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Refractive indices and birefringence of hybrid liquid crystal - nanoparticles composite materials in the terahertz region

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We show that a hybrid LC-ferroelectric nanoparticle suspension of liquid crystal E7 doped with $BaTiO_3$ nanoparticles leads to 10% increase in birefringence in the THz region of spectrum as compared to pure E7. Doped liquid crystals can be used to increase performance of THz modulators and waveplates. $BaTiO_3$ nanoparticles used in the mixture were synthesised with the sol gel technique, and their refractive index has been measured in THz in powder form and in solution. © *2015 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License.* [http://dx.doi.org/10.1063/1.4927392]

THz-time domain spectroscopy (THz-TDS) is a technique based on a near-IR ultrafast laser used to generate and measure THz pulses. The emission and detection mechanism is usually based on semiconductor photoconductivity or optical non-linearity. In THz-TDS the detection of the pulses provides both temporal and spectral information. The electric field is measured rather than the intensity of the EM wave; therefore the phase and the amplitude can be retrieved simultaneously. In this way, the real and imaginary part of the refractive index ($\tilde{n} = n + \iota k$) of a material can be determined, without using the Kramers-Kronig relations. As THz-TDS sources are usually linearly polarised, efficient polarisation control using THz liquid crystal (LC) devices such as wave plates and modulators, could provide additional, polarisation specific, spectroscopic information of tested samples.[1,2] LCs should have high birefringence to limit the necessary thickness of the devices as well as chemical stability for their reliable operation.[3–7] E7 is a well known, stable LC which has a relatively high birefringence in the THz range ($\Delta n_{E7} = 0.13$).[8] New LCs, specifically designed for THz have also been synthesised and the details of their chemical formulae reported.[9–11] The birefringence in the LC reported in Ref. 9 is $\Delta n = 0.28$ and in Ref. 10 it is $\Delta n = 0.3$, finally, in Ref. 11 the average birefringence is $\Delta n = 0.2$. Here we present a complimentary method for increasing the birefringence of LCs without changing the chemical structure of the material. It has been already reported that in the optical spectrum a hybrid LC and nanoparticle (NP) mixture, with a low concentration of ferroelectric NPs, can improve the birefringence of the material.[12–15] Doping of the LC with NPs, with size between 10-100 nm, can lead to significant increase of the dielectric anisotropy and of the birefringence of the suspension without disturbing the LC alignment. The enhancement of LC parameters is caused by the ferroelectricity of NPs, which produces large dipole moments, and thus large electric fields between the NPs. Furthermore, it has recently been suggested that additional charges resulting from the fabrication process of the suspensions (milling, sonication mainly) are also responsible for increased dielectric and optical anisotropy.[16,17] $BaTiO_3$ is a material with

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high dielectric constant and ferroelectric properties at room temperature with several applications in electronics devices.[18–20] Typically, the NPs are fabricated through the milling process of commercial powder.[21–23] However, the milling process is time consuming and requires dedicated, expensive equipment, so there is a clear need to develop alternative fabrication processes that could provide ferroelectric nanoparticles of similar specifications. In this paper, we used the sol gel method for the synthesis of the $BaTiO_3$ NPs.[19,20] Sol gel process offers a higher purity, chemical homogeneity and better control of the particle dimensions compared to other chemical techniques such as solid state reaction, coprecipitation and hydrothermal reaction.[24] The birefringence in the THz range of a hybrid LC, containing the liquid crystal E7 and sol-gel $BaTiO_3$ in mixture is measured and presented here, demonstrating an increase of the birefringence in frequencies between 0.3 to 3 THz. For the benefit of future fabrication and optimisation of NP/LC mixtures, we also measured the refractive index in the THz range of the $BaTiO_3$ NPs in solution with heptane and as powder.

For the synthesis of the $BaTiO_3$ powder,[20] we used as main compounds titanium(IV) t-butoxide $Ti(OC_4H_9)_4$ (99.95%), and barium acetate $Ba(CH_3COO)_2$ (99%) both from Strem Chemicals. The formula applied to produce $BaTiO_3$ powder, used 1.73 grams of $Ti(C_4H_9)_4$ and 1.295 grams of $Ba(CH_3COO)_2$. The synthesis is based on two mixtures: the first mixture contained $Ti(C_4H_9)_4$, 1.75 ml of absolute ethanol (CH_3CH_2OH) and 0.83 ml acetic acid CH_3COOH (99.8 % - Acros Organics), and it was prepared by stirring. For the preparation of the second mixture, $Ba(CH_3COO)_2$ was dissolved with 1.62 ml CH_3COOH and 2.88 ml H_2O. The final material was obtained by combining the two mixtures (molar ratio 1:1) and vigorously stirred for one hour. The resulting suspension was a clear gel at room temperature and the xerogel was obtained by drying the precursor in a furnace at 120 °C. Then, the powder was obtained by a calcination performed at 700 °C for two hours. Finally, 1 gram of the powder was ball milled with 2 ml of oleic acid and 10 ml heptane for one hour. Milling of powder with oleic acid, as a surfactant, has been shown to remove aggregation and to provide nanosize particles.[24] Transmission electron microscopy (TEM) was used to estimate the NPs size which was between 20 and 60 nm. The NPs were characterised by Raman spectroscopy at 514.5 nm in a back scattering geometry system[25] using with Dilor XY triple mono-chromator spectrometers. The Raman spectrum and X-Ray diffraction (XRD), confirmed that the material was indeed $BaTiO_3$ and that it is ferroelectric. The Raman band at 305 cm^{-1} is the indicator of the tetragonal phase and the presence of this band indicates that the material was synthesised in the ferroelectric phase.[25,26]

