Declaration of Authorship

I, Elena Mavrona, declare that this thesis titled, ‘Functionalised Liquid Crystals for manipulating Terahertz radiation’ and the work presented in it are my own. I confirm that:

■ This work was done wholly or mainly while in candidature for a research degree at this University.

■ Where any part of this thesis has previously been submitted for a degree or any other qualification at this University or any other institution, this has been clearly stated.

■ Where I have consulted the published work of others, this is always clearly attributed.

■ Where I have quoted from the work of others, the source is always given. With the exception of such quotations, this thesis is entirely my own work.

■ I have acknowledged all main sources of help.

■ Where the thesis is based on work done by myself jointly with others, I have made clear exactly what was done by others and what I have contributed myself.

Signed: 

Date:

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Do not adventures ever have an end? I suppose not. Someone else always has to carry on the story . . .

J.R.R. Tolkien, The Lord of the Rings
New materials and techniques are needed to advance terahertz science and technology. Liquid crystals have been widely used for devices such as phase shifters and light modulators in the optical and terahertz regime. Liquid crystals doped with ferroelectric nanoparticles have improved the birefringence in the optical regime. In this work, the method of doping liquid crystals with ferroelectric nanoparticles in order to improve their birefringence in the terahertz regime is being investigated. The nanoparticles are synthesised using the sol gel technique and then characterised to check their ferroelectric properties. The new liquid crystals/nanoparticles suspensions were characterised with terahertz time domain spectroscopy and an algorithm was developed to determine the refractive index of the materials. In order to thoroughly understand the interactions between the liquid crystal molecules and the nanoparticles, several liquid crystals were doped with nanoparticles. After the doping of liquid crystals with nanoparticles the absorption spectrum of the new suspensions and the birefringence were measured. An increase in the birefringence of the liquid crystals was observed, most significantly in liquid crystals 2020 and E7. The other materials explored in this work are azobenzene complex dyes. The azobenzene complex dyes, PAADs, have been used for aligning of liquid crystals in the optical regime and also for manipulation of light polarisation and create complex beam shapes. Here I present a study of ultra-thin films of photo-aligning materials, in the optical regime with a future target to use them for applications in the terahertz spectral range. Finally, graphene is investigated as a zero-gap semiconductor for terahertz emission via the use of ultrafast diffusion carrier currents.
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To my mum . . .
Chapter 1

Introduction

In this work a variety of materials were characterised and identified with the aim of their application in Terahertz (THz) devices. Components for THz regime have not been fully developed yet, thus there is a need for new materials. The lack of devices to control and manipulate the THz radiation delays the advancement of THz technology. The project focuses on the development of materials for future liquid crystal (LC) based devices for manipulating THz radiation, for example as shown in figure 1.1. Selected materials were characterised, such as LCs, nanoparticles (NPs), azobenzene complex dyes in the optical and THz regimes with a range of methods. The LC technology has started developing rapidly, and LCs with high birefringence have been characterised in THz regime [4–7]. Since THz time domain spectroscopy (THz-TDS) sources are usually linearly polarised, efficient polarisation control using high birefringence of LCs is required; to limit the necessary thickness of the devices as well as chemical stability for their reliable operation. It has been suggested that ferroelectric NPs can increase the birefringence of LCs in the optical regime, and this technique, was applied during this thesis [8–10]. Other materials, such as azobenzene based complex dyes and their optical and physical properties, are characterised. Refractive indices, thicknesses and diffraction efficiencies of these materials were obtained. Azobenzene complex dyes from Beam.co (PAADs) are photo-aligning materials and can be used for the alignment of other functional materials such as LCs. Finally, graphene is a promising material for THz applications. Graphene was used for the development for lateral photo-Dember emitters due to its high mobility.

This introduction contains, the main description of THz science and the related applications. THz-TDS is being introduced as the method that was mainly used during this work. THz generation and detection are presented in this chapter. Moreover, the materials that were used during this thesis, for determination of efficient THz devices are
presented. LC technology and the applications, the optical properties of LCs, ferroelectric NPs and hybrid LC/NPs suspensions are core topics that are discussed. Finally, I outline the contents of this thesis.

![Diagram of a hybrid LC/NPs based THz modulator/beam steerer with photo-alignment layer for the alignment of the LC. The LC devices, due to their high birefringence and thickness, can create a phase shift in order of $\pi/4$ as shown.](image)

**Figure 1.1:** The schematic representation of a hybrid LC/NPs based THz modulator/beam steerer with photo-alignment layer for the alignment of the LC. The LC devices, due to their high birefringence and thickness, can create a phase shift in order of $\pi/4$ as shown.

### 1.1 Terahertz radiation

THz radiation includes the wavelengths from 30 $\mu$m to 3 mm (30 THz to 100 GHz) and energies from 40 meV to 0.4 meV. As shown in figure 1.2, the THz gap is the interface between optics and electronics because it is situated between the microwave and infrared regimes. It is called THz gap due to the lack of sources and detectors until recent years, and due to the late development of the THz area [3, 11]. The existence of vibrational and rotational modes of molecules within the THz regime has made THz an attractive area for further investigation and development.

#### 1.1.1 THz history

The history of THz radiation starts back in 1890s when Rubens and Nichols, with re-strahlen plates, built a spectrometer to isolate a very narrow wavelength band. They managed to produce wavelength beyond 50 $\mu$m by changing the reflecting plates and producing monochromatic light [12]. The work on quantum theory and on black body radiation by Max Planck and the collaboration with Rubens, on long wavelength results, helped to determine the Planck’s Radiation Law [12]. In 1950s Golay and numerous
experiments took place; with a milestone being the discovery of carbon bolometer [13] and more specifically the n-INSb electron bolometer [14] and the germanium bolometer [15] in 1960s. The 1960s was an important period due to the discovery of the pyroelectric detectors and the water vapour laser in 1964 by Crocker et al. [16]. However, it was only in 1984 that photoconductive antennas (PCA), emitters and detectors, were discovered by D.H Auston et. al. [17]. This was a revolutionary investigation for the THz regime that led to development of THz-TDS, a synchronous and coherent method for generating and detecting broadband THz radiation with detecting bandwidths between 0.1 to 100 THz [18]. The past 20 years have seen a significant progress in the THz regime also with the addition of THz quantum cascade lasers (QCLs) and frequency combs [19].

Nowadays, powerful methods have been demonstrated for generating THz radiation. First of all, PCAs and large aperture photoconductive antennas (LAPCAs), which are typical DC biased antennas with a few μm gap, with substrate materials such as GaAs, ZnSe, and lately 4H-SiC and 6H-SiC crystals [20, 21]. Surface emitters have demonstrated a simpler method of generating THz radiation, without applying any bias [22]. Another method is optical rectification which based on the second order nonlinear process with crystals such as ZnTe and 4-N-methylstilbazolium tosylate (DAST). Moreover, air plasma THz sources are used where the THz radiation is created in air by photoionisation. Finally, high intensity short pulse plasma interaction at relativistic intensities, are photon sources from X-rays to GHz [23].

Regarding the detection of THz, photoconductive antennas are the most common approach for the detection of THz pulses. Another method is the electro-optical sampling technique, which is based on the Pockels effect and can detect up to 5 THz depends on the crystal [23, 24].
1.1.2 THz applications

The rapid development of THz generation and detection techniques, has been the main reason for the exponential growth of THz applications in the past 30 years. THz radiation has an impressive role in biological, medical and pharmaceutical industries. THz spectroscopy is widely used for the studies of the intermolecular vibrational modes of proteins, viruses and DNA [25, 26]. THz-absorption spectra are being used for the classification of polymorphs in medicine and THz spectroscopy and imaging are methods that are in use for cancer diagnosis. There are several industrial applications as well. The semiconductor industry uses THz technology for inspection of silicon solar cells, nanocomposites, polymer films and dielectric films [27]. THz technology is also used for evaluating semiconductor wafer properties. Furthermore, THz imaging has been used for the inspection of the foam insulation in the space shuttles [28]. In security, THz has demonstrated impressive results in the detection of drugs and explosives [29–31]. THz QCLs, have provided a real time THz imaging of fingerprints [32]. THz cameras have been designed and are being used in airport security systems and THz sensing is being used for the hazardous gas detection [31]. THz technology has an important role in the environmental monitoring of the Earth, which monitoring the atmospheric chemical species, with the Earth Observing System Microwave Limb Sounder (EOS-MLS), on Aura satellite [32]. Today there are numerous THz instruments for space science [33]. Finally, the characterisation of an impressive range of materials in the THz regime has been an important component in the rapid development of THz technologies. Materials, such as LCs [34, 35], nanocomposites [36], metamaterials [37] have been characterised in THz regime and should promise for THz devices for controlling and manipulating THz radiation, such as phase shifters and THz modulators.

1.2 THz Time Domain Spectroscopy

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. 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 ($\tilde{n} = n + ik$) of a material can be determined, without using the Kramers-Kronig relations [38].

A schematic of a standard THz-TDS system is shown in figure 1.3. The beam of an ultrafast femtosecond laser, is split into two beams with a beam splitter. The one beam
Figure 1.3: Schematic representation of a typical THz-TDS setup.

is sent to the THz emitter, where the THz pulse is generated. The THz pulse propagates through the parabolic mirrors to the detector. The other beam is sent to the detector, where it gates it, and the detector is activated and can record the THz electric field at a small point in time relative to the length of THz pulse. Thus the delay stage is used to change the optical length between the beam splitter and the detector (either increase it or decrease it), and the THz electric field can be mapped out in time by the detector. The emitter is optically (by chopper) or electrically (AC) modulated and a lock-in amplifier is used for the detection of the THz electric field, which is increasing the signal to noise ratio. With a Fourier transform the information of the phase and the amplitude can be determined. In THz-TDS, the THz electric field of a reference and a sample is being measured. The information of the phase and the amplitude is used for the identification of the optical parameters of a sample [39]. THz-TDS have been widely used determining of the complex refractive index of materials, calculating the dispersion and the absorption of different materials in the THz regime [34, 40, 41].

1.3 THz generation

A variety of techniques have been introduced for the generation of THz radiation [42]. For THz-TDS, PCA emitters have demonstrated the most significant results. However
emitters based on optical rectification and surface emitters are popular as well [43].

1.3.1 Photoconductive

PCA are antennas that consist of a photoconductive semiconductor and two electrodes with some $\mu m$ gap (figure 1.4) on the top. Semiconductors such as GaAs (gallium arsenide) and InGaAs (Indium GaAs) have been used for photoconductive THz generation and detection [43–46]. An electric field, as 500 kV/cm is applied within some $\mu m$ of anode. For the generation of a THz pulse, an ultrafast pulse is focused on the semiconductor, where the wavelength of the ultrafast laser (Ti-Sapphire: 800 nm) is suitable with the band-gap of the semiconductor (GaAs: 870 nm). After the illumination of the semiconductor with the femtosecond laser, ultrafast carriers are generated and accelerate due to the presence of the electric field. This generation and acceleration of the carriers creates a photocurrent which starts to decay due to carrier and hole recombination. This fast changing dipole is the generator of the broadband THz radiation. Usually the gap in a PCA is just a few $\mu m$ which is less than a wavelength, thus the Hertzian dipole approximation can be applied by,

$$E_{THz}(r, t, \theta) = \frac{l_e}{4\pi \epsilon_0 c^2 r} \frac{\partial J(t)}{\partial t} \sin \theta \propto \frac{\partial J(t)}{\partial t}$$ (1.1)

where $J(t)$ is the photocurrent in the emitting dipole, $l_e$ is the effective length of the dipole, $\epsilon_0$ is the dielectric constant in the vacuum, $c$ is the speed of light in the vacuum.
and $\theta$ is the angle from the dipole. As shown in equation 1.1, the THz electric field is proportional to the time derivative of the photocurrent [39].

1.3.2 Optical Rectification

Optical rectification generates DC or a low frequency polarisation due to femtosecond near infrared beams that propagate through a nonlinear crystal. In order to achieve optical rectification it is necessary for the crystal to not be centrosymmetrical. The electric polarisation $P$ is given by,

$$P = \chi(E)E$$

(1.2)

$P$ is proportional to $E$ (applied electric field) where $\chi(E)$ is the electric susceptibility. The nonlinear optical properties are given by,

$$P = (\chi_1 + \chi_2 E + \chi_3 E^2 + ...)E$$

(1.3)

with optical rectification to be second order nonlinear optical effect. A second order nonlinear polarisation $P_2$ of two different electric field components, where the electric fields are $E_1(t) = E_0\cos(\omega_1 t)$ and $E_2(t) = E_0\cos(\omega_2 t)$, is described by

$$P_2 = \chi_2 E_1 E_2 = \chi_2 \frac{E_0^2}{2}(1 + \cos(\omega_1 - \omega_2)t + \cos(\omega_1 + \omega_2)t)$$

(1.4)

The term $\omega_1 - \omega_2$ is responsible for the generation of the THz radiation and the term $\chi_2 \frac{E_0^2}{2}$ is due to dc polarisation. The DC polarisation is due to the rectification of the incident optical electric field by the secondorder nonlinear electric susceptibility of the material [47]. A femtosecond pulse can generate a THz signal while it is propagating through a crystal due to the different frequency mixing frequencies and bandwidth of the ultrafast pulse. Zinc telluride (ZnTe), gallium phosphide (GaP) and gallium selenide GaSe are the most common crystal for nonlinear THz generation. However, organic crystals such as DAST have demonstrated high bandwidth in THz emission [24]. The crystals should be transparent in THz and have a high second order nonlinearity for efficient THz generation. Due to the different refractive indices of the crystals in THz regime and infrared regime, for achieving high bandwidth is necessary for the crystals to be thinner than the coherence length that creates the velocity mismatch [47, 48].
1.3.3 Photo-Dember emitters

Surface emitters, such as photo-Dember emitters, are the devices that generate THz radiation, after the excitation by a femtosecond laser, from the surface of bulk or film semiconductors without applying external electric field [49]. The photo-Dember effect was discovered by Dember in 1931 [50]. The generation of THz radiation with the photo-Dember effect happens due to the different mobilities of electron and holes in a semiconductor and a break in symmetry at the surface. Electrons and holes diffusion is generated after the illumination of the semiconductor with a femtosecond laser. The band gap of the semiconductor and the energy of the wavelength of the laser should match because this absorption creates a strong carrier concentration perpendicular to the surface [39]. The different mobilities of electron and holes create a net dipole perpendicular to the surface (fig. 1.5).

![Figure 1.5: Illustration of the photo-Dember with a symmetric electron and hole distribution.](image)

Lateral photo Dember (LPD) effect is the effect where THz radiation is generated by creating a metal mask on the surface of the semiconductor as is illustrated in figure 1.6. LPD emitters can give the same bandwidth as PCA emitters and they have demonstrated efficient signal to noise ratio [22, 51]. The THz generation is produced perpendicular to the surface so that the dipole is parallel to the surface and thus emitting perpendicular to it and can control carrier gradients [39]. The presence of the mask achieves the geometry rotation of carriers distribution. The metal mask on the top of the semiconductor sets the direction of the emitting current. The dipole that forms under the metal mask is suppressed and creates the anisotropy needed for net current because it experiences destructive interference from a reflected wave off the metal mask; due to the fact that after reflection it experiences a $\pi$ phase shift suppressing the dipole [52, 53]. The most important parameter is that there is no need for an external bias in LPD emitters so they have longer self life time compared with PCAs. Semiconductor such as Si-GaAs...
and LTG-GaAs have been used for the generation of THz pulses with LPD emitters. Multiplexed metal LPD emitters have been demonstrated by McBryde et al. [54]. These emitters were fabricated with periodic Au and Pb structures on GaAs and they exhibited 2 THz bandwidth. However, the THz emission was generated not only due to LPD effect but also from the different Schottky barrier heights of the Au and Pb.

![Figure 1.6: An illustration of the lateral photo-Dember effect.](image)

### 1.4 THz Detection

Regarding the detection of THz pulses, two methods are the most popular regarding THz-TDS. PCA for detection, which its function principle is the opposite of the PCA for emission and the electro optical detection which is based on nonlinear crystals and $\chi^{(2)}$ nonlinearity.

#### 1.4.1 Photoconductive Antennas

For detection with a PCA, an ultrafast laser pulse needs to generate the carries. However, the incident THz electric field, as it is shown in figure 1.3, accelerates the carriers [55] within the PCA. These accelerate carriers, produce a photocurrent which can be measured across the antennas gap, by a lock-in amplifier and the photocurrent is perpendicular to THz electric field. The carrier lifetime and the laser pulse length is shorter than the THz pulse and a delay stage is used to map the THz electric field, as it changes the path length between the emitter and the detector. This results in the carrier observing the THz electric field as a stationary DC field, and the detector measures only a
snapshot of the THz pulse. The time dependent photocurrent which is generated by the THz electric field is the convolution of the THz electric field with the time dependent conductivity of the detector \[39, 42\].

\[
j(t) = \frac{1}{T} \int_{0}^{T} E_{THz}(\tau) \sigma(t - \tau) dt
\]  

(1.5)

Where \(T\) is the laser repetition rate, \(E_{THz}\) is the incident THz electric field, \(\tau\) is the delay between the pump and probe pulse and \(\sigma\) is the conductivity of the detector.

### 1.4.2 Electro Optical Detection

The electro optical detection is based on the linear electrooptic effect that was suggested by F. Pockels in 1893 \[47\]. The detection is achieved by measuring the phase modulation of the femtosecond laser pulse due to the presence of a THz pulse, through a nonlinear \(\chi^{(2)}\) crystal. The nonlinear crystal, due to the presence of the THz electric field will became birefringent. Due to the birefringence of the crystal the polarisation of the femtosecond pulse will change. The measurement of the femtosecond pulse’s polarisation can be measured with a quarter wave plate (QWP), a wollaston prism (WP), balanced photodiodes (PA and PB) and of course the crystal (EO) as shown in the figure 1.7 \[56\].

![Figure 1.7: Illustration of nonlinear electro optical detection in THz TDS.](image)

### 1.5 Materials

LCs are materials have been widely tested in optical regime due to their physical and optical properties, in particular due to their high birefringence. High birefringence LCs have been attracting the interest in applications such as display devices and as tunable filters, phase shifters in the optical, THz and microwave regime \[57, 58\]. Recent studies have suggested that doping of LCs with ferroelectric NPs enhances the electrooptical properties of LCs and it can increase the birefringence of LCs in the optical regime. This
method can be applied in THz regime because high birefringence LCs are required, due to the size of the THz wavelength \[8, 59, 60\]. In this section the optical and the physical properties of LCs and LCs/NPs suspensions are introduced.

### 1.5.1 Liquid Crystals

For the purpose of this thesis a range of nematic LCs were characterised and functionalised. LC refers to a state of matter that has properties between those of conventional solid crystals and liquids, as shown in figure 1.8. A LC flows like a liquid, but its molecules are oriented in a crystalline manner \[61, 62\].

