chem. 66*, 2636–2642.
[13] Schönhals, A., & Kremer, F. (2003). in *Broadband Dielectr. Spectrosc.* (eds. Kremer, P. D. F. & Schönhals, P.-D. D. A.) 59–98 (Springer Berlin Heidelberg). at <http://link.springer.com/chapter/10.1007/978-3-642-56120-7_3>