After the synthesis of the NPs, the doped LC and NPs (in solution with heptane and oleic acid) mixture was prepared. The mixture contained $BaTiO_3$ NPs at 1% ratio by weight in the LC. A concentration of 1% w/w NPs in LC was used as it was the minimum in order to have an accurate estimation of the quantity of the NPs. We could not use higher concentrations because of aggregation effects. The suspension was heated to 60 °C on a hot plate for one day to evaporate heptane. The cells for the hybrid E7 - NPs suspensions were prepared using two 0.5 mm thick wires as spacers and electrodes. Quartz windows (1.5 mm thickness) were used as substrates; z-cut quartz was used as the absorption is low in the frequencies between 0.3 to 3 THz. The voltage applied to switch the orientation of LC was 400 V in AC field and with this voltage we obtained the alignment of the LC cells.[4]

The TPS Spectra 3000 TeraView ltd. THz -TDS system was used for the measurement of the LC/NP mixture. The samples were placed in the focus of the THz spectrometer for measurement. The ordinary (n_o) and the extraordinary (n_e) real refractive index and absorption, were calculated using the method for extraction of material parameters in THz-TDs.[27,28] This method is based on fitting a theoretical to the experimental transfer function using the Newton-Raphson method, so the complex refractive index can be determined. The reference measurement was the time domain scan of the terahertz pulse with the two windows in contact and the sample measurement was with the LC sample. When the polarisation of the THz wave was perpendicular/parallel to the LC director, the ordinary refractive index (n_o)/extraordinary refractive index (n_e) was determined.

First, we measured the average refractive indices of the E7,[8] which varied for different frequencies, the average values were $n_o = 1.60$ and $n_e = 1.73$ and for the doped E7 it was $n_o = 1.55$ and $n_e = 1.69$. Figure 1(a) shows the refractive indices for frequencies between 0.3 to 3 THz. The AC field aligned the LC solutions and stabilised their orientation, thus we obtained the maximum value
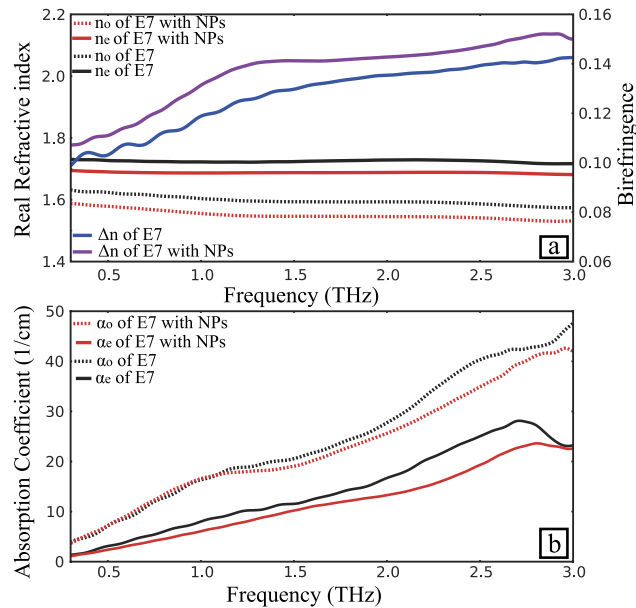
FIG. 1. (*a*) Ordinary (n_o) extraordinary (n_e) refractive indices and birefringence (Δn) of E7 and suspension of E7 and BaTiO$_3$ NPs.(*b*) Absorption in ordinary (a_o) and extraordinary (a_e) polarisations of E7 and suspension of E7 and BaTiO$_3$ NPs.