![Solid Liquid Crystals Liquid](image)

**Figure 1.8:** An illustration of the difference of the behaviour of solid, LC and liquid. A LC flows like a liquid, but its molecules are oriented in a crystalline manner

### 1.5.2 Types of LCs

There are different types of LC materials that exhibit liquid crystalline properties. The main materials are lyotropic LCs, polymeric LCs and the most important for this work, thermotropic LCs \[63\]. Lyotropic LCs exhibit liquid crystalline phase when a particular concentration of a material (such as soaps, detergent and lipids) is dissolved in a solvent \[1\]. Polymeric LCs are the LCs that form a polymer out of monomer LCs (such as aromatic) \[63\]. The important characteristic of the polymeric LCs is the degree of flexibility that distinguishes them in three different categories, vinyl type, Dupont Kevlar polymer and polypeptide chain. These LCs have higher viscosity compared with the monomers which is very important for optical storage applications.
1.5.2.1 Thermotropic LCs

Thermotropic LCs have been extensively investigated due to their linear and nonlinear properties and they can form different phases as a function of temperature [63]. Thermotropic LCs have two important characteristic temperatures. One is the temperature when they change from solid to LC phase and the other temperature when they change from LC phase to liquid phase. These molecules of the thermotropic LCs are described as rigid rods due to their shape. They are three different classes of thermotropic LCs: nematic, cholesteric and smectic. The LC molecules are aligned in the director axis ($\hat{r}$) which is the direction of preferred orientation of molecules [1].

Cholesteric LCs are the thermotropic LCs that are aligned in a helical way. Smectic LCs molecules form a positional order and are oriented in a more specific pattern. They are different subphases of smectics with smectic A and C being the most common. Smectic C molecules are optically biaxial and smectic A are uniaxial as shown in figure 1.9 [1, 63].

![Figure 1.9: An illustration of the three different classes of thermotropic LCs, nematic, cholesteric and smectic.](image)

1.5.2.2 Nematic LCs

For this work we used only nematic LCs. Nematic molecules have the same properties in the $+\hat{r}$ and $-\hat{r}$ directions; they are centrosymmetric. The individual molecules have a permanent electric dipole, but they are oriented such as the dipole moment is minimised. TL205 and E7 are commercial nematic LCs that have been used widely for applications such as display devices [64–67]. The chemical structure of TL205 and E7 are presented in figure 1.10 and they are both Merck Ltd. products. TL205 is a mixture of cyclohexane-fluorinated biphenyls and fluorinated terphenyls [68]. E7 is a mixture of four compounds. The main compound consists of 51% of 4-cyano-pentyl-4'-cyanobiphenyl molecules, 25% 4-cyano-4'-n-heptyl-biphenyl, 16% of 4-cyano-4'-n-oxyoctyl-biphenyl and 8% 4-cyano-4'-n-pentyl-p-terphenyl.

In this project, other nematic LCs were used, namely 6CHBT and 2,3',5'-trifluoro-4-(4-pentylcyclohexyl)-4'-(trifluoromethoxy)-1,1'-biphenyl (compound A), 1867, 2037. Their
Figure 1.10: Chemical structure of commercial LCs E7 and TL205 (Merck Ltd).

Figure 1.11: The chemical structure of the LCs 6CHBT, compound A, 2037 and 1867

chemical structures are shown in the figure 1.11 and LC 2020 [69, 70]. 6CHBT and compound A are single molecule LC and 1867, 2037 and 2020 are complex mixtures that were prepared only for THz applications. The LCs were provided by the Faculty of Advanced Technologies and Chemistry in Military University of Technology in Warsaw. The mixture 2020 is a complex mixer with isothiocyanato compounds with fluorine atoms substituted in the lateral position and phenyl rings. There are also acetylene bridge group (\(C \equiv C\)) between benzene rings and one compound possess cyclohexane ring. For the synthesis of high birefringence LCs for THz applications, complex mixtures of LC molecules are required as suggested by Herman et al [71].
1.5.3 Optical properties of LCs

Nematic LCs, are described as crystalline in form, and their molecules are aligned in a direction defined by the director $\hat{r}$. A uniaxial crystal, such as a nematic LC, can be characterised with two different refractive indices; ordinary and extraordinary refractive index. The ordinary refractive index ($n_o$), $n_o=n_x=n_y$ is determined by light polarised perpendicular to the optical axis and the extraordinary ($n_e$), $n_e=n_z$, is determined by light polarised in the direction of the optical axis. The refractive index of a uniaxial material when the light propagates through it in angle $\theta_i$ is given by,

$$n = n_o$$ \hspace{1cm} (1.6)

when the refractive index is independent of the direction of the propagation of the light and

$$n = n_{eff} = \frac{n_o n_e}{\sqrt{n_e^2 \cos^2 \theta_i + n_o^2 \sin^2 \theta_i}}$$ \hspace{1cm} (1.7)

when the refractive index is dependent on the direction of the propagation of the light. In the case that the light propagates, with wavelength $\lambda$, through a nematic LC, with thickness $d$, a phase lag ($\delta$) is created between ordinary and extraordinary waves, which depends on the angle $\theta_i$ and is given by [63],

$$\delta = \frac{2\pi}{\lambda} |n_o - n_{eff}(\theta_i)|d$$ \hspace{1cm} (1.8)

When $\theta_i=\theta_i(z)$ the total $\delta$ is

$$\delta = \frac{2\pi}{\lambda} \int_0^d |n_o - n_{eff}(\theta_i(z))|dz$$ \hspace{1cm} (1.9)

The deviation of the director orientation changes the effective refractive index and the phase lag between ordinary and extraordinary components of the light propagating through the LC. This method is important for detecting the nematic reorientation and is useful for determining of the birefringence of nematic LCs [1, 63].

The physical parameters that define the response of LCs to externally applied fields are the dielectric constants, refractive indices and the electric conductivities. The electro-optical measurements of LCs are based on the measurements of the birefringence ($\Delta n$) of the LC and the dielectric anisotropy ($\Delta \varepsilon$). These are two of the main properties of LCs that can be improved with the presence of NPs in the LC [9, 72].
1.5.3.1 Determination of birefringence

The aim of this experiment is to determine the birefringence of a LC. When a LC is being characterised, it is typically sandwiched between two transparent electrodes of Indium tin oxide (ITO). ITO is deposited on 1mm thick glass substrates (guard electrodes). The Freedericksz transition is the transition from a uniform director configuration to a deformed director configuration due to application of a magnetic or electric field. As the field value is gradually increased higher than Freedericksz transition, the director begins to rotate until it's aligned with the field (fig. 1.13) [73].

As regards to the measurement of the Freedericksz transition, the experiments by applying AC electric field. For the the Freedericksz transition experiment, guard electrode cells were used and the cross polarised intensity is recorded depending on the AC voltage applied to the cell as shown in figure 1.12. The cell is placed between two crossed polarisers, oriented at 45° with respect to the LC alignment. A frequency doubled YAG diode pumped laser (532 nm) from Laser Quantum was used for the illumination of the system. A photodiode was used for the motoring of the intensity of the beam after passing through the cell.

The crossed-polarised intensity depends on the AC voltages applied to the cell. An Agilent 33120A waveform generator generated an AC electric field at 1kHz and with 1% accuracy in the measurement of the amplitude. The cell had conductive ITO layers that served as electrodes, so voltages at rate 1 mV/s from 0 V to 10 V were applied to the cell. The normalised cross polarised intensity is being calculated by these measurements, which is the main component for the determination of the birefringence. An example of measuring the cross polarised intensity in TL205 shown in figure 1.13.

Figure 1.12: The schematic representation of the experimental setup for measuring the birefringence of a LC cell in optical regime.
Figure 1.13: Dependence of the normalised cross-polarised intensity on the AC Voltage measured in the nematic TL205 cell. The relative errors for the normalised intensity is 0.1% and for the AC voltage is 1% [1].

The phase lag between the ordinary and extraordinary components is related to the $n_{eff}$ as a function of $z$ due to the realignment of the director by the electric field [74]. The phase lag is given by,

$$\delta_{max} = \frac{2\pi d \Delta n}{\lambda} \quad (1.10)$$

where $d$ is the cells thickness, $\lambda$ is the wavelength of the laser beam that is passing through the cell and $\Delta n = n_e - n_o$ is the birefringence of the LC. The beginning of the LC reorientation happens at Freedericksz threshold fields when the intensity curves start to oscillate [1, 59]. When the polarisation of the incident beam is $\phi$ with respect to nematic director ($r$), the normalised intensity of the beam as detected by the photodiode when $\phi = 45^\circ$ [1] is given by,

$$I = \sin^2 2\phi \sin^2 \frac{\delta}{2} = \sin^2 \frac{\delta}{2} \quad (1.11)$$

The intensity oscillates with the change of the phase lag, as suggested by equation 1.11 and figure 1.13. The calculations are simplified when $\phi = 45^\circ$. With the calculation of the phase lag we can determine the birefringence of the LCs in optical regime with the equation 1.10.
1.5.3.2 Dielectric anisotropy of LCs

The LC cell can be assumed to be a capacitor with area $S_0 = 1 \times 1 \text{ cm}^2$ and thickness $d = 12 \mu m$. The capacitance ($C$) of a cell is determined using the equation,

$$C = \frac{\varepsilon S_0}{4\pi d}$$  \hspace{1cm} (1.12)

The effective dielectric constant $\varepsilon$, the area of the cell ($S_0$) and the thickness of the cell ($d$) are the parameters that the capacitance of a cell depends on. When the cell is empty $\varepsilon = 1$, the capacitance depends only on the $S_0$ and $d$. After this stage the LC cell is filled with LC. The difference of the capacitance of the empty cell ($C_0$) and the capacitance of the filled cell $C$ is due to the difference of the effective dielectric constant $\varepsilon$. The measurement of the capacitance at 1kHz of a cell is measured with a Wayne Kerr automatic precision bridge B905, with the capacitance bridge circuit shown in figure 1.14. The bridge applies an AC field around of 1 mV at 1 kHz frequency to the circuit and changes the value of the variable capacitor until a null is reached, in order that the variable capacitor and capacitance of the LC will be the same [75]. For changing the LC orientation, the setup applies a DC voltage on the LC electrodes. During the experiment the capacitance is recorded for DC voltages usually in the range of 0.1 to 50 V(depends on the LC). For the planar cell is $\varepsilon = \varepsilon_{\perp}$ and for the homeotropic cell is $\varepsilon = \varepsilon_{\parallel}$. When there is no applied voltage in the cell, the LC has planar alignment $\varepsilon = \varepsilon_{\perp}$. When the voltage has reached the threshold voltage the LC starts to reorient so that $\varepsilon$ changes. Finally, when the voltage is increased enough, the molecules of the LC are completely reoriented and $\varepsilon = \varepsilon_{\perp}$ [1].
1.5.4 Hybrid LC and NPs suspensions

It has been shown that some LCs, when doped with ferroelectric NPs, demonstrate improve in their optical and physical properties. The ferroelectric particles, in LC matrix, can decrease the Freedericksz transition threshold voltage and they also can increase the birefringence of the LCs in the optical regime [8, 76, 77]. NPs have stronger dipoles and they create an electric field around them (fig. 1.15). This electric field can affect the orientation of LCs and is proportional of the concentration and the size of the NPs [72]. The changes of the properties of the LC are due to the permanent polarisation of the ferroelectric particles which depends mainly on the size of the particles, their aggregation and mechanical treatment [72, 78]. Li et al. suggested a theoretical model where the ferroelectric NPs induce local dipoles whose effective interaction is proportional to the square of the orientational order parameter [60].

![Figure 1.15: Illustration of the alignment of LC/Nps suspension with the presence of electric field.](image)

Ferroelectric NPs such as BaTiO$_3$ (Barium Titanate) and Sn$_2$P$_2$S$_6$ (Tin Thiohypodiphosphate), synthesised by the milling process have been used for the doping of LCs and have demonstrated interesting results. In the work of Reznikov et al [10] was demonstrated that Sn$_2$P$_2$S$_6$ NPs in solution with nematic LC can increase the dielectric anisotropy from $\Delta \varepsilon = 1.9$ for pure LC to $\Delta \varepsilon = 4.9$ for the LC/NPs suspension. Herrington et al. [72] used BaTiO$_3$ ferroelectric NPs and they observed an increase of the dielectric anisotropy from $\Delta \varepsilon = 3.09$ to $\Delta \varepsilon = 6.01$, where measurements were determined by the method described in section 1.5.3.2, and increase of the birefringence from $\Delta n = 0.21$ to $\Delta n = 0.26$, where measurements were determined by the method described in section 1.5.3.1, in TL205. In the work of Kaczmarek et al., also was observed increase of the birefringence, dielectric anisotropy and decrease of the threshold voltage in LC/NPs suspensions with BaTiO$_3$ and Sn$_2$P$_2$S$_6$ NPs compared with the pure LCs [79].

However, the NPs, have used in all the previous works, have been fabricated with the milling process which is time consuming and requires dedicated and expensive equipment.
For this thesis BaTiO$_3$ NPs are fabricated with the sol gel process which offers higher purity, chemical purity and better control of the particles dimensions. The LC/NPs suspensions, also, are characterised with THz-TDS in order to investigate their optical parameters in THz regime.

1.5.5 Applications of LCs

LC technology has existed for already more than 100 years, thus there is a fair amount of applications that involve these exceptional materials, apart from LC displays which are the most common. In this work we will focus on high birefringence LCs for THz applications, but there are numerous applications of LCs in different areas. Firstly, LC lasers based on cholesteric LCs have be demonstrated using the cholesteric LC as an one dimensional photonic crystal [80]. LCs have been also used for organic electronics as organic semiconductor in solar cells. LC micro/nanofibres/fibers with a core of LC is an alternative method that has been introduced and the benefit of this method is that the fabrication of these fibres is easier compared with the glass fibres [81, 82]. Finally, LCs as organic materials are easy to use in biological bilogical applications, since the membranes of the cells in human body are in a lyotropic lamellar liquid crystalline state. There are many interesting applications of LCs in biology, biotechnology, food science and pharmacology, such as biodetection with LCs and drug delivery with LC cubosomes and creams [83–86].

1.6 Thesis outline

The following chapters focus on the investigation of a variety of materials for applications in THz regime.
In Chapter 2, the synthesis of ferroelectric NPs with the sol gel process is presented, with the aim of the preparation of effective ferroelectric BaTiO$_3$ NPs. Sol gel process is introduced for a first time as a method for synthesis of ferroelectric BaTiO$_3$, for the preparation of hybrid LC/NPs suspensions.

In Chapter 3, first an introduction of the parameter extraction with THz-TDS is presented. This algorithm was used in the most of this work for determining of the complex refractive index of the materials, such as LC and NPs. In the second part of this chapter the preparation and the characterisation of LC suspension doped with NPs is described, especially LCs with high birefringence, explicitly designed for THz regime that were used for the hybrid LC/NPs suspensions. Chapter 3 also includes the characterisation of BaTiO$_3$ NPs and powder, determined with THz-TDS.
In Chapter 4 contains the characterisation of the optical parameters of photo-aligning
materials, azobenzene complex dyes (PAADs) which forms an important part of this work. Azobenzene based complex dyes, have been used for the alignment of functional materials and the results of this part of the project can be applied efficiently in THz regime.

In Chapter 5, the characterisation and the fabrication of a lateral Photo-Dember emitter based on graphene, was demonstrated. The advantages of using graphene, a zero-gap semiconductor and has demonstrated high mobilities is highlighted.

In Chapter 6, the conclusions are discussed and the future work is covered.
Chapter 2

Nanoparticles, synthesis and characterisation

2.1 Introduction

This chapter is focused on the results of the fabrication of ferroelectric BaTiO$_3$ nanoparticles (NPs) with laser ablation [73] and the sol gel process [2, 87, 88]. The NPs were characterised with multiple methods.

In this work we mainly synthesised and characterised BaTiO$_3$, a material with high dielectric constant, approximately 7000, and ferroelectric properties, with spontaneous polarisation in order of $0.26 \text{ C/m}^2$ at room temperature, with several applications in electronic devices [87–91]. Typically, the ferroelectric BaTiO$_3$ NPs are fabricated through the milling process of commercial powder [78, 92, 93]. However, the milling process is time consuming and requires dedicated and expensive equipment, so there is a clear need to develop alternative fabrication processes that could provide ferroelectric nanoparticles of similar specifications. In order to prepare high quality ferroelectric BaTiO$_3$ NPs the ablation method and the sol gel methods were investigated. However, only the sol gel method demonstrated ferroelectric NPs. The sol gel process offers a higher purity, chemical homogeneity and better control of the particle dimensions as compared to the other chemical techniques such as solid state reaction, coprecipitation and hydrothermal reaction [38, 87, 88, 94].

The aim of the synthesis of high quality ferroelectric NPs is to prepare hybrid LC/NPs suspensions with higher birefringence compared with the pure LCs. The doping of LCs with ferroelectric NPs has demonstrated a significant increase in the dielectric anisotropy, birefringence and clearing temperature as well as the reduction in the Freedericksz transition [60, 95–98] compared with the undoped LCs. LC TL205 was doped with ablated
BaTiO_3_ NPs and the properties of the new suspension were investigated in optical regime in this chapter and NPs synthesised with the sol gel process were used for doping LCs and characterised in THz regime (chapter 3). It has been suggested that the significant effect on the LC matrix originates from the permanent polarisation of the ferroelectric particles [60, 78, 99, 100]. The range of the permanent polarisation of the ferroelectric NPs depends on the size of the particles, their aggregation, mechanical treatment, screening by free charges [93] and the presence or absence of permanent dipoles in NPs. Hence the interaction between the NPs and different LCs is complex and can lead to confusing results in the electro-optic performance of the nominally ferroelectric NPs/LC suspensions [78]. In order to increase the efficiency of such suspensions, the separation of NPs with and without permanent polarisation, have been introduced by the harvesting technique [101, 102]. In this chapter, the effects and the results of the harvesting technique will be discussed [2].

2.2 Characterisation methods

Presented in this section are the methods that were used for the identification and structural characterisation of BaTiO_3_ NPs. Transmission electron microscopy (TEM) was used for the identification of the shape and the size of the NPs. Raman spectroscopy was used for the characterisation of the material and to identify any impurities. X Ray Diffraction (XRD), was also used, a powerful method that can be used for the identification of the material and for determining the NPs size. Finally, the harvesting technique for the identification of the permanent polarisation/charges of the NPs and as a purification method that helps us to select only the ferroelectric NPs.

2.2.1 Transmission electron microscopy (TEM)

TEM is a powerful method for identification of the physical and chemical properties of NPs, the properties that are related to their crystal and surface structures [103]. TEM is a unique method that helps us identify the shape of NPs [104]. With TEM the information from a small region is collected using a focused beam. A TEM system is based on an illumination system (usually a lanthanum hexaboride -LaB_6), an objective lens, the magnification and the data recording systems. TEM measures the energy of the primary electrons after they have passed through the specimen. While the electrons are going through the specimen, they are loosing energy of the order of few tens of eV. The initial energy of these electrons is in the order of 100 to 200 keV and the spectrometers of the TEM, with a resolution limited to 0.1 eV, are able to measure the scattering energy
of the electrons [105]. In this project we used TEM for determining the size of NPs and the model used was a Hitachi H7000.

