# IC1208 MCM7 & WG meeting 2016

# INTEGRATING DEVICES AND MATERIALS: A CHALLENGE FOR NEW INSTRUMENTATION IN ICT

 $14^{th} - 15^{th}$  April, 2016







Vilnius University Vilnius Lithuania

## Thursday, April 14

08:00-09:00	Registration			
09:00-09:10	Opening			
09:10-10:00	MCM meeting			
10:00-10:20	Thomas Maurer	Building a consortium around plasmomechanics		
10:20-10:40	Leonid Gurevich	Nanolab Facilities at AAU		
10:40-11:00	Coffee break			
11:00-11:20	Kristiaan Neyts	Light emission and lasing in liquid crystal devices		
11:20-11:40	Giusy Scalia	Electro-optic switching with liquid crystal graphene		
11:40-12:00	Daniel Budaszewski	Photonic crystal fibers infiltrated with liquid crystals doped with metallic ewski nanoparticles		
12:00-12:20	Katarzyna Rutkowska	Integrated optic devices based on liquid crystalline materials		
12:20-12:40	Jan Lagerwall	Changing the nature of the isotropic-cholesteric transition in suspensions of cellulose nanocrystals by tuning the ionic strength of the solvent		
12:40-13:00	Anna Spadlo	Biopolymers as alignment layer for liquid crystal mixture		
13:00-15:00	Lunch			
15:00-15:20	Christophe Blanc	Particles at Nematic Liquid Crystal Interfaces		
15:20-15:40	Peter Salamon	Measurement of spontaneous polarization in novel types of polar liquid crystal materials		
15:40-16:00	Katalin A. Gillemot	Aggregation dynamics of elongated particles confined at liquid surfaces or in nematic phases, a numerical model development		
16:00-16:20	Vladimir Venediktov	Special features of electro-optics of composites with liquid crystal		
16:20-16:40	Yuri Panarin	Spontaneous Mirror-Symmetry Breaking in Different non-Chiral Liquid Crystalline Systems		
16:40-17:00	Coffee break			
17:00-17:20	Joseph Marae Djouda	Angular Plasmon Response of Gold Nanoparticles Arrays: Approaching the Rayleigh Limit		
17:20-17:40	Balazs Szabo	Electro- and magneto-optical studies of colloidal suspensions of anisometric particles		
17:40-18:00	Antonio Ferraro	Terahertz Characterization of Metamaterial		
18:00-18:20	Ugo Cataldi	Plasmon-exciton interaction study carried out on elastomeric template covered with Gold Nanoparticles and Rhodamine-6g		
18:00-19:00	Free time			
19:00-22:00		Social dinner		

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08:30-09:00	Registration		
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09:20-09:40	Trinh Bich Hoang	Development of Love wave mode device for glucose detection	
09:40-10:00	Mario De Miguel Ramos	Transparent thin film bulk acoustic wave resonators	
10:00-10:20	Michael Schneider	Pure and doped piezoelectric aluminium nitride thin films and their applications in MEMS devices	
10:20-10:40	Dimitrios Zografopoulos	Low-loss flexible terahertz polarizers with high extinction ratio	
10:40-11:00	Ngoc Nguyen	A New Design Method for The Improvement of FBAR Quality Factor at Anti-resonance Frequency	
11:00-11:20	Coffee break		
11:20-11:40	Mara Bernardo	Recent developments in the synthesis and microstructure of multiferroic materials based on BiFeO3	
11:40-12:00	Felicia Gheorghiu	Multiferroic diluted magnetic oxides: The influence of iron addition on the functional properties of BaTiO3 ceramics	
12:00-12:20	Nikola Ilić	Improvement of electrical and electronic properties, polarization and magnetization of BiFeO3 by modification of synthesis route and chemical composition	
12:20-12:40	Branimir Bajac	Dielectric properties of multiferroic BaTiO3/NiFe2O4 multilayer thin films: Interface effects	
12:40-14:20	Lunch		
14:20-15:20	Excursion/Free time		
15:20-15:40	Francesco viscomi	Nano fabrication processes for innovative plasmonic systems	
15:40-16:00	Santiago Esconjauregui	ago Co-based catalysts for the growth of carbon nanotube forests with controlled chirality	
16:00-16:20	Michał Czerwiński	Physicochemical and electrooptical properites of new orthoconic ferro- and antiferroelectric liquid crystalline materials	
16:20-17:00	Closing and farewell coffee		

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# April 14, Thursday

## **Building a consortium around plasmomechanics**

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The Laboratory of Nanotechnology and Instrumentation in Optics has been created 20 years ago and developed a strong expertise in near-field optics, plasmonics as well as in nanofabrication. Recently, we started investigating the use of metallic nanoparticles for material surface strain monitoring. This emerging research activity strats to attract pioneering research groups in Europe and we started building a research network involving different partners like the University of Calabria and the University of Geneva. The aim for us is to build a consortium around this emerging topics and to find partners which desire to join our consortium and apply to european calls.