of birefringence. The measurement was performed at 18 °C. The birefringence has increased as in the optical range;[12] for frequencies between 1 to 1.5 THz, the birefringence of the doped E7 was 0.138 and for the pure E7 was 0.125, the increase was approximately 10%. Between 0.3 to 3 THz, the average birefringence for the pure E7 was $\Delta n = 0.127$ and for the doped E7 was $\Delta n = 0.136$, which is equivalent to an increase of 6.6% (Figure 1(a)). Secondly, absorption of the ordinary and extraordinary polarisations in E7 and the doped mixture of E7 and BaTiO$_3$ NPs was measured and is presented on Figure 1(b). The absorption in the ordinary axis is higher compared to the extraordinary axis because of the rod-like shape of the nematic LCs (as E7); the rod like molecules can move around their long axis while the oscillations around the short axis are slower.[29] As it can be observed in Figure 1(b), the absorption coefficient increases linearly with frequency as it would be expected in a disordered medium where the absorption, $\alpha(\omega)$, is proportional to the vibrational density of states, $g(\omega)$, and a coupling coefficient, $C(\omega)$, which describes the coupling of the EM wave and the vibrational states and is considered to be constant in the low frequency limit, $\alpha(\omega) = C(\omega)g(\omega)$. The absorption dependence shows a Ioffe Regel transition frequency slightly above 1 THz.[30] The refractive indices of our NPs/LC suspension are decreasing and also the absorption of the NPs/LC mixture is decreased in comparison with pure E7. To understand the behaviour of the refractive index of the NPs/LC system molecular modelling is needed,[30] however, the electric field caused by the permanent polarisation of the BaTiO$_3$ NPs has to be taken into account.

In the next step, we measured the complex refractive index of our NPs in heptane solution using a custom THz-TDS system based on a Ti:Sapphire near-IR, 60 fs laser with GaAs photoconductive emitter and detector.[31] Firstly, we estimated the average refractive index for the heptane to be $n_{heptane} = 1.36$ between 0.3 to 1.5 THz. For the measurement of refractive indices of BaTiO$_3$ NPs in solution we designed a flask which has two silicon windows with thickness 5 mm per window to avoid multiple reflection effects of the THz pulse. The thickness of the flask was 3 mm. The flask was first filled with a solution of BaTiO$_3$ NPs in heptane and then, in a separate measurement, it was filled with pure heptane. The refractive indices of the solution and of heptane were measured. As reference, time domain scan was performed of two silicon windows in contact with each other. Before the characterisation of the solution, the oleic acid was removed with repeated centrifugation. Because the oleic acid has high and different refractive index to heptane, it would have been difficult to calculate the refractive index of the NPs if it was kept in solution. Three different concentrations

of NPs in heptane were prepared, namely 0.5, 1.5 and 3.0% v/v volume fraction solutions. Maxwell Garnett approximation, a well known method for the calculation of the dielectric function of a medium containing inclusions at low concentrations,[32] was used to extract the values of refractive indices of NPs. This approximation is particularly useful when one of the components can be assumed as host (heptane) and the other as inclusions (NPs) and is given in equation (1). The measurements were repeated four times for each sample.

$$\frac{\varepsilon_{eff} - \varepsilon_i}{\varepsilon_{eff} + 2\varepsilon_i} = \sum_{nps} f_{nps} \frac{\varepsilon_{nps} - \varepsilon_i}{\varepsilon_{nps} + 2\varepsilon_i} \tag{1}$$

where ε_{eff} as the effective permittivity of the mixture with spherical inclusions, ε_i the dielectric permittivity of the background medium and ε_{nps} the dielectric permittivity of the inclusions and f the volume fraction, we can determine the dielectric constant of the NPs knowing the dielectric constant of the medium. Maxwell Garnett can be used only when the size of the NPs is smaller than the incident wavelength and the multipolar interactions are neglected. For this reason, the distance between the NPs should be bigger than the size of the NPs. Otherwise, the electrostatic interaction between the inclusions should be taken into account when calculating dielectric properties of a system.[32] Therefore we used the equation (1) only for the 0.5% v/v volume fraction (f) solution. At higher concentrations, we had some evidence of aggregation, as will be discussed later and therefore Maxwell Garnett approximation may not be valid. A simpler model called effective medium approach (EMA) was used to estimate the refractive index of the NPs for samples with volume fractions 1.5% v/v and 3.0% v/v, using equation (2). The simple EMA gives the same results for volume fraction of 0.5% by volume as calculated with the Maxwell Garnett formula (eq. (1)). The anisotropic grains are randomly oriented, thus leading to an isotropic composite in EMA.[32,33]