2.2.2 Raman Spectroscopy

Raman spectroscopy is a very popular method for characterisation of materials [106]. In this project, Raman spectroscopy proved very useful for the identification of the NPs, to distinguish the characteristic bands of NPs. Moreover, with Raman spectroscopy it is possible to explore the existence of bands that are associated with the ferroelectricity (e.g. tetragonal peak for BaTiO$_3$ NPs) [96]. Raman Spectroscopy is one of the most common vibrational spectroscopic methods, which can detect local lattice distortions and crystallographic defects at the molecular level by measuring bond vibrations [107]. In Raman spectroscopy, the sample is irradiated by intense laser beams in the UV-visible or NIR at frequency $\nu_0$, and the scattered light is observed with back scattering. The scattered light consists of two types; one is called Rayleigh scattering, which is strong and has the same frequency as the incident beam $\nu_0$, and the other, called Raman scattering. It is very weak and has frequencies $\nu_0 \pm \nu_m$, where $\nu_m$ is the vibrational resonance frequency of the molecule. The $\nu_0 - \nu_m$ and $\nu_0 + \nu_m$ lines are called the Stokes and anti-Stokes lines, respectively. In Raman spectroscopy, the vibrational frequencies ($\nu_m$) [108] are measured. The Raman spectra in this project were recorded by two different

![Experimental setup of the micro Raman.](image)

*Figure 2.1: Experimental setup of the micro Raman.*
spectrometers, in order to in back scattering the first using a Dilor XY triple monochromator spectrometer conjunction with microscope, focussing a 514.5 nm $\text{Ar}^+\text{Kr}^+$ laser beam onto a 1 $\mu$m spot as shown in figure 2.1 and the second using a Horiba Scientific Labram HR800 spectrometer coupled with microscope which focused a 784 nm Laser diode beam to 2 $\mu$m spot [96]. The difference between the two Raman spectrometers is the use of Notch filter in the Horiba Scientific Labram HR800 spectrometer instead of a monochromator box. The quantity of light in the CCD is higher with this system which improves the sensitivity and the accuracy of the measurements.

### 2.2.3 X ray Diffraction

X Ray Diffraction (XRD) is being used for the recognition of the atomic and the molecular structure of a crystal and it is based on crystalline atoms can diffracting a beam of incident X-rays into many directions, revealing the lattice of the crystal [109, 110]. For XRD patterns, we used the Ultima IV Rigaku diffractometer [111]. The configuration is the Bragg−Brentano $\theta−\theta$ configuration in which the sample is stationary while the X-ray tube and the detector are rotated around it (fig. 2.2). XRD patterns are recorded using a step size of 0.02$^\circ$ and a scanning rate of approximately 0.3$^\circ$/min. X-ray radiation is produced by the photoelectric effect. For the calculation of the shape and the size of the crystals, the Bragg formulation of XRD is widely used. The rays interfere constructively (fig. 2.2 b), so Bragg’s law of diffraction is [109],

$$2d \sin \theta = m\lambda$$  \hspace{1cm} (2.1)

where $m$ is an integer, $\lambda=1.54 \AA$ the wavelength of the X-ray, $d$ the lattice constant and $\theta$ the scattering angle. During this work, XRD was used for the identification of the NPs and for the estimation of the size of NPs.

### 2.2.4 Harvesting

Harvesting of single ferroelectric domain NPs from a large quantity of NPs is based on that free charges in nonconductive fluid media can be physically separated through the use of electric field gradients [77, 95]. The harvesting concept is based on the fact that dipoles experience a translational force only when exposed to a field gradient. The net translational force vector $\vec{F}$, is given by the equation 2.2, where $\vec{p}$ is the net average dipole moment of the nanoparticle and $\vec{E}$ is the electric field. For a given electric field and particle size, the translational force is maximised when average dipole moment is
Incident X-rays
Sample
2θ
X-ray Detector
Transmitted 
Beam 
2θ
θ
θ
mλ=2dsinθ
Incident 
plane wave
\[\vec{F} = (\vec{p} \cdot \vec{\nabla})\vec{E}\] (2.2)

The harvesting was performed in the experimental setup proposed in paper by Cook et al. [95] as shown in figure 2.3. The suspension of ferroelectric particles (solvent, e.g. heptane, with NPs) and surfactant (oleic acid) were put in a glass vial. There was a thin, inner wire electrode at the centre of the vial and an external, radial foil electrode, wrapped around the bottle. The inner wire electrode was put inside a thin-walled, sealed glass capillary tube. A high DC-potential, $V$ (10 to 20 kV), was applied to the inner wire electrode, while the outer foil electrode was grounded. The distance between the electrodes was 1 cm and the thickness of the vial walls was 1 mm. In such geometry, a strong gradient of the field was produced in the direction of the inner electrode. The lack of contact between the electrodes and the dispersion meant that electrophoretic effects could be excluded. Such harvesting process is being used to separate the ferroelectric NPs with the non ferroelectric NPs as the ferroelectric NPs, due to their dipole moments, either collect on the inner electrode or on the walls of the device. Non ferroelectric NPs remain in the solution. Figure 2.4 shows the set up that was used for the harvesting of the ferroelectric BaTiO$_3$ NPs.
Figure 2.3: Harvesting setup before applying the voltage. The NPs are in uniform solution.

Figure 2.4: The harvesting setup that was used for the harvesting of the ferroelectric BaTiO$_3$ NPs. The safety box that contains the device and the voltage generator is presented. In this figure, also, the outer electrode of the harvesting system inside the safety box can be seen.

2.3 Results on fabrication and characterisation of NPs with different methods

For this work, laser ablation and the sol gel processes were used for the fabrication of BaTiO$_3$ NPs. In fact, two different sol gel methods were initially used. The first method is based on n-butoxide [87], which is less expensive, and the second is based on tetrabutil titanate [88]. The materials were characterised with Raman spectroscopy, XRD and
TEM. However, the sol gel process based on n-butoxide, did not demonstrate promising results so the method based on tetrabutil titanate was mainly used in this thesis for the synthesis of the NPs. These NPs were then used for the preparation of LC/NPs suspensions. Finally, the ferroelectric NPs, Sn$_2$P$_2$S$_6$, synthesised with milling process were characterised with the harvesting technique and the results are being discussed here.

2.3.1 Ablated BaTiO$_3$ nanoparticles

The first method of the synthesis of BaTiO$_3$ NPs, relied on laser ablation of a BaTiO$_3$ pellet that was placed at the bottom of a glass vessel filled with toluene. The average size of the ablated BaTiO$_3$ nanoparticles was estimated to be around 30±5 nm, with sizes ranging from 1 nm to 80 nm (measured by TEM). The ablated BaTiO$_3$ nanoparticles were prepared by Dr. Stratakis in FORTH Crete [112]. We used the harvesting process and Raman spectroscopy for the identification of the NPs ferroelectricity. Their Raman spectrum, showed a band at 305 cm$^{-1}$, however, the peaks were attributed to the tetragonal phase (ferroelectric peak) of BaTiO$_3$, the spectra was not the same as the commercial BaTiO$_3$ powder as can been seen in the figure 2.5 [96]. During the harvesting process, no NPs were attached to the electrodes, all the NPs stayed in the solution. This result indicates that our NPs did not have any dipole moments, as has been observed by Cook in [101]. The results were negative, so we conclude that the NPs do not possess a permanent polarisation. The non-ferroelectric NPs were used for the comparison of ferroelectric NPs with non ferroelectric NPs in work of Podoliak et al. [73]. These NPs, as not ferroelectric, were used for the preparation of LC/NPs suspensions and the changes in birefringence and the dielectric anisotropy were compared with ferroelectric BaTiO$_3$ NPs fabricated by milling process.

For the next step, I doped LC TL205 with ablated BaTiO$_3$ NPs. The electro-optical properties of this new hybrid LC suspension (1% w/w NPs in LC) was measured as it was described in the section 1.5.3. The cells were created with glass substrates, ITO (indium tin oxide) electrodes and polyamide, as alignment layer. Measurements of the capacitance and the birefringence of TL205/NPs suspension and pure TL205 were performed. The dielectric anisotropy for pure LC was $\Delta \varepsilon = \varepsilon_\| - \varepsilon_\perp = 2.45$ and for TL205 doped with the ablated NPs was $\Delta \varepsilon = 2.70$. In previous works by Herrington et al. a relatively high increase of the dielectric anisotropy of TL205 was observed ($\Delta \varepsilon = 6.01$) [8].

The electrically induced birefringence of the liquid crystals cell was measured using applied AC electric field (freq. of 1 kHz) to reorientate the LC. The cross-polarised intensity of pure TL205 and doped TL205 was measured and the birefringence of these samples was determined as $\Delta n = 0.25 \pm 0.01$ and $\Delta n = 0.23 \pm 0.01$ respectively (fig,
2.6) [1]. Previous results [8] with BaTiO$_3$ fabricated with the milling method, however have shown small increased birefringence ($\Delta n = 0.26$). The fact that birefringence did not significantly change can imply that the presence of NPs creates a disorder in the LC matrix [9].

2.3.2 Synthesis of BaTiO$_3$ NPs with the sol gel method based on n-butoxide titanate

For the synthesis of the first BaTiO$_3$ powder [87], titanium (IV) n-butoxide titanate (Ti(OC$_4$H$_9$)$_4$) (99.0%), and barium acetate Ba(CH$_3$COO)$_2$ (99%) both from Strem Chemicals were used as main compounds. The Ti(OC$_4$H$_9$)$_4$ was mixed with acetic acid
CH₃COOH (99.8 % - Acros Organics) (mixer 1) and the Ba(CH₃COO)₂ with CH₃COOH (mixer 2). Mixer 1 and the mixer 2 were mixed together until we obtained a clear solution. The solution was stirred vigorously for 1 hour in molar ratio 1:1. Stearic acid (CH₃(CH₂)₁₆CO₂H) and 2-Methoxyethanol (C₃H₈O₂) were added. After a while, gel was formed at room temperature. Then, the powder was obtained by a calcination performed at 700 °C for two hours. The final powder was characterised with Raman spectroscopy and XRD and we identified that they were BaTiO₃ NPs. However there was some evidence of carbon contamination which leads to the presence of barium carbonate (BaCO₃).

2.3.3 Synthesis of BaTiO₃ NPs with the sol gel method based on tetrabutil titanate

For the synthesis of the BaTiO₃ powder [88], we used as main compounds titanium(IV) t-butoxide Ti(OC₄H₉)₄ (99.95%), and barium acetate Ba(CH₃COO)₂ (99%) both from Strem Chemicals. The formula applied to produce BaTiO₃ powder, used 1.73 grams of Ti(OC₄H₉)₄ and 1.295 grams of Ba(CH₃COO)₂. The synthesis is based on two mixtures: the first mixture contained Ti(OC₄H₉)₄, 1.75 ml of absolute ethanol (CH₃CH₂OH) and 0.83 ml acetic acid CH₃COOH (99.8 % - Acros Organics), and it was prepared by stirring. For the preparation of the second mixture, Ba(CH₃COO)₂ was dissolved with 1.62 ml CH₃COOH and 2.88 ml H₂O. 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, can remove aggregation and obtain smaller size particles [2, 94].

Transmission electron microscopy (TEM) was used to estimate the BaTiO₃ NPs size which was between 20 and 60 nm as can be seen in figure 2.7. Aggregation can be also observed, because for the TEM characterisation the oleic acid had to be removed by washing with ethanol during the centrifugation. The oleic acid is an organic surfactant, and it would prevent the observation of the NPs with TEM.

Afterwards, the NPs were characterised by Raman spectroscopy at 514.5 nm in a back scattering geometry system [96] using Dilor XY triple monochromator spectrometers. The Raman spectrum and X-Ray diffraction (XRD) confirmed that the material was tetragonal BaTiO₃ and was 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 [96, 113] shown in figure 2.8. The bands that are indicative to BaTiO$_3$ are at 180 cm$^{-1}$, 250 cm$^{-1}$, 515 cm$^{-1}$ and 728 cm$^{-1}$ [114, 115].

In order to estimate their size, XRD technique in addition to TEM, was used. The measurement of the Bragg peak broadening observed in XRD pattern gave the average size of particles as 54 ± 4 nm. The Scherrer method using the full width of half maximum (FWHM) gives the ratio of the root-mean-fourth-power to the root-mean-square value of the thickness. The size of the particles was estimated using the Scherrer’s formula, from the half-minimum width (111) peaks of the XRD (fig. 2.9) [109, 110],

$$\beta_{exp}^2 = \beta_{sample}^2 + \beta_{ins}^2$$  \hspace{1cm} (2.3)
where, $\beta_{exp}$ is the measured peak width, $\beta_{sample}$ is the full-width-half-max of the peak after correcting for peak (111) broadening which is caused by the diffractometer for BaTiO$_3$, and $\beta_{ins}$ is the peak broadening due to the machine. The peak (111) is peaks combined for the cubic and tetragonal phases [110]. The Gaussian profile is,

$$\beta_{sample} = \sqrt{\beta_{exp}^2 - \beta_{inst}^2} \quad (2.4)$$

Thus Bertaut’s equation [109] is being used to calculate the size of the NPs,

$$t_{NPs} = \frac{c \lambda}{\beta_{sample} \sin \theta} \quad (2.5)$$

where $t_{NPs}$ is the size of the NPs and $c$ is a crystal shape factor from 0.9 -1.

![Figure 2.9: XRD of BaTiO$_3$ NPS. The (111) diffraction peak was used for the determination of the size.](image)

The particle size was measured at different temperatures because the size of the NPs is temperature (T) dependent and for 700 $^\circ$ the size is 54.3 nm as shown in table 2.1, which agrees with the results of the TEM (20-60 nm).

<table>
<thead>
<tr>
<th>T ($^\circ$)</th>
<th>$\alpha$ (degree)</th>
<th>FWHM</th>
<th>$\beta_{exp}$</th>
<th>$\beta_{inst}$</th>
<th>$\beta_{sample}$</th>
<th>$t_{NPs}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>700</td>
<td>38.88</td>
<td>0.3500</td>
<td>0.501</td>
<td>0.11</td>
<td>0.0085</td>
<td>54.30</td>
</tr>
<tr>
<td>800</td>
<td>38.86</td>
<td>0.2892</td>
<td>0.468</td>
<td>0.11</td>
<td>0.0079</td>
<td>58.38</td>
</tr>
<tr>
<td>900</td>
<td>38.91</td>
<td>0.2354</td>
<td>0.390</td>
<td>0.11</td>
<td>0.0065</td>
<td>70.66</td>
</tr>
<tr>
<td>1000</td>
<td>38.93</td>
<td>0.2099</td>
<td>0.314</td>
<td>0.11</td>
<td>0.0051</td>
<td>90.17</td>
</tr>
<tr>
<td>1100</td>
<td>38.87</td>
<td>0.1382</td>
<td>0.203</td>
<td>0.11</td>
<td>0.0030</td>
<td>155.36</td>
</tr>
</tbody>
</table>

Table 2.1: The results of the calculation of the NPs’s size using the Bertaut equation, at different temperatures (T).
Harvesting technique was then used to confirm ferroelectric properties. The NPs with weight concentration, $c_{\text{part}} \approx 10^{-2}$, were in solution with heptane. Before the experiments, the NPs were sonicated for 5 mins, however, after the sonication most of the particles gravitated to the bottom of the bottle. For this reason, a small quantity of oleic acid, $c_{\text{oa}} \leq 10^{-3}$, was added to make a more stable solution. After the sonication, the solution was more uniform. For this experiment the harvesting setup was used, as described in figure 2.3. The electrode was grounded and + or − potentials were applied to the other electrodes. Voltage of $13 \text{kV}$ was applied for 30 s in the harvesting setup, for concentration of oleic acid $c_{\text{oa}} \leq 10^{-3}$ in the solution of the NPs/heptane. Afterwards, clearing of the suspension and the deposition of the NPs on both walls to which the electrodes were attached, was observed. A larger amount of the NPs was deposited on the live electrode as compared with the outer foil electrode, with different polarity. NPs were being attracted to the live electrode, due to the fact they were a mix of ferroelectric and non ferroelectric NPs. After the change of the direction of the electric field, the same effect was observed. This result confirms that both positive and negative particles were present in the suspension. An increase of the oleic acid concentration, $c_{\text{oa}} \leq 3 \times 10^{-3}$, changed the ratio of the NPs concentrations on the electrodes such that almost all the particles were deposited on the grounded electrode, when the live electrode was positive, and almost all the particles were deposited on the live electrode, when it was negative. Such outcome shows that the majority of particles had positive charges. Thus we can consider that ferroelectric NPs BaTiO$_3$, made by sol gel technique, are charged. At small concentration of the oleic acid, both positive and negative particles were in the suspension, however when we increased the oleic acid concentration, we observed an increased concentration of the positively charged NPs which might be due to protonation of the BaTiO$_3$ surface by oleic acid molecules.

The harvesting of BaTiO$_3$ ($c_{\text{part}} \approx 1\% \ c_{\text{oa}} \leq 10^{-3}$) for 30 s created the separation of the NPs in the dispersion and increased the transparency of the solution. Some NPs were collected on the vial walls, moving opposite to the field gradient. Some NPs were collected on the walls at any polarity of the field, which means that both positively and negatively charged particles are in the suspension [2]. The increase of the oleic acid concentration ($c_{\text{oa}} \approx 10^{-3}$) changed the ratio of the particles concentrations on the electrodes. In the case of the negative inner wire electrode, most of the particles were collected on the wire and the change of the polarity resulted most of the NPs are collected on the walls. Thus, the NPs behave as positively charged and dipole moment of the particles is less important at this concentration of the oleic acid.
2.3.4 Characterisation of Sn$_2$P$_2$S$_6$ with harvesting technique

The ferroelectric particles, tin thiohypodiphosphate (Sn$_2$P$_2$S$_6$), produced by the milling technique, where also tested with the harvesting technique. Sn$_2$P$_2$S$_6$ crystals were ground together with oleic acid in a weight ratio 4:1 in a Fritsch 00-502 vibration micro-mill. The particles were milled for 8-10 hours per day for 130 h [102]. The concentration of Sn$_2$P$_2$S$_6$ particles in heptane was around 0.3% by weight. The particle's size was in the range 20-50 nm and aggregation in order of several hundred nanometers has been observed due to the absence of oleic acid during the TEM measurement. These NPs have been used for LC/NPs suspensions and have demonstrated improvement of the physical properties compared with the pure LCs [79]. The Sn$_2$P$_2$S$_6$ particles exposed to homogeneous field, showed that they are charged because the application of the voltage $V \geq 4$ kV to the cuvette with outer electrodes caused clearing of the suspensions almost instantly and the majority of the NPs were attached to the live electrode. Afterwards, the NPs that attached on the live electrode, were sonicated and returned to the solvent. Electric field applied and the Sn$_2$P$_2$S$_6$ particles were separated again. For the next step of this experiment, the electrode was attached to the inner sides of the opposite walls. The electrode plates were pulled out from the cell after the voltage was switched off. Most of the particles attached to the positive electrodes and the thickness of the layer of the NPs was several micrometers, as can be seen in the electrodes in figure 2.10.

![Figure 2.10: Pictures of the inner electrodes after the separation of Sn$_2$P$_2$S$_6$ NPs. Left electrode is grounded, right electrode is positive. Yellow colour indicates deposition of a layer of Sn$_2$P$_2$S$_6$ NPs [2].](image)

The experiments show that the charge of the particles is also evident in a harvesting technique and allows the separation of the particles with and without a permanent polarisation [95, 101]. In the harvesting technique, the separation of the polarised and no-polarised particles occurs in the gradient of a DC-field, applied to the dispersion in
an isotropic solvent [2]. When the NPs are ferroelectric and have dipole moments are collected on the surface of the electrode because the electric field gradient is the strongest (inner electrode). However, the NPs without dipole moments remain in a solvent or sediment [101].

![Figure 2.11](image-url)  

**Figure 2.11:** a) The NPs are attaching the electrode in the inner sides. b) The NPs are attaching the electrode in the outer sides.

The harvesting of the Sn$_2$P$_2$S$_6$ particles ($c_{\text{part}} \approx 0.3\%$) revealed their charging, and their ferroelectricity. The application of the voltage $V \geq 10$ kV to the electrodes resulted in the separation of the NPs. The dispersion of NPs in heptane turned transparent within a few minutes of the voltage application as shown in figure 2.10. When the wire electrode was charged negatively, only a small fraction of the particles didn’t attach on this electrode. Thus, the Sn$_2$P$_2$S$_6$ NPs behaved as negative objects.