In this talk, I will briefly introduce the research activity of the LNIO and then I will mainly present the preliminary results that we obtained about plasmomechanics. The technological objective of our work is to develop colour-cahanging strain sensors based on plasmonic coupling between NPs. To achieve this objective, we have to adress several scientific challenges in terms of nanofabrication, sample design and instrumentation. I will thus strive to detail these challenges to maybe make you want to work with us.

## Nanolab Facilities at AAU

### Leonid Gurevich

Aalborg University, Department of Physics and Nanotechnology, Aalborg, Denmark

## Light emission and lasing in liquid crystal devices

### Kristiaan Neyts

ELIS Department, Ghent University, Ghent, Belgium

The light emission from within an anisotropic medium is influenced in polarization, spectrum and emission pattern. We have measured and numerically simulated light emission and lasing from dye-doped nematic and chiral nematic liquid crystal after optical excitation. Liquid crystal can also be used to modify the emission from Vertical Cavity Surface Emitting lasers. Finally, we discuss the alignment of semiconductor nanorods in an electric field. Individual nanords emit polarized light and when en ensemble of nanorods can be aligned parallel to a given axis, then the total emission is polarized to a high degree.

### Electro-optic switching with liquid crystal graphene

### **Giusy Scalia**

Luxembourg University, Luxembourg

Graphene oxide (GO) particles in aqueous dispersions can form liquid crystal (LC) phases at extremely low concentrations due to the extremely high aspect ratio of the flakes and noticeably, they possess an extremely large Kerr coefficient attractive for low power consumption electro-optic devices. Reduced graphene does not easily form LC phases in water due to its hydrophobic nature but here we show that stable dispersions of reduced graphene oxide can be realized with surfactants and that they exhibit birefringence upon shearing as well as under application of electric fields. The performance of the system is largely superior to GO LC possessing longer time stability and drastically improved electro-optic properties with an induced birefringence twice as large at the same field strength thanks to the almost recovery of graphene properties upon reduction.

## Photonic crystal fibers infiltrated with liquid crystals doped with metallic nanoparticles

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A preliminary results of spectral properties of photonic crystal fibers (PCFs) infiltrated with liquid crystals (LCs) doped with metallic nanoparticles (NPs) are reported.

LCs are materials with an unceasing interest, because of their exceptional properties as: electric field-induced reorientation of molecules, relatively broad range of optical anisotropies, or existence of spontaneous polarization in some types of LCs. All these properties made LCs to be broadly used in optoelectronic applications as e.g. LC display devices, LC fiber optics filters, attenuators, etc. Nevertheless, these devices are relatively slow in comparison to electroluminescent devices, and there is a need for improvement of their electro-optical response times. Over the last years, a lot of research efforts have been devoted to improve properties of LCs by doping them with different materials as: polymers, dyes, or carbon nanotubes [1-2].

Recently, there has been a growing interest in dispersing NPs in LCs. Even a small amount of metallic NPs should be sufficient to influence the dielectric anisotropy and threshold voltage of LCs [3]. The most common dopants are gold and silver NPs [4]. Both have been shown to improve electro-optical properties and increased thermal stability of LC. Combining the ease of physical properties tuning of LCs and structure of PCFs, a new type of fiber, i.e. Photonic Liquid Crystal Fiber (PLCF) was proposed over 10 years ago. These structures are characterized with an enhanced control of spectral, polarization, and guiding properties [5]. It appeared that the use of LCs as a infiltrating material greatly improved optical properties of PCFs.

In the following research work, we infiltrated an isotropic PCF 061221 (UMCS, Lublin, Poland) with 6CHBT nematic LC doped with gold NPs (MUT, Warsaw, Poland). Two different concentrations of gold nanoparticles were used: 0.1% and 1% wt/wt. The light propagation, electro-optical response to external electric field and thermal tuning through infiltrated PCF samples were analyzed. Obtained results were compared with properties of PCF infiltrated with pure 6CHBT LC.

- C. V. Rajaram, S. D. Hudson, L. C. Chien, "Morphology of Polymer-Stabilized Liquid Crystals", Chem. Mater. Vol. 7, pp. 2300-2308, (1995).
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## Integrated optic devices based on liquid crystalline materials

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Nowadays, the liquid crystal technology is a subject to many advanced areas of science and engineering. Specifically, a significant number of applications involving LC-based photonic devices have been successfully demonstrated in the area of telecommunications, optical data processing, sensing systems, free-space beam steering systems, and optoelectronic neural networks. Optically active and easily reconfigurable liquid crystalline structures and materials can be considered as a promising medium for the functional optical circuits. Liquid crystals at different phases and structures exhibit electro-, magneto-, acusto-optic, as well as opto-optic coefficients that are orders of magnitude higher than those of any other materials. Moreover, LC is the high-class nonlinear optical material, playing thus an important role in nonlinear optics and in having thus a great impact on information technology and industrial applications. While interaction between light and LCs can be used in many ways, the optical properties of photonic devices strongly depend on the particular liquid crystalline structure and/or material applied. Structures of nematic LCs (NLCs), as well as polymer stabilized LCs (PSLCs) in nematic, cholesteric and smectic phases may be considered as perfect candidates for possible applications in LC-based waveguides and other elements for integrated optical circuits.