$$f n_{nps}^2 = n_{eff}^2 - (1 - f) n_i^2 \tag{2}$$

The refractive index of the NPs (fig. 2(a)) was estimated to vary between 1.4 to 1.8 for the frequencies and the concentrations studied. As can be seen on Figure 2(a), the refractive index is similar for all concentrations of NPs considered, but the samples with higher concentrations have higher absorption. This result is consistent with the process of aggregation that is likely to occur for higher NP concentrations, leading to stronger scattering. Possible aggregation was indeed expected due to the
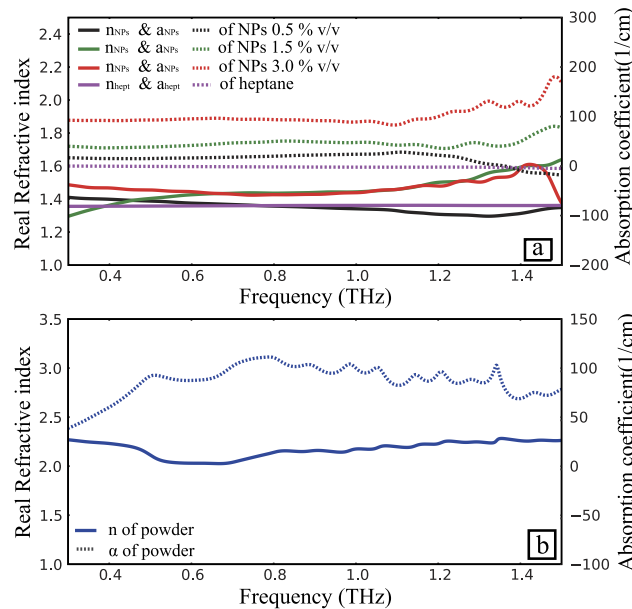

FIG. 2. (*a*) The real refractive index and absorption of heptane and BaTiO$_3$ NPs while in a heptane solution. NPs in volume fractions 0.5%, 1.5% and 3.0% in heptane were characterised. (*b*) Refractive index and absorption of the BaTiO$_3$ powder.

TABLE I. Values of the birefringence of the E7 and NPs suspension, refractive index of NPs and powder in the frequencies of 0.5 THz, 1THz and 1.5 THz.

Sample	0.5 THz	1.0 THz	1.5 THz
Δn_{E7+NPs}	0.112	0.131	0.141
n_{NPs}	1.41	1.41	1.48
n_{powder}	2.12	2.17	2.3

removal of oleic acid. Further, at higher frequencies the wavelength may be comparable with the size of the aggregations leading to increased scattering which is manifested in the measurement as increased absorption. The negative absorption of the 0.5 % v/v above 1.3 THz that can be seen in Figure 2(a) can be explained due to the assumption of the MG equation and the fact that the refractive index of the heptane is higher compared with the refractive index of the NPs for volume fraction 0.5% v/v. Finally, the refractive index of the $BaTiO_3$ powder was determined, for completeness of our investigation and as a reference for future fabrication of NPs. For $BaTiO_3$ powder measurements we used the same THz-TDS as with the measurement of NPs in heptane solution and we used two quartz windows with thickness 1.5 mm and wires with thickness 1 mm as spacers. The reference THz scan was the windows of the cell in contact. As mentioned, in the description of the fabrication, the powder was ball milled in order to produce NPs, and therefore it contains larger particles as compared to the NPs. The complex refractive index of $BaTiO_3$ powder was measured to be $n_{powder} = 2.2$ in frequencies 0.3 to 1.5 THz (Figure 2(b)). Our measurements give similar results to previous works where the refractive index was estimated to be 2.4.[18] The measured difference of the refractive index between powder and NPs can be explained due to NPs higher surface reactivity, the larger surface volume ratio, which is a consequence of their smaller dimensions. This enables the surface atoms in NPs to be bound by weaker forces and this influences the optical properties between different size particles.[33] The measurements were repeated which allowed us to confirm the values and estimate the error of measurements to be $\delta_{n_{powder}} = 0.02$. In the Table I, the results of the increased birefringence of the hybrid suspension (Δn_{E7+NPs}), the refractive index of the $BaTiO_3$ NPs (n_{NPs}) and the $BaTiO_3$ (n_{powder}) in the frequencies 0.5, 1 and 1.5 THz are summarised. In conclusion, we demonstrated hybrid LC suspensions with sol-gel $BaTiO_3$ NPs. We have used the sol gel process which is a method which offers high purity and chemical homogeneity. The hybrid mixture shows an increase of up to 10% in birefringence in comparison with the pure E7. Therefore, we demonstrate that enhanced birefringence can be observed without synthesis of new LC mixtures. The measurements presented can be used as reference in future fabrication of ferroelectric NPs and LC mixtures. By measuring the THz optical properties of the powder, NPs solution in heptane and NPs/LC mixture, we completed a comprehensive characterisation of the fabrication process of the LC/NP mixture, that can aid future repeatability and research on hybrid materials for the THz range.

ACKNOWLEDGMENTS

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