### 2.4 Conclusions

In this chapter we detailed the fabrication techniques and the characterisation of different BaTiO$_3$ NPs. Also, Sn$_2$P$_2$S$_6$ were characterised with harvesting technique. Regarding ablated BaTiO$_3$, the ablated process did not create efficient ferroelectric NPs as was proved by Raman spectroscopy and by the harvesting technique. The ablated BaTiO$_3$ however, were characterised with multiple methods and the birefringence and the electric anisotropy of the ablated NPs/TL205 suspension was measured. BaTiO$_3$ NPs, synthesised by the sol gel methods, based on tetrabutil titanate, were characterised with Raman spectroscopy, XRD, TEM and finally the method of harvesting. It was indicated that we fabricated small NPs with size between, 20-60 nm, ferroelectric and without any contaminations.
The results of the harvesting experiments in BaTiO$_3$ and Sn$_2$P$_2$S$_6$ show that ferroelectric particles may be charged. Depending on the material, particles can be positively charged (chemically synthesised BaTiO$_3$ particles in presence of oleic acid), negatively charged (ground Sn$_2$P$_2$S$_6$ particles in presence of oleic acid) or the suspension can have comparable amounts of the positively and negatively charged particles (BaTiO$_3$ particles, almost no oleic acid) [2]. In the case of the particles made by sol gel technique, the NPs were affected during the process of the sonication, and through the milling process, a strong mechanical impact creates the charges on the NPs, during their fabrication. Thus, as demonstrated in this chapter, the final charge distribution in the suspension strongly depends on the ferroelectric material, surfactant agents, solvent, size of the particles and details of the suspension preparation. The addition of oleic acid shifts the balance between positively and negatively charged BaTiO$_3$ particles, created by the sol gel process, and the ferroelectric NPs covered with oleic acid are negatively charged.

The previously accepted understanding and qualitative model that usually describes the suspensions of ferroelectric NPs in LCs assumed a strong, dipole-originated electric field around the particles which increases the order parameter of the LC and its effect on the physical and electro-optic properties of the LC. However, after the experiments described here, we know that the presence of charge on the particles modifies this explanation significantly [60, 99, 100]. The ordering of the LC molecules neighbouring to the NPs, should strongly depend on the density of the accumulated charge, thus new theories should investigate the changes of order parameter, the clearing temperature, birefringence and dielectric anisotropy in the suspension of ferroelectric NPs in LCs/NPs suspensions. Also, the presence of electric charge should be taken into account in the experimental and theoretical studies of electro-optical effects in the suspensions [2]. Furthermore, the stability of the LC suspensions should be reconsidered. It shows, also, the importance of the harvesting method for NPs preparation. The BaTiO$_3$ NPs prepared in this way were used in the next chapters in the THz regime.
Chapter 3

Parameter extraction and THz properties of liquid crystals doped with ferroelectric BaTiO$_3$ nanoparticles

3.1 Introduction

In this chapter, I will discuss my latest results on characterisation of the BaTiO$_3$ NPs (nanoparticles) in the THz regime and the preparation of hybrid LCs (liquid crystals) and NPs suspensions for THz applications. The doping of LCs with NPs can improve LC properties, such as birefringence; with higher birefringence materials, thinner LC devices can be achieved. We can also reduce the value of the control voltage and improve LC tunability, which is useful in the case of THz modulators.

In the first part of this chapter, I will describe the parameter extraction, which is an algorithm that calculates the complex refractive index of materials with THz-TDS. The algorithm is based on an experimental transfer function, which is calculated using the measurement of a sample in a THz-TDS in comparison to a reference measurement. A comparison with a theoretical transfer function which is the model of the THz electric field propagation is needed to identify the complex refractive index of the sample. Such an algorithm has been developed during my work on this project.

LCs specifically designed for THz of which the details of their chemical formulae has been reported in previous works [6, 7, 116]. The birefringence in the LC reported in [6] is $\Delta n=0.28$ and in [7] it is $\Delta n=0.3$. In the second part of the chapter, we present a complimentary method for increasing the birefringence of LCs without changing the
Chapter 3: Parameter extraction and THz properties of liquid crystals doped with ferroelectric BaTiO$_3$ nanoparticles

chemical structure of the material. Producing high birefringence LCs for THz with new chemical synthesis is time consuming and expensive. Furthermore, designing LCs for THz application is a complex procedure and more than ten chemical components are required and also due to the number of these components it is hard to predict the material properties. It has been already reported that in the optical spectrum a hybrid LC/NPs mixture, with a low concentration of ferroelectric NPs, can improve the birefringence of the material [59, 95]. Doping of the LC with NPs with size between 10-100 nm can lead to significant increase of the dielectric anisotropy and the birefringence of the suspension without disturbing the LC matrix [8, 79]. 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. I present the results on the characterisation of hybrid LC/NPs materials in the THz regime, and I start presenting my work on LC E7 and ferroelectric BaTiO$_3$ NPs. The birefringence of the hybrid LC E7 and sol gel BaTiO$_3$ suspension demonstrated an increase in the birefringence in frequencies between 0.3 to 3 THz. E7 is a well known, stable LC which has a relatively high birefringence in the THz range ($\Delta n_{E7}=0.13$) [117]. This work is based on the work that has been published in [38].

In the last part of the chapter I present NP doping of other LCs specifically designed for THz regime (2020, compound A, 2037, 1867). We created hybrid LC/NPs suspensions, with the NPs that are described in the sections 2.3.3 (harvested and no harvested) and 2.3.2. In addition LC 6CHBT and 6CHBT doped with BaTiO$_3$ are characterised. The aim of this work is to understand better the LC/NPs interaction and to understand how the chemical structure of the LCs can benefit the increase of birefringence due to the presence of NPs as suggested by Podoliak et al. [73].

3.2 THz-TDS Extraction of the refractive index and the absorption coefficient in the THz regime

The extraction of the complex refractive index can be obtained by modelling the propagation of the THz electric field. During THz-TDS scans, information about the phase and the amplitude of the electric field can be acquired. In the simplest case a sample scan is a THz-TDS scan that we measure a sample and a reference scan is a time domain scan of the system without anything in the THz beam path. The differences between a reference and a sample scan are the information that we use to extract the optical properties of a material in the THz regime. The THz-TDS sample scan depends on the dielectric properties of the material that is being measured, due to the changes of the THz electric field when a material is present. In this thesis, I calculate the complex refractive index of the materials, (eq. 3.1) which is frequency dependent, where $n(\omega)$ is the
refractive index, $\kappa(\omega)$ is the extinction coefficient and $\omega$ is the angular frequency. The real part of the refractive index depends on the speed that the THz pulse is travelling through the sample and the imaginary part depends on the change in the amplitude of the THz pulse. The parameter extraction starts by calculating an experimental transfer function by dividing the frequency spectra of the sample scan by the frequency spectra of the reference scan. The next step involves the modelling of the THz propagation through the sample using propagation and the Fresnel coefficients, which is the theoretical transfer function, $H_{\text{theo}}(\omega, \tilde{n})$ [118]. Finally, the fitting of the experimental and the theoretical function, usually with Newton Raphson method, helps us to determine the complex refractive index (equation 3.1).

$$\tilde{n}(\omega) = n(\omega) + i\kappa(\omega)$$ (3.1)

In general a transfer function is a relation that depends on the output and input of a system which is linear and time invariant, and used for determining the output when an arbitrary input is provided.

$$Y(\omega) = H(\omega)X(\omega)$$ (3.2)

In the equation 3.2, the equivalence between the transfer function $H(\omega)$, the input $X(\omega)$ and the output of a system $Y(\omega)$ is shown. The time dependent equivalent of the transfer function, the impulse response $h(t)$, is given by,

$$h(t) = \int_{-\infty}^{+\infty} H(\omega) e^{-i\omega t} d\omega$$ (3.3)

The THz-TDS are of course in the time domain therefore it would be equivalent to work with the impulse response instead of the transfer function. However, to avoid convolution and de-convolution we usually work in the frequency domain where everything can be calculated with multiplication and division. For the experimental transfer function, two measurements are taken in the THz setup, a measurement of the THz electric field of a reference and of a sample [3, 119].

The construction of the transfer function cancels (by dividing out) the propagation terms to and from the sample, which allows a simpler equation, under the assumption that the conditions of the THz beam path to and from the sample remain the same between scans. For the final calculation the equation 3.4 is used [3]:

$$H_{\text{theo}}(\omega, \tilde{n}) = H_{\text{exp}}(\omega)$$ (3.4)
3.2.1 Experimental transfer function

As mentioned before for the extraction of the complex refractive index, with a THz-TDS, the measurement of the electric filed of the THz pulse which propagates through a reference and a sample is required. There are numerous THz-TDS setups, such as the TPS Spectra 3000 TeraView ltd. THz-TDS system, which was used for some of our measurements. The setup in (fig. 3.1) is based on two photoconductive antennas, an emitter and a detector. During a measurement, the sample and the reference are placed on the path of the THz beam between the parabolic mirrors. In the simplest scan the reference is the THz signal in the absence of a sample. A delay stage is being used to map the THz signal as a function of time in a certain time range. In order to measure an average refractive index for the sample we can use just the time delay between the reference and sample scan, the average refractive index is given by the following equation when the reference is air,

\[
n_a = 1 + \frac{c \Delta t}{L}
\]  

(3.5)

where L is the sample thickness, c is the speed of the light and \( \Delta t \) is the time delay between reference and sample THz pulse. The electric fields of the THz pulses as measured by the detector are shown in figures 3.1 and 3.3.

If we take the fast Fourier transform of the sample and reference THz electric field scans, \( E_s(\omega, \tilde{n}(\omega)) \), and \( E_{ref}(\omega, \tilde{n}(\omega)) \) respectively, the transfer function can be built. The experimental transfer function is given by,

\[
H_{exp}(\omega, \tilde{n}(\omega)) = \frac{E_s(\omega, \tilde{n}(\omega))}{E_{ref}(\omega, \tilde{n}(\omega))}
\]  

(3.6)
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**Figure 3.2:** Schematic representation of the transmission, reflection and propagation in cases of air, windows and windows with a material in between.

**Figure 3.3:** The THz electric field of a reference and a sample as it was measured with THz TDS. The average refractive index of a sample can be estimated knowing the $\Delta t$ between a reference and a sample measurement.

In this work the reflections in the sample of the THz pulses have been neglected and where possible we have used thick windows in order to avoid to have reflections in the THz scans as they complicate unnecessarily the analysis of the data. In order to determine the complex refractive index, we truncated the data with a window function. The window function starts after the main THz pulse with aim to remove reflections. After the window function, the data is replaced with zeros, and the original data length is kept because consistent frequency resolution between scans is important to divide the two
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In order to achieve the correct complex refractive index phase unwrapping of the experimental transfer function is required.

### 3.2.2 Phase unwrapping of the experimental transfer function

The extraction of the complex refractive index of a material strongly depends on the measured THz electric field, its amplitude and its phase. The phase of the spectra of the experimental transfer function is wrapped between $\pm \pi$. For this reason, phase unwrapping is required for the determination of the correct complex refractive index of the samples. In the figure 3.4 the logarithm of the amplitude of the Fourier transform of the sample and reference are being presented. As can be seen, the bandwidth is 0.1 to 2 THz.

The phase of the theoretical transfer function is unwrapped because the logarithm of the theoretical transfer function is calculated. The phase of the experimental transfer function should be unwrapped as well for correct fitting. The correction of the phase can be done either by detecting jumps in the phase that denote wrapping or by using the difference phase of adjacent points in the transfer function, assuming that the differences are small. During my thesis, at the beginning the phase unwrapping was based on detecting the discontinuities in the phase that can been seen in figure 3.6. To calculate the phase we use the imaginary part of the logarithm of the transfer function.

![Figure 3.4: THz spectra of 3 mm quartz window (sample) and air (reference) between 0.2 to 2 THz.](image)

In figure 3.5 the phase of the experimental transfer function is shown, $H_{\text{exp}} = \text{imag}(\log(\mathcal{L}\{E_{\text{sample}}(t)\})$ in comparison with the phases of the reference $\text{imag}(\log(\mathcal{L}\{E_{\text{reference}}(t)\})$ and the sample $\text{imag}(\log(\mathcal{L}\{E_{\text{sample}}(t)\})$. In general, in order to obtain the phase the
four quadrant inverse tan \((\arctan 2)\) of the real and imaginary components is calculated. The complex number which defines the phase is given in Cartesian form as,

\[
x + iy = Ae^{i\phi}
\]  

(3.7)

where \(\phi\) is the phase and the four quadrant inverse tan is used to calculate the phase as,

\[
\phi = \arctan 2(y, x)
\]  

(3.8)

In this project the phase unwrapping was achieved using the following algorithm, we set the phase of the next point \(e^{i\phi(j+1)}\), using the phase of the previous point \(e^{i\phi(j)}\) and adding to it the difference of the phases of the two points. To find the phase difference we calculate firstly, the conjugate of the experimental transfer function at a specific point (usually the point that has the higher signal to noise ratio-SNR) and then this is multiplied by the transfer function at the next point. We continue loop for all the points of the transfer function. If we start the loop from the point with the higher SNR then the phase at frequency zero will not be zero but a positive number, for the refractive extraction to work we have to shift the phases so at zero frequency we have zero phase. As it can been seen in the figure 3.5 the phase of the reference is different to the phase of the sample and in order to obtain the correct refractive index the phase of the sample and reference sample scan should tend to zero in zero frequency, such as the experimental transfer function. A THz pulse when it propagates through a material can be interpreted by the combinations of frequency components. The wavelength will increase to infinity when the frequency of the components reduces to zero and the phase of the frequency components that is being detected will be also zero [3]. In the end the new transfer function is reconstructed with the original amplitude and the new phase.

The results of the phase unwrapping of the experimental transfer function can be seen in the figure 3.6. The black line describes the phase of the experimental transfer function before the phase unwrapping and the green line presents the phase after the phase unwrapping. The discontinuity around 1.6 THz is due to the absorption of water vapour in the air.

The comparison of the original phase, the unwrapped phase with non zero intercept and the unwrapped phase with extrapolated zero intercept shown in figure 3.7. The refractive index extraction also is shown in figure 3.8 in cases of the original phase, the unwrapped phase with non zero intercept and the unwrapped phase with extrapolated zero intercept. As shown in figures 3.7 & 3.8 for the correct extraction of the refractive index the phase unwrapping is necessary.
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3.2.3 Modelling of the theoretical transfer function

The theoretical transfer function is a model that describes the THz electric field which propagates through a reference and a sample in a THz-TDS setup. In this work the reference was two windows (one next to the other-slab) and the sample was the two...
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Figure 3.7: Phase unwrapping of the experimental transfer function for a 500 $\mu$m quartz sample showing the original phase, unwrapped phase with non-zero intercept and unwrapped phase with zero intercept that was extrapolated using a linear regression on the unwrapped phase [3].

Figure 3.8: Refractive index extracted with original phase and unwrapped phase [3].
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windows with the material that was characterised in between as shown in figure 3.9. These models are based on a further study of the previous works of Chung and Duvillaret et al. [3, 119].

For the modelling of the theoretical transfer function the propagation (P) coefficient and Fresnel transmission (T) and reflection (R) coefficients are calculated. The equations when an EM wave is incident on a material with refractive index, $\tilde{n}_a$, to another with refractive index, $\tilde{n}_b$, are,

\[
T_{ab}(\omega) = \frac{2\tilde{n}_a(\omega)}{\tilde{n}_a(\omega) + \tilde{n}_b(\omega)} \tag{3.9}
\]

\[
R_{ab}(\omega) = \frac{\tilde{n}_a(\omega) - \tilde{n}_b(\omega)}{\tilde{n}_a(\omega) + \tilde{n}_b(\omega)} \tag{3.10}
\]

\[
P_a = e^{-i\tilde{n}_a(\omega)\omega L/c} \tag{3.11}
\]

3.2.3.1 Extraction of the refractive index of the windows

We are working here for the case that can been seen in figure 3.10 where we are interested to calculate the refractive index of the windows using as reference the air, the THz electric
field through a sample can be described with the equation,

\[
E_s(\omega) = P_{01}(\omega, L_1)T_{01}(\omega)L_1\nu_1(\omega, L_1)P_{02}(\omega, L_2)
\]

\[\sum_{k=0}^{\infty}\{R_{10}(\omega)L_1(\omega, L_1), R_{10}(\omega)L_1(\omega, L_1)\}^k E(\omega)
\] (3.12)

where \(R_{01}\) is the reflection coefficient for the electric field from the window to the air and \(k\) is the number of reflections. Regarding the propagation terms, \(P_{01}\) is the propagation of the electric field from the THz emitter to the sample, \(P_1\) is the propagation through the sample and \(P_{02}\) the propagation from the sample to the detector. The transmission coefficients, \(T_{01}\) is the transmission through the first sample interface and \(T_{10}\) through the second. \(E(\omega)\) is the frequency dependent THz electric field. Finally, \(L_1\) is the distance between the sample and the emitter, \(L\) is the thickness of the sample and \(L_2\) is the distance between the sample and the detector. The THz electric field through the air for the reference measurement can be determined as,

\[
E_{\text{ref}}(\omega) = P_{01}(\omega, L_1)L_0(\omega, L_1)L_1(\omega, L_1)E(\omega)
\] (3.13)

where \(P_{01}\) is the propagation between the emitter and the sample, \(P_0\) is the propagation in the area that the sample will be placed and \(P_{10}\), the propagation term between the sample and the detector as is described in figure 3.10.

**Figure 3.10:** Schematic representation of the calculation of the THz electric field. Transmission, reflection and propagation coefficients are describing in cases of air and a sample (windows).

Using the above relations now for the electric field the theoretical transfer function can be described now as,
\[ H_{\text{theo}}(\omega, \tilde{n}(\omega)) = \frac{E_s(\omega, \tilde{n}(\omega))}{E_{\text{ref}}(\omega, \tilde{n}(\omega))} = \frac{T_{01}(\omega)P_1(\omega, L)T_{10}(\omega)}{P_0(\omega, L)} \]

\[ + \sum_{k=0}^{+\infty} \{R_{10}(\omega)P_1(\omega, L), R_{10}(\omega)P_1(\omega, L)\}^k \] (3.14)

For the determination of the theoretical transfer function of a window (e.g., quartz), the propagation coefficient in the air is given by,

\[ P_{\text{air}} = e^{-i\tilde{n}_{\text{air}}\omega L/c} = e^{-i\omega L/c} \] (3.15)

because the refractive index of the air is \( n_{\text{air}} = 1 \). The propagation coefficient in the window is given by,

\[ P_{\text{w}} = e^{-i\tilde{n}_{\text{w}}\omega L/c} \] (3.16)

where \( \tilde{n}_{\text{w}} \) and \( \tilde{n}_{\text{air}} \) are the complex refractive indices of the window and the air respectively. In the case of the air, the transmission and the reflection coefficient are \( T_{\text{air}} = R_{\text{air}} = 1 \) whereas, in the case of the window,

\[ T_{\text{w}} = \frac{2\tilde{n}_{\text{w}}}{\tilde{n}_{\text{w}} + \tilde{n}_{\text{air}}} \] (3.17)

\[ R_{\text{w}} = \frac{\tilde{n}_{\text{w}} - \tilde{n}_{\text{air}}}{\tilde{n}_{\text{w}} + \tilde{n}_{\text{air}}} \] (3.18)

In this work, the etalon effects were neglected for the estimation of the complex refractive index. According to this assumption the equation 3.14 is simplified and the theoretical transfer function is given by,

\[ H_{\text{theo}} = e^{-i(\tilde{n}_{\text{w}} - \tilde{n}_{\text{air}})\omega L/c} \frac{4\tilde{n}_{\text{w}}\tilde{n}_{\text{air}}}{(\tilde{n}_{\text{w}} + \tilde{n}_{\text{air}})^2} \] (3.19)

### 3.2.3.2 Extraction of the refractive index of a sample in between of two windows

In the case the sample is a different material between two windows, such as LC, the theoretical function is defined differently where the sample scan is the windows with the sample in between and the reference scan are the windows adjacent to each other
as shown in figure 3.9. In this calculation, etalon effects were neglected again, and the propagation coefficient for the reference is given by,

\[ P_w = e^{-i\tilde{n}_{\text{air}} \omega L_s/c} \]  

(3.20)

and for the sample,

\[ P_s = e^{-i\tilde{n}_s \omega L/c} \]  

(3.21)

The sample displaces propagation in air equal to its thickness as shown in the figure 3.9 thus for the propagation coefficients the refractive index of the air is being used instead of the refractive index of the windows.

The transmission coefficients for the reference is given by,

\[ T_w = \frac{2\tilde{n}_w}{\tilde{n}_w + \tilde{n}_{\text{air}}} \]  

(3.22)

but they divide out between reference and sample scan. The transmission coefficients for the sample are given by,

\[ T_s = \frac{2\tilde{n}_s}{\tilde{n}_s + \tilde{n}_w} \]  

(3.23)

where \( \tilde{n}_s \) is the refractive index of the sample between the two windows. The theoretical transfer function is given by,

\[ H_{\text{theo}} = e^{-i(\tilde{n}_s - \tilde{n}_{\text{air}}) \omega L/c} \frac{4\tilde{n}_s \tilde{n}_{\text{air}}}{(\tilde{n}_s + \tilde{n}_{\text{air}})^2} \]  

(3.24)

For the extraction of the complex refractive index was assumed that the transmission coefficient in the sample and the reference was the same. The last part of the parameter extraction is the fitting of the theoretical and experimental transfer function.

### 3.2.4 Newton Raphson

After the determination of the correct phase of the experimental transfer function and the modelling of the theoretical transfer function, the next step is to determine the complex refractive index by comparing these two functions. In order to achieve this, the Newton Raphson method is employed. This method finds the \( x \) intercept of a certain function \( f(x) \). The Newton Raphson method is described in equation 3.25. This method uses the function, \( f(x) \) and the derivative of the function \( f'(x) \), in order to determine a value of the \( x \) intercept [3].
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$$x_{i+1} = x_i - \frac{f(x_i)}{f'(x_i)}, i = 1, 2, 3... \quad (3.25)$$

The $\tilde{n}$ is the solution of,

$$\ln(H_{\text{theo}}) - \ln(H_{\text{exp}}) = 0 \quad (3.26)$$

For the determination of the complex refractive index the natural logarithm is used for the function required and given by,

$$f(\omega, \tilde{n}(\omega)) = \ln(H_{\text{theo}}) - \ln(H_{\text{exp}}) \quad (3.27)$$

where $H_{\text{exp}}$ is the experimental transfer function and $H_{\text{theo}}$ is the theoretical transfer function as it was described before. The derivative of the function is also analytically calculated [3].

The Newton Raphson method uses a starting point, $\tilde{n} = 2.0 - 0.005 \ j$, for the complex refractive index and when consecutive iterations reach a difference of $10^{-7}$ the algorithm returns the value of the complex refractive index.

The algorithm was described in this section has been compared with other commercial algorithms (TeraView) and has successfully determined similar, if not identical, results. The calculation of the complex refractive indices of BaTiO$_3$ NPs and powder and the birefringence of the LC E7 and E7 with BaTiO$_3$ NPs were calculated with this algorithm.

### 3.3 Characterisation BaTiO$_3$ NPs and powder with THz TDS

The characterisation and the extraction of the complex refractive index of the BaTiO$_3$ NPs in THz was the first step on this project. The BaTiO$_3$ NPs used in this work were prepared by the sol gel method as described in section 2.3.3. We measured the complex refractive index of NPs in solution with heptane solution using a custom THz-TDS system based on a Ti:Sapphire near-IR, 60 fs laser with GaAs photoconductive emitter and detector (fig. 3.11) [120]. The THz beam was focused and collimated with Tsurupica lenses. Tsurupica lenses, are transparent in the THz and optical regime, with similar refractive indices.
3.3.1 Different concentrations of nanoparticles

Firstly, regarding the characterisation of BaTiO$_3$ NPs in solution, we estimated the average refractive index for the heptane to be $n_{\text{heptane}} = 1.36$ 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 between the two windows 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, a TDS scan was performed of two silicon windows in contact with each other (fig. 3.12). 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 they were 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 [121], was used to extract the values of refractive indices of the 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 3.28.

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

(3.28)
where $\varepsilon_{\text{eff}}$ is the effective permittivity of the mixture with different spherical inclusions, $\varepsilon_i$ the dielectric permittivity of the background medium and $\varepsilon_{\text{nps}}$ the dielectric permittivity of the inclusions and $f$ the volume fraction. In this work only one type of NPs was used for these measurements. 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 [121]. Therefore we used the equation 3.28 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 3.29. The simple EMA gives the same results for volume fraction of 0.5% by volume as calculated with the Maxwell Garnett formula (eq.3.28). The anisotropic grains are randomly oriented, thus leading to an isotropic composite in EMA [121, 122].

\[
f n_{\text{nps}}^2 = n_{\text{eff}}^2 - (1 - f)n_i^2
\]  

(3.29)

Where $n_{\text{nps}}$ is the refractive index as was calculated with EMA and $n_{\text{eff}}$ is the refractive index was measured with THz-TDS and $n_i$ is the refractive index of heptane.

The refractive index of the NPs (fig.3.13) was estimated to vary between 1.4 to 1.8 for the frequencies and the concentrations studied. As can be seen, 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 removal of oleic acid. 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 figures 3.14 (grey area) is due to the low signal to noise ratio after 1.3 THz. Due to the low signal to noise ration in frequencies above 1.2 THz, the absorptions and the refractive indices are not precise as shown in the grey area in figures 3.14 and 3.13, only the measurements before 1.2 THz were taken into account.
3.3.2 BaTiO$_3$ powder

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 two quartz windows 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 $n_{\text{powder}}=2.2$ in frequencies 0.3 to 1.5 THz as shown in figure 3.15. Our measurements give similar results to previous work where the refractive index was estimated to be 2.4 [89]. The measured difference of the refractive index between powder and NPs in solution can be explained due to NPs higher surface reactivity and the larger surface volume ratio, which is a consequence of their smaller dimensions. The surface atoms in NPs are bound by weaker forces and this influences the optical properties between different size particles [122]. The measurements were repeated which allowed us to confirm the values and estimate the error of measurements to be $\delta n_{\text{powder}}=0.02$.

![Figure 3.15: Refractive index and absorption of the BaTiO$_3$ powder.](image)

The characterisation of the NPs in THz regime was very important for the estimation of the absorption of the NPs and to identify the existence of any resonances.

3.4 Characterisation of LCs and LC/NPs in the THz regime

LC E7 is a commercial LC that has been characterised in the THz regime [117]. For this reason, firstly LC E7 was doped with ferroelectric BaTiO$_3$, and characterised in the
THz regime. Other LCs were also characterised namely 2020,1867 and 2037, 6CHBT and compound A. The reference measurement was a TDS scan of the THz pulse with the two windows of the substrate in contact and the sample measurement was with the LC sample between the two windows. When the polarisation of the THz wave was perpendicular/parallel to the LC director, the ordinary refractive index \((n_o)\)/extraordinary refractive index \((n_e)\) were determined.

### 3.4.1 Birefringence of E7/NPs mixture

In order to prepare hybrid E7/NPs suspension, after the synthesis of the NPs, I mixed the LC with NPs (in solution with heptane and oleic acid). 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 \(^\circ\)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].

First, we measured the average refractive indices of the E7 [117], which varied for different frequencies. The refractive indices were calculated with the algorithm presented in section 3.2. The average values for the undoped liquid crystal were \(n_o = 1.60 \pm 0.02\) and \(n_e = 1.73 \pm 0.02\) and for the doped E7 they were \(n_o = 1.55 \pm 0.02\) and \(n_e = 1.69 \pm 0.02\). Figure 3.17 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 of birefringence. The measurement was performed at 18 \(^\circ\)C. The birefringence did increase for frequencies between 1 to 1.5 THz, the birefringence of the doped E7 was 0.138 and for pure E7 was 0.125, the increase was approximately 10% (Figure 3.16). Between 0.3 to 3 THz, the average birefringence for the pure E7 was \(\Delta n = 0.127 \pm 0.02\) and for the doped E7 was \(\Delta n = 0.136 \pm 0.02\), which is equivalent to an increase of 6.6% (shown in Figure 3.16).

Secondly, absorptions of the ordinary and extraordinary polarisations in E7 and the doped mixture of E7 and BaTiO\(_3\) NPs were measured and are presented on figure 3.18. 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 [123]. As it can be observed in Figure 3.18, 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 [34]. 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 [34], and the electric field caused by the permanent polarisation of the BaTiO\(_3\) NPs has to be taken into account.

In the table (3.1), the results of the increased birefringence of the hybrid suspension (\( \Delta n_{E7+NPs} \)), the refractive index of the BaTiO\(_3\) NPs (\( n_{NPs} \)) and the BaTiO\(_3\) (\( n_{powder} \)) in the frequencies 0.5 and 1 THz are summarised.
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3.4.2 Characterisation of THz LCs with ferroelectric BaTiO$_3$

We demonstrated with E7 that enhanced birefringence can be achieved without synthesis of new LC mixtures. Here we present further experiments based on the same idea but with LCs explicitly designed for high birefringence in the THz regime to see if we can increase their birefringence when they are doped with BaTiO$_3$ NPs.

In this section, the results of the THz measurements of LC, with birefringence between 0.07 to 0.3 and doped with ferroelectric BaTiO$_3$ NPs from 0.3 up to 3.0 THz are presented. We used ferroelectric BaTiO$_3$ NPs synthesised by two sol gel processes, in one of which also the harvesting was applied resulting three different types of BaTiO$_3$ NPs; for simplicity we named them as $n_{ps1}$, $n_{ps2}$ and $n_{ps3}$. The first sol gel process we used was based on tetrabutyl titanate Ti(OC$_4$H$_9$)$_4$ and barium acetate Ba(CH$_3$COO)$_2$ as was described in section 2.3.3 and they were also used in the previous work with LC E7. This sample of NPs refers as $n_{ps3}$. Furthermore, a harvesting technique was applied [2, 101]. The harvested BaTiO$_3$ NPs based on Ti(OC$_4$H$_9$)$_4$ and barium acetate Ba(CH$_3$COO)$_2$ are labelled as ($n_{ps1}$). Finally, we used a second sol gel method for the synthesis of BaTiO$_3$, which is based in n-butoxide titanate Ti(C$_8$H$_{17}$O)$_4$ and barium acetate Ba(CH$_3$COO)$_2$, as described in the section 2.3.2, refers as $n_{ps2}$. Five LCs were used for the suspensions; two single compounds: 6CHBT and compound A; and three mixtures: 1867, 2037 and
2020. LCs 2037, 2020 and 1867 have high birefringence and they have been designed for THz applications. It has been previously reported that the presence of fluorine atoms and cyclohexane rings in the LC matrix can benefit the increase of the birefringence due to the presence of NPs. In this work we study how these molecules affect the LC-NPs interaction.

For these experiments we used in total 11 different solutions with LC/NPs. For the LC 2020 and 6CHBT we used the NPs: \( nps_1 \), \( nps_2 \) and \( nps_3 \). However, with NPs \( nps_1 \) and \( nps_2 \) we did not obtain promising results, thus the LCs, compound A, 2037 and 1867 were doped only with \( nps_3 \), because \( nps_3 \) have demonstrated the most interesting results both for E7, 6CHBT and 2020. The LC/NPs mixtures and the concentrations of the NPs \( \text{(w/w)} \) that they used for this work can been shown in the tables 3.2 and 3.3. As it can been seen for the compound A and LC 2020 we used two different concentrations of \( nps_3 \) in aim to see how the LC properties change in different concentrations of NPs.

<table>
<thead>
<tr>
<th>LC</th>
<th>( nps_1 ) (w/w)</th>
<th>( nps_2 ) (w/w)</th>
<th>( nps_3 ) (w/w)</th>
<th>( \Delta n )</th>
</tr>
</thead>
<tbody>
<tr>
<td>2020</td>
<td>0.2%</td>
<td>0.2%</td>
<td>0.2% &amp; 0.5%</td>
<td>0.32</td>
</tr>
<tr>
<td>6CHBT</td>
<td>0.2%</td>
<td>0.2%</td>
<td>0.2%</td>
<td>0.17</td>
</tr>
</tbody>
</table>

Table 3.2: Concentrations of NPs that were used for the hybrid LC and NPs mixtures and the average birefringence \( \left( \Delta n \right) \) from 02-3.0 THz before the doping for the LCs 2020 and 6CHBT.

<table>
<thead>
<tr>
<th>LC</th>
<th>( nps_3 ) (w/w)</th>
<th>( \Delta n )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compound A</td>
<td>0.2% &amp; 1%</td>
<td>0.9</td>
</tr>
<tr>
<td>2037</td>
<td>0.2%</td>
<td>0.25</td>
</tr>
<tr>
<td>1867</td>
<td>0.2%</td>
<td>0.27</td>
</tr>
</tbody>
</table>

Table 3.3: Concentrations of NPs that were used for the hybrid LC and NPs mixtures and the birefringence \( \left( \Delta n \right) \) from 02-3.0 THz before the doping for the LCs compound A, 2037 and 1867.

A TeraView Time-Pulsed Spectrometer 3000 (TPS) [124] was used for these measurements. The parameter extraction of this section was calculated by the TeraView algorithm and the preparation of the cell was the same as in the case of E7 in section 3.4.1.

For simplicity, in the following figures the term \( \Delta n \) defines the birefringence. The terms \( o \) and \( e \) refer to ordinary and extraordinary directions.

### 3.4.2.1 6CHBT and hybrid 6CHBT/NPs suspensions

In figure 3.19 the birefringence of 6CHBT and hybrid 6CHBT/NPs can be observed. As it can be seen the birefringence of pure 6CHBT is higher than the birefringence of the hybrid LC/NPs suspensions. This effect can indicate that ferroelectric NPs, instead of increasing the order parameter, create disorder in the LC matrix. This can
be clearly seen in figure 3.19b, the ordinary refractive indices are higher while the extraordinary refractive indices are lower than pure 6CHBT. The highest birefringence in the hybrid LC/NPs suspensions, was observed in $6\text{CHBT}/\text{nps3}$ mixture and the lowest in $6\text{CHBT}/\text{nps2}$. This indicates the sol gel process that the nps3 were prepared is more suitable for fabrication of ferroelectric NPs. The ordinary absorption coefficients are higher for the hybrid 6CBHT/NPs suspensions compared with pure 6CHBT. The extraordinary absorption coefficient for pure 6CHBT is higher than for $6\text{CHBT}/\text{nps2}$ and $6\text{CHBT}/\text{nps3}$ suspensions, but equal or lower than $6\text{CHBT}/\text{nps1}$ suspension. It is obvious that the harvested NPs ($\text{nps1}$) are showing a different behaviour in comparison with the suspensions $\text{nps3}$ and $\text{nps2}$. For the $6\text{CHBT}/\text{nps1}$ suspension, the absorption is higher than that for $6\text{CHBT}/\text{nps3}$ in both ordinary and extraordinary directions.
This can be explained due to the additional charges that the harvesting process creates to NPs as it was discussed in section 2.3.3. These charges can effect the dipole moments between the LC and NPs and the interaction with the THz radiation.

**Figure 3.21:** a) The birefringence of 2020 and the hybrid 2020/NPs suspensions. b) The difference of the birefringence between the different mixtures.

### 3.4.2.2 2020 and hybrid 2020/NPs suspensions

The results of the THz characterisation of the complex mixture 2020 are presented in figures 3.21 and 3.23. The extraordinary refractive indices for the 2020/nps1 and 2020/nps2 suspensions are lower compared with the pure 2020, however the extraordinary refractive index of nps3/2020 was higher than pure 2020. The birefringence of 2020/nps3

**Figure 3.22:** Ordinary and extraordinary refractive indices of 2020 and 2020 doped with ferroelectric NPs
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was better than the other suspensions and the pure 2020. We prepare two suspensions with different concentrations of 0.2% w/w and 0.5% w/w, respectively because with the suspension 2020/nps3 interesting results were observed. The birefringence of suspension of 0.5% of 2020/nps3 is lower in the range of frequency 0.3-1.5 THz and higher between 1.5-3.0 THz compared with the suspension of 0.2% of 2020/nps3. However, the birefringences of the other suspensions, 2020/nps1 and 2020/nps2 are lower than pure 2020 as it can be seen in the figure 3.21 (b). nps3 seem to change the order parameter and to improve the properties of the LC. As shown in figure 3.23, the ordinary absorption coefficient of the suspension 2020/nps3 is lower or similar to the absorption of pure 2020, while the other suspensions (2020/nps1 and 2020/nps2) have higher absorption than pure 2020 above 0.7 THz. The extraordinary component of absorption for pure 2020 is lower than all the other suspensions between 0.7 and 2.5 THz. The extraordinary absorption coefficients of all the LC/NPs suspensions have a maximum around 1.5-1.7 THz, while the pure 2020 have only a less pronounced maximum around 1.6 THz. This might indicate that the presence of the NPs affects the chemical structure of the LC matrix and thus there is a change in the absorption component. Also, the absorption coefficient increased only in the cases that we did not observe increase of the birefringence, which indicates that nps1 and nps2 most likely created a disorder in LC matrix.

LC/NPs suspensions, in the optical regime, are related to the ferroelectric NPs affecting the order parameter of the host LC [79]. For this reason, we prepared ferroelectric suspensions of LC materials with simpler structure and with compounds similar to LC 2020 in order to explain the effects due to the presence of NPs. It was suggested in the work by Podoliak et. al in [73], LCs with fluorine atoms and cyclohexane rings

![Figure 3.23: Ordinary and extraordinary absorption coefficients of 2020 and 2020 doped with ferroelectric NPs](image)
are more likely to increase their birefringence with the doping with ferroelectric NPs in optical regime. Compound A was the first LC that was investigated because it is a single compound and consists only of one type of molecule.

![Figure 3.24: a) The birefringence of compound A and the hybrid compound A/NPs suspensions. b) The difference of the birefringence between the different mixtures.](image)

**Figure 3.24:** a) The birefringence of compound A and the hybrid compound A/NPs suspensions. b) The difference of the birefringence between the different mixtures.

![Figure 3.25: Ordinary and extraordinary refractive indices and absorption coefficients of compound A and compound A doped with ferroelectric NPs with different concentrations](image)

**Figure 3.25:** Ordinary and extraordinary refractive indices and absorption coefficients of compound A and compound A doped with ferroelectric NPs with different concentrations

### 3.4.2.3 Compound A

Two suspensions were prepared with the compound A and nps3 with concentrations 0.2% and 1%, in order to see the effects of different concentration of NPs in the LC. The THz
properties of the compound A and the compoundA/nps3 suspensions are presented in figures 3.24 and 3.25. As it can be seen, the birefringence of the LC/NPs suspensions and pure compound A were similar. However in the frequencies between 2 THz and 2.6 THz, the birefringence of compoundA/nps3 with 0.2% of NPs is slightly higher than the birefringence of pure compound A. The extraordinary absorption coefficient of the LC/NPs suspensions have a maximum around 1.5 THz and 2.6 THz. For the compoundA/nps3 suspension with 1% of nps3, the absorption is higher due to the aggregation of the NPs and the interactions between the NPs and the LC molecules. The ordinary absorption coefficient of compoundA/nps3 suspension with 1% of nps3, is similar with the compound A, while for the suspension with 0.2% of NP the ordinary absorption is higher compared to the pure compound A in the range of frequency 0.7-3.0 THz. The results are different for the extraordinary absorption coefficient, for the compoundA/nps3 with 0.2% of NPs is similar to the pure compound A, while for the compoundA/nps3 with 1% of NPs the extraordinary absorption coefficient is higher than the compound A. The increase of the absorption coefficient it can be due to the aggregation of the NPs, especially with concentration of NPs 1% w/w.

3.4.2.4 LCs 2037 and 1867 and hybrid suspensions

In figures 3.26 and 3.27, THz properties of mixtures 2037 and 2037/nps3 can be seen and the results of 1867 shown in figures 3.28, 3.30 & 1867/nps3. These LCs have high values of the birefringence $\Delta n_{2037} = 0.27$ and $\Delta n_{1867} = 0.30$ in 1.5 THz respectively. However, as it can be seen in figure 3.26 we observed a small decrease of the birefringence for the 2037/nps3 suspension, in comparison with 2037. In 1867 we observed a lower
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Figure 3.27: Ordinary and extraordinary refractive indices and absorption coefficients of 2037 and 2037 doped with ferroelectric NPs

Figure 3.28: Birefringence of 1867 and 1867 doped with ferroelectric NPs

Birefringence for the 1867/nps3 between 0.3 to 0.8 THz and higher birefringence 0.8 THz to 2.8 THz compare with the pure 1867. The extraordinary absorption coefficient of 2037/nps3 suspension is similar to pure 2037 however the ordinary absorption coefficient is higher for the 2037/nps3 suspension. The 1867/nps3 suspension has higher ordinary and extraordinary absorption coefficient than the pure 1867.

The LCs 1867 and compound A have the same molecules and for the LC/NPs suspensions we observe the increase of absorption coefficient for the extraordinary direction and a stronger local absorption maximum compared with the pure LC materials. The reason for this change in extraordinary absorption coefficient could be due to strong dipole-dipole interactions between the ferroelectric NPs and the LC molecules. The molecules
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that 1867 and compound A share might be responsible for such effects. The extraordinary absorption coefficients for pure LCs are similar or lower than their ferroelectric suspensions except 6CHBT where the extraordinary absorption coefficient for the pure LC is higher than for hybrid LC/NPs suspensions. The difference between 6CHBT and the rest LCs is that 6CHBT does not contain any fluorine atoms substituted in lateral position, 2020, 2037, 1867 and compound A contain fluorine atoms. This might be the cause of this difference in the behaviour of the extraordinary absorption coefficient.

3.5 Conclusion

In conclusion, I developed during my thesis a robust algorithm for the extraction of THz refractive indices. This algorithm, can successfully extract the refractive indices of materials in case of a single layer or a sample in between two windows. The algorithm was
used to determine the parameters of BaTiO$_3$ NPs powder, LC E7 and the hybrid E7/NPs suspension in THz regime. 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 regime. The MG equation and the EMA, were also used to identify the $n_{NPs}$ and the $\alpha_{NPs}$, for low concentrations. We also demonstrated hybrid LC suspensions with solgel 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 increase of the birefringence can be achieved without synthesis of new LCs. In addition, the LC mixtures 2020, compound A, 1867, 6CHBT and 2037 were characterised with THz-TDS. We observed an increase of the birefringence in materials 2020, compound A and 1867. These materials have molecules with longer cores compared with 2037 and 6CHBT. We prepared hybrid LC/NPs suspensions with harvested nanoparticles ($nps_1$). These results were different compared with the results for the LC/NPs suspensions with the $nps_3$, that confirms that the harvesting method does not collect only the ferroelectric domains but can collect charged domains which were made during the synthesis of the suspension [2]. Moreover, we compared two sol-gel synthesis methods: the synthesis described in section 2.3.3 is a more suitable process for synthesis BaTiO$_3$ ferroelectric NPs compared to the fabrication method described in section 2.3.2 for the $nps_2$ labeled nanoparticles. Future modelling is required for further explanation of the interaction between LC molecules and ferroelectric NPs in the THz regime. In this chapter we demonstrated the increase of the birefringence of LC with doping of ferroelectric BaTiO$_3$ NPs, with the birefringence $\Delta n_{E7/NPs}$ to be 10\% higher compared to the pure E7 and for 2020 $\Delta n_{2020/NPs}$ to be 14\% higher. In the next chapter new materials will be introduced namely photo-aligning azobenzene based complex dyes. These materials can align LCs for applications in optical regime and can be used as photoaligning materials for THz devices.
Chapter 4

Azobenzene based photo-aligning complex dyes

4.1 Introduction

In this chapter, I discuss the optical properties of thin films based on photoaligning materials. These materials have been demonstrated successfully when used for the alignment of functional materials [125, 126], and they may eventually be used as aligning materials for LC/THz modulators and phase shifters. Azo-material THz properties have not been fully investigated, so the starting point was to characterise the photoaligning layers in more detail, including establishing their minimum thickness while still photosensitive in optical regime. The photo-aligning complex dyes PAAD materials, 22D, 22N and 22E, were deposited on different substrates and the minimum thicknesses were determined. The absorption and the light induced changes in these materials were also observed. Moreover, the information on the thickness and the absorbance, was used for modelling and the calculation of the refractive index and the absorption coefficient with ellipsometry. In the last part of this chapter the diffraction efficiency of 22D, 22N and 22E was determined. Finally, AFM was performed for the investigation of the presence of surface relief.

4.2 Introduction to Photo-aligning materials

Thin films of azo compounds align in the direction perpendicular to the optical electric field and they can also align other functional materials [125, 127–129]. Various photodrawing materials have been demonstrated with a thickness that varies between 100
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nm to 500 \( \mu m \) [130–132]. Photo-aligning materials presented here are azobenzene based complex dyes (PAAD) [126, 133]. The PAAD materials came from Beam Co. These materials are proprietary mixtures with patents being submitted by Beam Co. and therefore their detailed structure is not known. It is known that the dyes were obtained by azo coupling of the diazonium salt of 4,4’-diaminobiphenyl – 2,2’-disulfonic acid with the derivatives of phenol and aniline having different numbers and positions of such pendants as -chloro, -hydroxy, -alkyl, -carboxyl groups or in the phenol ring or at the nitrogen atom in aniline. PAADs are new photoaligning materials that have been successfully demonstrated results in the aligning of LCs [125]. The alignment axis of PAAD complex dyes is perpendicular to the polarisation and this orientation process is reversible. In fact, these materials provide high resolution patterns which are being used for polarisation gratings and spiral phase wave-plates [125, 126].

The past 30 years azobenzene based materials have been used as photoalignment materials [134, 135]. Priimagi et al have suggested photoalignment materials for aligning LC materials [136] with different methods such as photoinduction of anisotropy in thin alignment layers, so-called command surfaces, or incorporating photoresponsive units into the bulk of the LC material [133, 137]. They show photochemical isomerisation between trans- and cis- forms [135]. Cis- and trans- azobenzene have three excited singlet states that are related with their absorption bands in near UV and visible regime [138]. Azobenzene materials determine trans form to less stable cis form under the radiation with UV or visible light to achieve a photostationary composition that is wavelength and temperature dependent and the thermal isomerism from the photogenerated cis to the trans form is shown in figure 4.1. Azobenzene isomerisation is based on the rotoresistant property of the \( N = N \) bond and proceeds with large structural change as reflected in the dipole moment and change in geometry. This effect involves a decrease of the distance between the para carbon atoms (1 nm) in azobenzene form to cis form (0.6 nm) [139]. Photo-aligning complex dyes require low exposure energy, they have absorption extended after 400 nm, and the deposition methods in substrates is very simple.

4.2.1 Preparation of thin PAAD films

For the solution of the complex dyes, methanol was used as a solvent together with a concentration of 1% g/ml dye powder, as recommended. The dye powder was sonicated in methanol for 5 mins, until a very clear form was obtained. A variety of solvents were also tested, such as toluene and heptane, however, these solvents were not able to dissolve the polymer powder well. Water and dimethylformamide were also tested, demonstrating promising results in dissolving the dyes. Afterwards, the thin films were deposited on the substrate by spin coating.
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Figure 4.1: Schematic representation of the photochemical isomerisation between trans- and cis- forms in azobenzene based materials.

The substrate used for our characterisation was 30 nm ITO (indium titanium oxide) on glass (1 mm). ITO/glass substrate was preferred because the difference in the refractive index (n) between the ITO (average n=2.2) and the dye is higher, compared to glass (average n=1.5) which improves the accuracy of the ellipsometry results due to the higher phase shift. For this project were used in total eleven samples. 22D, 22E and 22D were deposited in silicon, glass and ITO/glass and also two thicker samples of 22N were prepared on ITO/Glass substrate. In figure 4.2 the different surface roughness of 22D in ITO and glass can be observed. Silicon substrate due to its high refractive index, was used as well, but it was difficult to obtain an uniform thin film due to the hydrophobic behaviour of PAAD dyes. The first step for determining thin films, was the deposition of the films with spin coating. The film was annealed on a hot plate for 10 minutes at 90 °C after the spin-coating. Finally, in order to observe the range of the thicknesses we can determine with these materials with spin coating deposition, we attempted to increase the thickness with two different methods. In the first method, I deposited the solution 22N in methanol (1% w/v) on a ITO/Glass substrate followed by spin coating for 10 mins on the hot plate. I followed the same procedure 5 times. The maximum thickness that I observed with this technique was approximately 80 nm. In the second method, in order to determine the maximum thickness, I increased the concentration of the solution of PAAD 22N in methanol from 1% to 5% and 10% w/v. The maximum thickness obtained was 70 nm.
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4.3 Determination of the optical parameters of PAAD materials

The determination of the refractive index of the PAAD thin films with the method of ellipsometry is described in this section. Ellipsometry is based on optical measurements of the reference and the sample and a model that determines the complex refractive index and the thickness of the films using these measurements [140]. Additional measurements of the thickness and absorption peaks can confirm the ellipsometric results for the refractive index and is usually necessary due to the uncertainty of the the ellipsometric modelling. For this work, we measured the film thickness with profilometry and the absorption peaks with spectrophotometry of the films. The values of the thickness and the absorption peaks were used to confirm the ellipsometry results. We observed the same results for the thicknesses of the films using profilometry and ellipsometry and the same absorption peaks using spectrophotometry and ellipsometry.

4.3.1 Thickness and roughness of PAAD/films

To obtain very thin and uniform films, different speeds (rounds per minutes-RPM); 1000, 2000, 3000, 4000, were tested and the different thicknesses are presented in table 4.1 and figures 4.3, 4.4 and 4.5. The thicknesses of all the films were measured with profilometry (KLA Tencor P-16 Stylus Profiler) in all the stages of the experiments and the thicknesses were also confirmed with ellipsometry (M2000DI ellipsometer). In these figures the black line represents the roughness which was determined with measuring the thickness of the thin films in different areas of the same sample 4 times. The
22N and 22D dyes were more uniform and their surface roughnesses were low compared with 22E. 22E has higher surface roughness and the thin films were not uniform. 22D and 22N obtained very thin of less than 20 nm with very low roughness. The lowest thickness was observed for 22E was 30 nm. For 22N and 22D the roughness was higher with 1000 and 2000 RPM, compared to 3000 and 4000 RPM because these materials’s films were very uniform. However, for 22E that the films were not so uniform; the roughness was very high even with 3000 and 4000 RPM.

<table>
<thead>
<tr>
<th>Sample</th>
<th>1000 RPM</th>
<th>2000 RPM</th>
<th>3000 RPM</th>
<th>4000 RPM</th>
</tr>
</thead>
<tbody>
<tr>
<td>22D</td>
<td>150 nm</td>
<td>35 nm</td>
<td>20 nm</td>
<td>15 nm</td>
</tr>
<tr>
<td>22N</td>
<td>90 nm</td>
<td>70 nm</td>
<td>25 nm</td>
<td>15 nm</td>
</tr>
<tr>
<td>22E</td>
<td>65 nm</td>
<td>35 nm</td>
<td>45 nm</td>
<td>45 nm</td>
</tr>
</tbody>
</table>

Table 4.1: The thicknesses of the three different materials (22D, 22N and 22E), as they spin coated with different speeds. The surface roughness of 22E is observed. The measurements were recorded with KLA Tencor P-16 Stylus Profiler.

Figure 4.3: Thickness and roughness of 22D. The minimum thickness of 22D was 20 nm.

Figure 4.4: Thickness and roughness of 22E. The minimum thickness was 35 nm, the surface roughness was very high.
4.3.2 Absorbance and light induced absorbance of 22D, 22E and 22N

The next step of this work involved the measurement of the absorbances. Absorbance spectroscopy (spectrophotometry) measures the light is absorbed by the sample in given wavelengths in range between 200 to 2500 nm [141]. The decadic absorbance ($A$) is defined by Beer-Lambert law,

$$A = -\log_{10}\frac{I_T}{I_o}$$  \hspace{1cm} (4.1)

where $\frac{I_T}{I_o}$ is the transmittance of the sample. The absorbance is determined with measuring the light intensity between a reference and a sample.

The absorbance of the three different materials were measured when deposited on glass substrates with a spectrometer using unpolarised light (UV/VIS/NIR JASCO). The error of the system is approximately 2%. The materials were characterised between 300-1500 nm. As shown in the figure 4.6, the absorbance peak of the 22E is broad reaching to the wavelength of 1000 nm, compared with 22D and 22N. The main absorption peaks were at 375 and 450 nm for 22D, 380 and 470 nm for 22N and 375 and 440 nm in 22E. 22E demonstrated higher absorption and the wider spectra response compared with 22N and 22D, which is likely to be caused due to its larger thickness. The measurements of the absorbance were also used to verify the ellipsometry fitting.

For the study of the photosensitivity, thin PAAD films, were illuminated by a 405 nm (100 mW) diode laser with 5 mm spot size for 1 minute and the absorption spectra was determined after the illumination. In figures 4.7, 4.8 and 4.9 the results are being
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Figure 4.6: Absorbance of 22N, 22E and 22D as measured with an UV/VIS/NIR JASCO spectrometer. 22E has a higher and wider absorption compared with 22N and 22D. Light induced change in absorption create different trends at different wavelengths. This effect is likely be caused by different wavelength causing reorientation with different effective cis-concentration.

Figure 4.7: Absorbance of 22D after and before illumination. A 14 % reduction in absorption at 375 nm and 7% increase in absorption at 450 nm after illumination was determined.

For the PAAD 22D a 14 %, reduction in absorption at 375 nm and 7% increase in absorption after illumination at 450 nm shown. For 22N, 37 % reduction in absorption at 380 nm and 20 % reduction of the absorption after illumination at 470 nm was determined. For 22E 14 % reduction in absorption after illumination at 375 nm was observed. The most significant results were observed in 22N and these results can be due to the different chemical structure of the materials. The measurements of the thickness and the
**Figure 4.8:** Absorbance of 22E after and before illumination. A 14% reduction in absorption after illumination at 375 nm was observed.

**Figure 4.9:** Absorbance of 22N after and before illumination. A 37% reduction in absorption at 380 nm and 20% reduction of the absorption after illumination at 470 nm was determined.

Absorbance were very important for the correct determination of the refractive index of the PAADs.

### 4.3.3 Determination of the refractive index and the absorption coefficient with ellipsometry

In this work ellipsometry was used to determine the complex refractive index of the PAAD complex dyes. Ellipsometry is widely used to measure the thickness and the optical constants of materials, especially thin films [140, 142]. For the following demonstration, the wave equation of a plane wave propagating along the z-axis is given,

$$E(z, t) = \frac{E_x}{E_y} e^{i(k_z z - \omega t)}$$  \hspace{1cm} (4.2)
where $E_x$ and $E_y$ are the amplitudes of the electric field along the $x$-axis and $y$-axis respectively, $k_z$ is the wave vector ($k_z = \frac{\omega}{c} \tilde{n}$), with $c$ is the speed of light, $\omega$ is the angular frequency and $\tilde{n}$ is the complex refractive index. Ellipsometry measures the light’s change in polarisation, when either transmitted or reflected from a sample as shown in figure 4.10. The change in the polarisation is estimated when the light is oriented in $p$− (parallel) and $s$− (perpendicular) polarisations relative to the incidence plane, by the amplitude ratio ($\tan \Psi$), and the phase difference ($\Delta$). Ellipsometry measures the ratio of change in polarisation of reflected light [140].

\[ \varrho = \tan(\Psi)e^{i\Delta} = \frac{R_p}{R_s} \]  

(4.3)

Where $R_p$ and $R_s$ are the Fresnel coefficients for $p$− and $s$− polarisations and are given by,
where \( R_p \) is the reflection coefficient, in the \( p- \) polarisation and \( R_s \) is the corresponding coefficient in the \( s- \) polarisation. The case of total reflection is not included in the ellipsometry measurements [143].

Ellipsometry follows the Kramers-Kronig relations,

\[
\begin{align*}
R_p &= \left( \frac{E_r}{E_i} \right)_p = \frac{n_t \cos(\theta_t) - n_i \cos(\theta_i)}{n_i \cos(\theta_i) + n_t \cos(\theta_t)} \\
R_s &= \left( \frac{E_r}{E_i} \right)_s = \frac{n_i \cos(\theta_i) - n_t \cos(\theta_t)}{n_i \cos(\theta_i) + n_t \cos(\theta_t)} 
\end{align*}
\] (4.4)

Ellipsometry follows the Kramers Kronig relations,

\[
n(\omega) = 1 + P \int_{-\infty}^{+\infty} \frac{d(\omega')k(\omega')}{\pi(\omega' - \omega)} 
\] (4.5)

\[
\kappa(\omega) = -P \int_{-\infty}^{+\infty} \frac{d(\omega') n(\omega') - 1}{\pi \omega' - \omega} 
\] (4.6)

where \( P \) is the Cauchy principal value. The Kramers-Kronig equations, (4.5) and (4.6) show that the refractive index \( (n(\omega)) \) and absorption coefficient \( (\kappa(\omega)) \) are dependent. As ellipsometry is strongly dependent on the model used; the sets of parameter values may not be unique [144, 145]. A full Kramers-Kronig analysis requires a complete optical spectrum of either the reflection or absorption coefficients, as the integrals suggest.

In this work, we estimated the absorbance spectrum and we compared it with the ellipsometric results of the absorption coefficient. Moreover, an accurate measurement of the thickness of the films was used from profilometry measurements. For the following ellipsometric characterisation, I estimated the refractive index and the absorption coefficient of the thin films of PAADs, after having estimated the optical properties of the ITO/glass substrate which used as a reference. The absorbance spectra was used for the correct modelling with ellipsometry, because the absorption peaks and the absorbance peaks need to be equal. The optical properties of PAADs were determined between 300 to 1800 nm. For the estimation of these parameters, two different methods were used to confirm the same values, a) B-Spline [146], which based on a mathematical calculation and b) Lorentz oscillator [147]. Lorentz oscillator model is based on the Lorentz classical theory of interaction between light and matter and it describes frequency dependent polarisation due to the bound charge, where the bindings between electrons and nucleus are similar to a mass-spring system [147]. For more accurate results, the Cauchy model was used to estimate the thickness of the material in the transparent regime (between
800-1200 nm), as described in the work of Weber et al. [146]. The Cauchy relationship is given by,

\[ n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4} \]  

(4.7)

\[ \kappa(\lambda) = 0 \]  

(4.8)

with A,B,C fitting parameters. The complex dielectric function for multiple Lorentz oscillators is given by,

\[ \tilde{\varepsilon}(\omega) = \varepsilon_{\infty} + \frac{(\varepsilon_s - \varepsilon_{\infty})\omega_t^2}{\omega_t^2 - \omega^2 + i\Gamma_0\omega} + \sum_{j=1}^{2} \frac{f_j\omega_{0j}^2}{\omega_{0j}^2 - \omega^2 + i\gamma_j\omega} \]  

(4.9)

where \( \tilde{\varepsilon} \) is the complex refractive index, \( \omega_t \) is the resonant frequency of the oscillator, \( \Gamma_0 \) is the damping factor, the broadening of each oscillator, and \( \omega \) the frequency of the light. \( f_j \) is the oscillator strength, \( \omega_{0j} \) is the resonant energy of an oscillator for a collection of several Lorentzian oscillators and finally \( \gamma_j \) is the broadening parameter corresponding to the peak energy of each oscillator.

For the calculation of the refractive index of PAADs, a double Lorenz oscillator model was used because of the two main absorption peaks of PAADs. For the value of \( \omega_t \) was used the value of the first resonance, as it was determined with absorbance spectroscopy and as \( \omega_{01} \) was used the value of the second resonance. For example, for the correct modelling of the complex refractive index of 22D with absorption peaks in 375 nm (3.3 eV) and 450 nm (2.7 eV) the values of \( \omega_t \) and \( \omega_{01} \) were 2.7 and 3.3 eV respectively. The average refractive index is presented in table 4.2. The 22N refractive index was higher in comparison with 22E and 22D (4.11). The refractive indices at 400 nm were the same for all PAADs (n=2.0), between 400 and 500 nm there were strong peaks and increases in n. These results are related to the absorbance; 22E has higher absorption and lower refractive index and 22D and 22N have similar refractive indices in all regimes. The refractive index of azobenzene polymers as determined by other groups [148] was \( n_{azo}=1.77 \), a value that agrees well with our measurements. The measurements of the refractive indices are important because they can be used for the calculation of the maximum effect of the phase modulation in the surface relief which is introduced in section 4.5 (theoretical calculation in Appendix A).
Chapter 4: Azobenzene based photo-aligning complex dyes

Table 4.2: The absorption peaks of the three different polymers as it was measured with the UV/VIS/NIR JASCO spectrometer and confirmed with ellipsometer M2000DI ellipsometer. The ellipsometric results of the average refractive index in the regime 300 to 1800 nm.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Absorption peaks±5 (nm)</th>
<th>Refractive index ±0.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>22D</td>
<td>375 &amp; 450</td>
<td>1.9</td>
</tr>
<tr>
<td>22N</td>
<td>380 &amp; 470</td>
<td>1.8</td>
</tr>
<tr>
<td>22E</td>
<td>375 &amp; 440</td>
<td>1.6</td>
</tr>
</tbody>
</table>

Figure 4.11: The determination of the complex refractive index of 22D on ITO/glass substrate as it was determined by ellipsometry. The same absorption peaks as they were observed with absorption spectroscopy in 375 nm and 450 nm, they were determined in ellipsometric model.

4.4 Diffraction efficiency of azobenzene complex dyes

For the investigation of the phase induced properties of the PAADs the diffraction efficiency (\( \eta \)) was measured. Michelson interferometer based setup was used for the determination of \( \eta \) and the time response. The sample was illuminated with a 514 nm Ar\(^+\) laser at 500 mW/cm\(^2\) [149]. The Ar\(^+\) laser was linearly and perpendicularly polarised, with the incident angle of the pumping beam in respect to the sample fixed at 37° in Bragg angle; and the grating period was 1 \( \mu m \) as shown in figure 4.12. For monitoring the \( \eta \), a He-Ne laser at 632.8 nm was used with power 1100 mW/cm\(^2\) which transmitted through a polariser (P) and a quarter waveplate (\( \lambda/4 \)).

The diffraction efficiency was calculated with equation 4.10 [150] where \( I \) is the the power...
A 514 nm Ar$^+$ laser was used for writing the gratings and a He-Ne laser at 632.8 nm was used for monitoring the diffraction efficiency ($\eta$). For the measurements of $\eta$ the PAAD films were deposited on ITO/glass substrates.

The intensity of the first order diffracted beam and $I_o$ is the power of the incident beam. The intensity of the diffracted beam was measured by a photodiode connected to an oscilloscope.

$$\eta = \frac{I}{I_o}$$

(4.10)

The measurements took place in real time and in room temperature. The pattern written in the film was able to be deleted using a single beam. $\eta$ was measured in two different polarisations, parallel ($\eta_\parallel$) and perpendicular ($\eta_\perp$) to the incident beam. I investigated the maximum effect in the refractive index due to phase modulation with the assumption that no surface relief gratings were created. Equation 4.11 was used to determine the maximum effect on the refractive index due to the two beam illumination [151].

$$\Delta n = \frac{\lambda \cos \theta}{2\pi d} \ln \left( \frac{1 + \sqrt{\eta}}{1 - \sqrt{\eta}} \right)$$

(4.11)

Where $\lambda$ is the wavelength of the probe beam, $d$ is the thickness of the polymer, and $\theta$ is the Bragg angle. The 22N gave the highest $\eta$ with $\eta_{22N}$ estimated as $7 \cdot 10^{-5}$ while for 22D and 22E $\eta$ was of the order of $10^{-6}$, as is summarised in table 4.3. Thus, the refractive index modulation for 22N was higher with $\Delta n_{22N} = 3.5 \cdot 10^{-2}$ while for 22E and 22D it was the same with $\Delta n_{22D&22E} = 7 \cdot 10^{-3}$. The time response of the 22N was slower compared with the other two polymers, this effect can be seen in figures 4.13 & 4.14. In order to evaluate how the diffraction efficiency depends on the thickness of the material, we measured the diffraction efficiency of 22N PAAD with thicknesses of 60 nm and 70 nm (with increasing the concentration of the 22N powder in methanol for 5% and 10 % w/v respectively). For 60 nm thickness, the maximum $\eta$ was $8 \cdot 10^{-6}$ and $\Delta n_{22N} = 0.028$. However, for thickness 70 nm the maximum $\eta$ was $6 \cdot 10^{-6}$ and $\Delta n_{22N} =$
0.02. The grating can form within some thickness only and PAAD films, since they had limited thickness, were likely not thick enough to create surface relief [152, 153]. The writing time for 22N was 300 s and for 22D and 22E it was 10 s. The change of $\eta$ was polarisation dependent. $\eta$ in perpendicular polarisation was higher compared with the horizontal polarisation.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thickness ±5 (nm)</th>
<th>$\eta_{\perp} \pm 0.1 \cdot 10^{-6}$</th>
<th>$\eta_{\parallel} \pm 0.1 \cdot 10^{-9}$</th>
<th>$\Delta n \pm 0.002$</th>
</tr>
</thead>
<tbody>
<tr>
<td>22D</td>
<td>20 ±5</td>
<td>10$^{-7}$</td>
<td>5$\cdot 10^{-9}$</td>
<td>7$\cdot 10^{-3}$</td>
</tr>
<tr>
<td>22N</td>
<td>35 ±5</td>
<td>7$\cdot 10^{-6}$</td>
<td>10$^{-8}$</td>
<td>3.5$\cdot 10^{-2}$</td>
</tr>
<tr>
<td>22N</td>
<td>60 ±5</td>
<td>8$\cdot 10^{-6}$</td>
<td>5$\cdot 10^{-9}$</td>
<td>2.8$\cdot 10^{-2}$</td>
</tr>
<tr>
<td>22N</td>
<td>70 ±5</td>
<td>6$\cdot 10^{-6}$</td>
<td>5$\cdot 10^{-9}$</td>
<td>2.0$\cdot 10^{-2}$</td>
</tr>
<tr>
<td>22E</td>
<td>35 ±15</td>
<td>3$\cdot 10^{-7}$</td>
<td>2$\cdot 10^{-9}$</td>
<td>7$\cdot 10^{-4}$</td>
</tr>
</tbody>
</table>

Table 4.3: Diffraction efficiency and refractive index

![Figure 4.13: Time response of 22D and 22E as it was recorded during the diffraction efficiency measurement.](image)

4.5 Atomic force microscopy

The investigation of surface modulation can be carried out with AFM. The diffraction efficiency can be either due to refractive index modulation, or the surface modulation of the PAADs, such surface relief grating (SRG). After the measurement of the diffraction efficiency, it is likely the surface of azobenzene films to change due to cis and trans isomerisation. Azobenzene based materials with large birefringence obtain high $\eta$ and response time [154] and the SRG depends on the intensity and the thickness of the
Figure 4.14: Time response of 22N as it was recorded during the diffraction efficiency measurement.

For the determination of the sinusoidal SRGs, AFM was performed in the 22N polymers which has been widely used for the determination of the SRGs [128, 131, 154, 155]. AFM is a scanning probe microscope and measures the force between the probe, a sharp tip, and a sample [152, 153]. For this work, AFM maps were acquired by a MultiMode Nanoscope V AFM (Veeco Metrology Group) in contact mode using commercial Al coated Si tips (Budget sensors, Tap300Al-G) with 125 µm long cantilevers, resonant frequency of 300 kHz and force constant of 40 N/m [156]. With our current results we were not able to observe any surface relief which indicates that the \( \eta \) is primarily due to the modulation of the refractive index. As shown in figures 4.15 a and b, any SRGs cannot be observed and no clear periodicity on the surface of the films was observed. In figure 4.15b the evidences of roughness can also be observed, due to the higher thickness of the film. The absence of SRGs is likely due to the low thickness of these films, since they were between 20-70 nm. Very thin azobenzene materials are not able to form SRGs as it has previously reported by Barrett et al and Fucuda et al [157, 158].

4.6 Conclusion

In this work three different photo-aligning materials, PAADS: 22D, 22E and 22N were studied. Different substrates were tested ITO/glass, glass and silicon as substrates for the thin films. Films on glass and silicon substrates showed high roughness, most likely due to the wetting surface and due to the fact that azobenzene dyes are hydrophobic.
ITO/glass substrate was selected as a substrate of choice. For all three PAAD samples, absorption spectroscopy peaks agreed with the peaks detected in ellipsometry and the refractive index at 400 nm was the same for all PAADs at around 2.0. The absorbance spectra are in agreement with the ellipsometric results, the absorption peaks and the thickness as calculated by the ellipsometer, were the same as estimated by profilometry and the UV/VIS/NIR spectrometer. The light induced behaviour of the azobenzene materials was studied as well. The change of the absorption due to the illumination with 405 nm diode laser was as expected in these photosensitive materials. Moreover, the $\eta$ of thin films was characterised. The different chemical structures of these materials can affect the time response and the refractive index modulation. 22N likely due to the longer molecules, demonstrated higher effective refractive index of the order of 0.025, but had a response time of 300 s. 22N also shown significant change of the absorption (decrease) under illumination which shows its different chemical structure compared with 22E and 22D. With 22E was obtained a higher absorption peak at higher wavelengths, however, the film deposition of uniform films proved difficult and high roughness was observed. Finally, the $\Delta n$ and the SRGs due to the phase modulation were studied. The absence of SRGs suggests that the phase modulation is only due to the $\Delta n$. This characterisation of PAAD optical and physical parameters is the first step in adapting them for LC components for the other regions of spectra, in particular in THz.
Chapter 5

Graphene based lateral photo Dember emitters

5.1 Introduction

There are various methods for THz radiation generation [159], such as photoconductive antennas [160], emitters based on optical rectification [161], THz quantum cascade lasers (QCLs) [162, 163] and surface semiconductor emitters. For THz-TDS, photoconductive antennas have been widely used for generating THz radiation due to the bandwidth (approximately 0.1-4 THz) and signal to noise ratio (SNR > 50). In this chapter we suggest the surface lateral Photo-Dember (LPD) emitters as an alternative method for generating THz without applying any electric bias. Numerous semiconductors, such as GaAs and InGaAs, with high electron-hole mobility asymmetry have been used for the fabrication of LPD emitters [22, 39, 51, 53, 164, 165].

Further investigation of new materials can improve the efficiency of the LPD emitters. Graphene is a single atom of carbon thick and has demonstrated interesting electro optical properties [166]. In this chapter, we demonstrate our first work on fabrication and characterisation of LPD emitters based on graphene. The graphene was deposited on doped silicon with a silicon oxide buffer layer so it is working in reflection geometry.

5.2 Graphene based lateral Photo-Dember emitters

The Photo-Dember (PD) effect is a well understood surface THz emission effect that was used a lot to understand semiconductor dynamics but was not an established THz emission mechanism because of the problems of outcoupling the radiation. LPD is a novel
geometry for PD emission which solves the problem of out-coupling for generating THz radiation and it was suggested by Klatt et al. [51]. This method is based on generating THz radiation from lateral photo-Dember currents, by partially masking a semiconductor surface with a metal layer, when the spot of an ultrafast laser is focused half on the semiconductor surface and half on the metal mask (fig. 5.1) [22, 39]. As, Barnes et al proposed [39], the THz generation is produced perpendicular to the surface and the carriers diffuse laterally in opposite directions due to the metal mask as it was described in the section 1.3.3. In LPD emitters dipoles are formed from difference in mobilities between hole and carrier. GaAs and InAs have been suggested as semiconductor for LPD emitters, because the difference between the mobilities between hole and carrier is relatively high; GaAs has carrier mobility $\mu_e=8500 \text{cm}^2\text{V}^{-1}\text{s}^{-1}$ and hole mobility $\mu_h=400 \text{cm}^2\text{V}^{-1}\text{s}^{-1}$ [167]. New materials with high mobilities and a large asymmetry between the electron and hole mobilities need to be characterised for the better performance of such devices.

Graphene started being the focus of interest after Novoselov, Geim and co-workers, manage to obtain a single layer of graphene using a simple mechanical exfoliation method in 2004 [168, 169]. Graphene is a two dimensional material (2D), which forms from a single layer of carbon atoms in a honeycomb lattice [170] and it has been used for numerous applications in the optical and THz regimes. It has demonstrated interesting results from high-frequency transistors and photodetectors [166] to graphene based electrodes [171] and broadband THz modulators [172, 173].

Graphene can be produced by methods such as dispersion and exfoliation of graphite
with solvents [174], chemical vapour deposition (CVD) from graphene oxide [175] and CVD on to flexible cooper (Cu) substrates [171, 176]. The 2D material has been the centre of the attention due to the high ambipolar electric field, which with high concentrations of electrons and holes \( (n > 10^{10} \text{cm}^{-2}) \) can achieve mobilities in the order of \( \mu = 15000 \text{ cm}^2\text{V}^{-1}\text{s}^{-1} \), temperature dependent. Graphene is a zero gap semiconductor with low energy quasiparticles, massless Dirac fermions that can be described with the Dirac equation [177].

Due to the electron-hole symmetry, graphene does not seem a suitable semiconductor for LPD emitters. However, as it has been suggested by Liu et. al [167], it is claimed that graphene can be a promising material for LPD THz generation due to its electro optical properties. In [167] graphene as a 2D material with spatial confinement, has a lateral diffusion of hot carriers and a low electronic specific heat capacity which creates a high carrier temperature and enhances the diffusion speed of hot carriers due to high carrier mobility. Therefore the small difference of mobilities of the carrier and holes in graphene can be increased rapidly due to the high carrier temperatures. The diffusion coefficient is described by the Einstein relation,

\[
D = \frac{\mu k_B T}{2q}
\]

where \( D \) is the diffusion coefficient, \( \mu \) is the excited charge mobility, \( T \) the temperature and \( k_B \) Boltzmann constant and \( q \) is the electrical charge of the particle. Finally, in [167] it is claimed that due to the small thickness of the graphene single layer, there is a strong light coupling which creates high photo-carrier density, however in [167] THz emission was not reported. In our group we have worked a lot in the LPD effect and we wanted to investigate if graphene can be really a material for LPD emitters.

### 5.3 Fabrication and characterisation of graphene lateral Photo-Dember device

For the fabrication of the graphene/LPD emitters for this work, the monolayer graphene was grown with the CVD method from the company 2D-tech. The graphene was deposited on n-doped (silicon) Si. Si is a conductive material and thus a layer of silicon dioxide (SiO\textsubscript{2}) was used as an insulator, to isolate the graphene from the Si. We used a Si substrate because we wanted to change the gate Voltage \( (V_g) \) and to observe how the THz radiation is being affected. At zero \( V_g \) the Fermi level is at the Dirac point, with applied Voltage \( (V_g > 0 \text{ and } V_g < 0) \), the Fermi level moves into the valence and conduction band respectively, and this can increase or reduce the THz radiation [172].
The figure 5.2, is a schematic representation of the device. 2D-tech used a n-doped Si wafer (1 cm²) 525 µm with 290 nm thick SiO₂ for the deposition of the graphene single layer. The Au partial mask on the top of the graphene and the back gate were deposited by thermal evaporation. Since the Si is not transparent in THz, for this work a reflection setup was used for the characterisation of the graphene LPD emitter. The setup is presented in figure 5.3. As a pump we used a 100 fs Ti:Sapphire laser with wavelength at 800 nm and repetition rate of 80 MHz and a photoconductive antenna from Menlo GMBH for the detection. The optical beam was modulated using an optical chopper for the synchronous detection with a lock-in amplifier.

The THz-TDS scan in figure 5.4 (a), shows the THz emission from the monolayer graphene LPD emitter. The THz signal that was generated by these emitters, was very low compared to previous works on Si-GaAs based LPD [22]. In figure 5.4(b), the
relating Fourier transform of the electric field that was measured is presented. The signal to noise ratio and the bandwidth, which is lower than 300 GHz, were very weak compared with other LPD emitters as well. In the work of Barnes et. al [11] demonstrated that Si-GaAs LPD emitter generates THz signal with bandwidth approximately 1.5 THz. The negative results on graphene LPD emitter are more likely to the pump beam absorption and to the low absorption of graphene due to the material thickness [170]. The absorption of GaAs at 800 nm is approximately 68% [178] and for a monolayer graphene is approximately 2 to 3% [179].

![Graphene LPD emitter](image)

**Figure 5.4:** a) The THz electric field was recorded in the time domain by the graphene LPD emitter. b) The Fourier transform of the THz electric field. The bandwidth is lower than 300 GHz.

For the next step of this project we applied gate voltage to the graphene/LPD device because with applied voltage \( V_g > 0 \) or \( V_g < 0 \), the Fermi level moves into the valence or conduction band, and this effect can increase or reduce the THz radiation that the emitter generates. Thus, we applied \( V_g \) of \( V_g = 10\) V and \( V_g = 20\) V. However, as it can be seen in the figures 5.5 (a) and (b), the change of the bias did not affect the signal of the THz pulse most likely due to the device’s performance and a current leakage or saturation [180].

In order to confirm that the results are due to LPD emission, we wanted to check if the net dipole will form in the opposite direction due to the suppression under the metal as it has proposed by Barnes [11]. However, we could not measure reproducibly the effect, which is mainly due to the very weak THz signal we observed with the graphene/LPD device.
Figure 5.5: a) The THz electric field was recorded in the time domain by a graphene LPD emitter. b) The Fourier transform of the THz electric field. Any effect due to the increasing bias can be observed, mainly due to the current leakage of the device.

5.4 Conclusion

LPD emitters are emitters that generate THz pulses without applying any external bias and although they give similar bandwidth to photoconductive emitters they still lack in SNR [22, 39, 51, 53, 164, 165]. Graphene is a promising material due to its electrooptical properties but because of the low absorption at 800 nm and the electron-hole symmetry is not very effective yet as material for LPD emitter. Here, I have presented LPD emitters based on monolayer graphene. In the work by Liu et. al [167] has been suggested that the THz emission from graphene LPD emitters is possible due to the high carrier temperature can increase the difference between the carrier and holes mobilities. However the THz emission we observed with graphene/LPD emitters was very weak compared to previous works on other semiconductors (for example Si-GaAs). The signal to noise ratio and the bandwidth that we determined with these emitters were very low and future work is required. For the advancement of this work, multi-layer graphene can be used instead of monolayer graphene. Multi-layer graphene has higher absorption and the carrier mobility of bilayer graphene has been confirmed 1000 $cm^2V^{-1}s^{-1}$ [181]. There was also a current leakage, which can be reduced with increasing the layer of $SiO_2$ and create current channels in the surface of LPD device. This can help on applying bias, since it will limit the current leakage, and we can increase the bandgap of graphene. Combining an efficient LPD emitter with other THz components, we could also design devices to control the THz radiation, such as lenses based on LC [182], tunable filters [183], LC based beam steering devices [184].
Chapter 6

Conclusions and future work

In this chapter I am presenting the conclusions of this work and a brief introduction of preliminary results regarding future work. The aim of this thesis was the investigation and the characterisation of new materials for components in THz spectroscopy. THz technology has been developed in the past 30 years and there is still a lack of devices for manipulation of polarisation. In this work we demonstrated new materials and techniques that can be used for the future development of THz apparati. In the second chapter I presented the fabrication of ferroelectric BaTiO$_3$ NPs with the sol gel method for LC/NPs suspensions. The doping LCs with sol gel NPs was explored for the first time for the THz spectral range. This method has been demonstrated by various groups [8, 78, 95, 96, 185] in the optical regime. LC/NPs suspensions have demonstrated improvements of the optical parameters of LCs. LCs/NPs suspensions have developed higher birefringence and dielectric anisotropy compared to the pure LCs. However in these works the NPs were mainly fabricated with milling technique, the milling technique which is time consuming and requires expensive equipment. For this work, BaTiO$_3$ were fabricated by Dr Stratakis with laser ablation, though BaTiO$_3$ fabricated with the ablated method were not ferroelectric; as we proved during their characterisation. We used these non ferroelectric materials and we compared them to ferroelectric in the work by Podoliak et al. [73]. The sol gel process, that we investigated in the process of this work, offers a higher purity, chemical homogeneity and better control of the particle dimensions compared to milling. I fabricated these materials in the Unité de Catalyse et de Chimie du Solide (UCCS Artois) in Lens with the help of Dr S. Saitzek and Mrs A. Gumienny. For the fabrication of the most effective BaTiO$_3$ NPs, we used two different synthesis. Only the synthesis based on tetrabutil titanate, demonstrated sufficient results; hence NPs based on this method were used for the most of the LC/NPs suspensions during this work. The method of harvesting also was presented and discussed, in order to investigate its efficiency in the separation of ferroelectric with non ferroelectric NPs.
In the third chapter, I developed an algorithm for the parameter extraction with the help of Dr M. Barnes and Dr Geoff Daniell, based on previous work by Dr Aaron Chung. The new algorithm calculates the optical properties of materials and was used for the majority of the THz parameter extraction during this thesis. The BaTiO$_3$ NPs and BaTiO$_3$ powder were characterised with THz-TDS and the refractive indices of these materials were determined using the algorithm I presented in the section 3.2. Hybrid LC/NPs with ferroelectric NPs also were demonstrated for first time in THz regime. I doped LC E7 with BaTiO$_3$ NPs and the new LC/NPs suspension developed an increase in the birefringence in the order to 10%. The next stage of this set of experiments was the doping of high birefringence LC materials, designed especially for THz radiation, with ferroelectric NPs. LCs such as 2020, 6CHBT, 2037 and 1867 have been developed from the Military University of Technology in Poland for THz devices and their birefringence is higher than 0.20 and were doped with NPs. I prepared the suspensions and with Dr U. Chodorow we characterised the samples. 2020/NPs suspension demonstrated increase of the birefringence in order of 14% compared with pure LC. However, we did not observe an increase in the birefringence in all the LC/NPs suspensions. We tried to use only LCs with cyclohexane rings fluorinate atoms that have indicated an increase of the birefringence in optical regime [73], but the results were not as effective as we expected. The idea that dipole moments are being created between the LCs and NPs and change the order parameter of the LC molecules more likely is not applied to all the LCs mixtures [8]. Viscosity, chemical structure, phase transition temperature of LCs are some of the parameters that affect the LCs/NPs suspensions. For this project further modelling is required to explain the LCs-NPs interactions and how that affects the birefringence.

In the fourth chapter PAADs, photo-aligning azobenzene complex dyes, were characterised. I determined the thickness, refractive index absorption and diffraction efficiency (with Dr Mailis) of these materials. Different optical parameters were determined with 22D and 22N to be able to create very uniform thin films. 22N exhibited higher diffraction efficiency compared with 22D and 22E and demonstrated longer time response. The aim of this project was the determination of the thinnest layer of PAADs while they still keep their photo induced properties. These materials can find use in THz regime as photo-aligning materials.

In the last chapter, I explored graphene as a potential THz material for LPD emitters and I characterised it with THz-TDS. Graphene is a zero gap semiconductor which has high carrier mobilities for its thickness but due to the carrier-hole symmetry it is difficult to obtain THz emission. The signal to noise ratio and the bandwidth of our devices was too limited when compared with Si-GaAs emitters and future work is required to determine if graphene can really develop a diffusion photo-curent.
6.1 Future work

Important future work on the characterisation of LC doped with NPs in the THz regime is the modelling of the chemical interactions between the LC and NPs. A variety of LCs can be doped with NPs in order to understand how different LC molecules interact with the ferroelectric NPs and change the order parameters of LCs and improve the LC properties. However work on this subject needs interdisciplinary collaborations and collaboration of theorists with experimentalist, in order to be successful. After the characterisation of PAAD materials in the optical regime, the next step will be the characterisation of the PAADs materials in THz regime. PAADs can be used in THz to manipulate THz light, one important application would be to create q-plates for the fabrication of THz vortex light. These materials have shown high diffraction efficiency and birefringence can find use in THz and optical regime for applications such as beam steering and phase shifters. I would be interesting to use graphene as a THz emitter, mostly to understand diffusion and drift currents in graphene. Multi-layer or bilayer graphene should be used so an unambiguous THz signal from graphene to be detected. Bilayer graphene has demonstrated higher absorption and thus the THz signal can be increased. Also, with the improvement of the device, the application of gate voltage can be achieved which will help us understand more the mechanism of generation of in the graphene/LPD device.

**Characterisation of water, proteins and salts in THz regime:** Towards the end of my thesis I was interested and worked on the characterisation of proteins in the THz regime and the preliminary results of this work will be given here.

During the last part of my work, I started to investigate other materials in THz regime. In recent years, an interest of the properties of bio molecules in THz regime has ben developed [25, 186, 187] due to multiple resonances of the molecular bonds and vibrational modes that can be identify in THz regime.

For the following measurements the box setup that was presented in section 3.3 and shown in figure 3.11 was used. The algorithm described in the section 3.2 determined the optical parameters of the tested materials. Furthermore, a microfluidic device was designed by Dr Rowe for the characterisation of the samples as shown in figure 6.1. Microfluidic devices have been demonstrated before and they are transparent with near-zero dispersion in the THz frequency range [188]. The microfluidic device, we used for our experiments is based on two 5 mm thick teflon windows of 1x1 inch² dimension. Teflon was suggested due to its low absorption in THz regime [189]. One teflon window had thickness 4.600 mm in the middle in order to create a gap (roughly 0.400 mm) for the characterisation of the samples.

For the purpose of this work and for the extraction of the refractive index and the absorption coefficient of the tested samples; firstly the refractive index of the teflon was
Figure 6.1: A schematic representation of a device similar with the device used for the characterisation during this work. In the device was used for this set of experiment there were two teflon windows.

determined. Figure 6.2 shows the results of the absorption coefficient (a) and refractive index (b) of teflon (Polytetrafluoroethylene). The absorption of this material in THz regime it is very low (<10 cm\(^{-1}\)) and the refractive index is estimated as \( n_t=1.46 \).

![Graphs](image1.png)

**Figure 6.2:** a) The refractive index of teflon b) The absorption coefficient of teflon.

The measurements of water and PBS (phosphate buffered saline) in solution with water were determined. PBS contains NaCl, KCl, Na\(_2\)HPO\(_4\) and KH\(_2\)PO\(_4\). Water is used in solution with proteins and PBS [190, 191]. For the PBS sample 10 mM of PBS was used in solution with water. In figures 6.3 (a&b), the refractive indices of the water and the PBS are shown. The average refractive index of water is \( n_w=2.7 \) and the refractive index of PBS is slightly higher than the refractive index of water. However the absorption of the water is higher compared to the absorption of PBS and this should be due to the presence of the PBS molecules in the water solution and the lower presence of water molecules.

For the last part of this work the protein BSA (bovine serum albumin) was characterised in solution with water and in PBS (with water). For the preparation of the suspension
we used 4 mM BSA in 10 mM water. The refractive index of BSA is lower than water and the absorption coefficient of the water in higher than the refractive index of BSA. This is due to the different vibrations of the protein molecules in the BSA solution [192].

During these measurements we managed to optimise our system for measuring more complex materials with high absorption in the box setup. These results agree with results that have been previously reported from other groups. After these measurements we are confident to start measuring new proteins in THz-TDS and to investigate how protein THz resonances can be affected by oxygenation and also by optical irradiation. For the continuation of this project different proteins and biomolecules can be characterised in

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure6_3}
\caption{a) Refractive index of water and PBS/water b) Absorption coefficient of water and PBS/water.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure6_4}
\caption{a) Refractive index of BSA/water and water b) Absorption coefficient of the BSA/water and water.}
\end{figure}
THz regime. The characterisation can give us more information of the vibrational modes of the proteins and the results can be applied in the biological and medical industries.
Appendix A

Theoretical investigation of the phase modulation

This appendix is an addition to chapter 4. We present the approach to model the maximum effect of the diffraction efficiency ($\eta$) on the surface and refractive index modulation. For the PAADs we did not observed any evidence of surface relief as demonstrated in the section 4.5.

A.1 Raman-Nath model

Two beams in a bulk photorefractive crystal create a sinusoidal interference pattern that produces a periodic modulation of the phase. The phase modulation created due to the presence of the photosensitive material and this can be estimated with the $\eta$ measurements. The $\eta$ can estimate the level of the phase modulation and it can estimate the maximum effect on the surface relief grating (SRG) and the maximum effect on the refractive index modulation. As was suggested by Kogelink [193], the Raman-Nath model can be used in the case where $q << 1$, where $q$ is given by equation (A.1).

$$q = \frac{2\pi \lambda d}{n_{PAAD} \Lambda^2} < 10^{-9}$$  \hspace{1cm} (A.1)

where $\lambda$ is the wavelength of the probe beam of HeNe (532.8 nm), $n_{PAAD}$ is the refractive index of the polymer, and $\Lambda$ is the grating period (1 \( \mu \text{m} \)) in our measurements. For the calculation of the phase modulation in the Raman-Nath diffraction modelled with the assumption that the grating is thin and the material is isotropic. Two different approaches were determined in this section, as effect of the phase modulation, a) SRG b)
the modulated refractive index [194–196]. The incident plane wave is given by equation (A.2).

\[ E = Ae^{i(k \cdot x - \omega t)} \]  

(A.2)

Where \( n_0 \) is the refractive index of the polymer, \( k \) is the wave vector of the incident and \( \omega \) is the optical angular frequency. The wave at the far side of the medium can be expressed as

\[ E = Ae^{i[n_0 k \cdot x + \Delta \Phi \sin K \cdot x - \omega t]} \]  

(A.3)

where \( K = k_1 - k_2 = \frac{2 \omega \Lambda}{\pi} \), with regards to the different phases of the incident beams and \( \Delta \Phi \) is the phase modulation. The Jacobi -Anger expansion for Bessel functions, is an expansion of exponentials of trigonometric functions in the basis of their harmonics and it is given by,

\[ e^{i \Delta \Phi \sin x} = \sum_{m=-\infty}^{\infty} J_m(\Delta \Phi) e^{imx} \]  

(A.4)

where \( J_m \) is the \( m^{th} \) order Bessel function of the first kind and \( i \) is the imaginary unit [197].

For the \( m^{th} \) order, \( k_m = k + mK \) is the wave vector and \( \sin(\theta_m) = m\lambda/n_0\Lambda \). The intensity of the diffraction beams is given by the equation .

\[ I_m = E_0^2 J_m^2(\Delta \Phi) \]  

(A.5)

Finally, the diffraction efficiency can be calculated using equations (4.10) and (A.5) as shown the relative intensities depend on the phase modulation \( \Delta \Phi \).

\[ \eta = \frac{|J_1|^2}{|J_0|^2} \]  

(A.6)

We first investigated the maximum height of SRG in the case that the \( \Delta \Phi \) will create only SRGs and modulation of the refractive index (fig.A.1) [194]. The modulation of the phase is periodic and is given by,
Chapter 6: Conclusions and future work

Figure A.1: Schematic representation of the SRGs on the surface of a PAAD polymer. The diffraction efficiency was recorded with a 632.8 nm HeNe laser.

\[
\Delta \Phi(z) = k[d + h \sin(K \cdot x)]n_{PAAD} + k(Z - D - h \sin(k \cdot z))n_{air} \rightarrow
\]
\[
\Delta \Phi(z) = k(n_{PAAD} - n_{air}) = kzn_{air} + kh(n_{PAAD} - n_{air})\sin(k \cdot x) \rightarrow
\]
\[
\Delta \Phi_{PAAD} - \Delta \Phi_{air} = kh(n_{PAAD} - n_{air}) \tag{A.7}
\]

Where, the \(x\) axis is parallel to the surface of the PAAD and the \(z\) axis perpendicular to the surface of the PAAD and parallel to the direction of the beam. \(n_{PAAD}\) and \(n_{air}\) are the refractive indices of the PAAD and the air, respectively and \(h\) is the maximum change of the thickness of the PAAD due to the phase modulation and the SRG. The relative intensities are given by,

\[
J_1(\Delta \Phi) \simeq \frac{\Delta \Phi}{2}, \Delta \Phi \ll 1
\]
\[
J_0(\Delta \Phi) \simeq 1, \Delta \Phi \ll 1 \tag{A.8}
\]

\[
\eta = \frac{J_2^2(\Delta \Phi)}{J_0^2(\Delta \Phi)} \simeq \frac{(\Delta \Phi)^2}{4}
\]
\[
\Delta \Phi \simeq 2\sqrt{\eta} \tag{A.9}
\]

Finally,

\[
h = \frac{\Delta \Phi}{(n_{PAAD} - n_{air})k} \simeq \frac{2\sqrt{\eta}}{(n_{PAAD} - 1)k} \tag{A.10}
\]
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\[ h = \frac{\sqrt{\eta} \lambda}{\pi (n_{PAAD} - 1)} \]  
(A.11)

The maximum \( n \) modulation due to the phase modulation should be:

\[ \Delta \Phi = dk \Delta n = \frac{2\pi d \Delta n}{\lambda} \]  
(A.12)

\[ 2\sqrt{\eta} = \frac{2\pi d \Delta n}{\lambda} \Rightarrow \Delta n = \frac{\lambda \sqrt{\eta}}{\pi d} \]  
(A.13)

Table A.1 shows the calculated values of the SRG and the refractive index modulation for PAADS 22N, 22D and 22E for the parameters that measured in chapter 4. As it can be seen, the maximum height of the SRG is 1nm for the material 22N. However we did not observe such evidences with AFM.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thickness (nm)±5 (nm)</th>
<th>( n_{PAAD} \pm 0.1 )</th>
<th>( \eta \pm 0.1 \cdot 10^{-6} )</th>
<th>( h \pm 0.01 \cdot 10^{-9} ) (nm)</th>
<th>( \Delta n \pm 0.002 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>22D</td>
<td>20</td>
<td>1.9</td>
<td>1.5 \cdot 10^{-6}</td>
<td>0.3</td>
<td>0.012</td>
</tr>
<tr>
<td>22N</td>
<td>35</td>
<td>1.8</td>
<td>8.1 \cdot 10^{-9}</td>
<td>1</td>
<td>0.05</td>
</tr>
<tr>
<td>22E</td>
<td>35</td>
<td>1.6</td>
<td>2.6 \cdot 10^{-6}</td>
<td>0.27</td>
<td>0.009</td>
</tr>
</tbody>
</table>

**Table A.1:** The values and the results of the theoretical calculations of the SRGs and the refractive index modulation.
Appendix B

Journal and Conference publications

Journal publications:


Conference presentations:


European Quantum Electronics Conference (CLEO®/Europe-EQEC), June 2015, poster presentation

Bibliography


[69] Urszula Chodorow, Janusz Parka, Przemyslaw Kula, Jakub Herman, Olga Chojnowska, Roman Dabrowski, and Vladimir G. Chigrinov. Terahertz properties


[128] Fengxiang You, Marvin Y. Paik, Michael Häckel, Lothar Kador, Daniela Kropp, Hans Werner Schmidt, and Christopher K. Ober. Control and suppression of


[161] T. Löﬄer, T. Hahn, M. Thomson, F. Jacob, and H. G. Roskos. Large-area electro-

[162] Mikhail A. Belkin, Federico Capasso, Feng Xie, Alexey Belyanin, Milan Fischer,
Andreas Wittmann, and Jérôme Faist. Room temperature terahertz quantum
cascade laser source based on intracavity difference-frequency generation. *Ap-
2919051. URL http://scitation.aip.org/content/aip/journal/apl/92/20/10.1063/1.2919051.

1002/lpor.200810030.

[164] D. McBryde, M. E. Barnes, S. A. Berry, P. Gow, H. E. Beere, D. A. Ritchie,
and V. Apostolopoulous. Fluence and polarisation dependence of gaas based lateral
1364/OE.22.003234. URL http://www.opticsexpress.org/abstract.cfm?URI=
oe-22-3-3234.

R. Huber, and T. Dekorsy. Photo-dember terahertz emitter excited with an er:fiber
1.3543627. URL http://scitation.aip.org/content/aip/journal/apl/98/2/10.1063/1.3543627.


[167] Chang-Hua Liu, You-Chia Chang, Seunghyun Lee, Yaozhong Zhang, Yafei Zhang,
Theodore B. Norris, and Zhaohui Zhong. Ultrafast lateral photo-dember effect in
graphene induced by nonequilibrium hot carrier dynamics. *Nano Letters*, 15(6):
4234–4239, 06 2015. doi: 10.1021/acs.nanolett.5b01912. URL http://dx.doi.
org/10.1021/acs.nanolett.5b01912.