Taking into account basic physical and chemical properties of LCs, and basing on a long-term experience of both research groups (in Rome and Warsaw) in development of LC-based photonic elements and devices, we have proposed a STSM aiming for a discussion of ideas and configurations of liquid crystalline structures and materials exhibiting special properties particularly dedicated for integrated optic circuits. In particular, we have aimed to discuss efficient methods (based e.g. on photo-orientation and photo-polymerization) to form liquid crystalline structures with particular spatial distribution of refractive index within in order to obtain functional elements typical for integrated optics (e.g. waveguides of different shape, logic gates, y- and x-junctions, switches, couplers, etc.). Such a solution allows for further miniaturization and simplification of the design, as well as its independence of external bias. The expertise of Prof. d'Alessandro's Research Team has been merged with that brought to Rome by Dr. Rutkowska towards a better understanding of prospective liquid crystalline photonic elements and devices for more stable, better controlled and adjustable linear and nonlinear waveguides. Nonlinear optical effects in liquid crystals, numerical methods for designing guided wave devices, fabrication technology and experimental tests on liquid crystal-based guided wave optical devices are the main subjects to be discussed in this communication.

## Changing the nature of the isotropic-cholesteric transition in suspensions of cellulose nanocrystals by tuning the ionic strength of the solvent

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While the interest from academia and industry in cellulose nanocrystals (CNC) is growing rapidly [1], our understanding of some of the fundamental processes that govern their ability to self-assemble into long-range ordered structures is still far from satisfactory [2-4]. This knowledge gap has applied importance, because many proposed schemes for exploiting CNC in advanced functional composites or cellulose films with structural color rely on the ability of cholesteric liquid crystalline CNC suspensions to self-assemble with a helical superstructure. Likewise, the transition into a kinetically arrested non-equilibrium state upon evaporation of the solvent plays a crucial role in utilizing the self-assembled arrangement. The questions at the heart of this knowledge gap are also highly stimulating from a fundamental soft matter physics point of view. Thus, the physics and physical chemistry of CNC suspensions has grown into a very fertile research field of modern physics, chemistry and materials science.

Here we demonstrate that the ionic strength of the solution in which the CNC nanorods are suspended is important not only for the helix pitch and onset concentrations for liquid crystalline order and kinetic arrest, respectively, but it also influences the nature of the isotropic-cholesteric phase transition [5]. The strong first-order character normally associated with lyotropic liquid crystalline colloidal suspensions is seen at low ionic strength, but as the ionic strength increases, whether due to added inorganic salt or to increased CNC surface charge, the barrier between isotropic and cholesteric phases appears to be weakened. The effect is strong enough that critical fluctuation-like scattering is seen towards the liquid crystalline end of the two-phase regime in case of high ionic strength.

Y. Habibi, L. Lucia, and O.J. Rojas, *Chem. Rev.*, **110**, *6*, pp. 3479-3500 (2010); S.J. Eichhorn *et al.*, *J. Mater. Sci.*, **45**, *1*, pp. 1-33 (2010); D. Klemm *et al.*, *Angew Chem Int Edit*, **50**, *24*, pp. 5438-5466 (2011); J.A. Kelly *et al.*, *Acc Chem Res*, **47**, *4*, pp. 1088-1096 (2014); M. Giese *et al.*, *Angew. Chem. Int. Ed.*, **54**, *10*, pp. 2888-2910 (2015)

<sup>[2]</sup> J.P.F. Lagerwall *et al.*, *NPG Asia Mater*, **6**, *1*, p. e80 (2014)

<sup>[3]</sup> J.H. Park et al., ChemPhysChem, 15, 7, pp. 1477-1484 (2014)

<sup>[4]</sup> C. Schütz *et al.*, *Langmuir*, **31**, *23*, pp. 6507-6513 (2015)

<sup>[5]</sup> C. Honorato-Rios et al., submitted to Frontiers in Materials (2016);

http://journal.frontiersin.org/researchtopic/3856/anisotropy-in-deformable-biomaterials

### **Biopolymers as alignment layer for liquid crystal mixture**

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Optical devices using liquid crystalline materials (LC) are important in the field of information and communication technologies. The deoxyribonucleic acid (DNA) and its derived materials with its unique properties derived from a double-helix structure are considered as a key materials for numerous application in photonics and organic molecular electronics, including: devices based on nonlinear optical effects, optical waveguides, holography, bioorganic field effect transistors or organic lasers [1-5]. The LC surface interaction with the double-stranded helical DNA aligned film is an interesting task for LC materials developers.

DNA as non-conventional alignment layers for LC materials can be good alternative in the field of biological cell detection using liquid crystals or to develop photonic devices based on biologic substances. Furthermore some applications of LC using substrate which require less curing temperatures, could be appropriate the use of this type of DNA as alignment layer.

A set of experiments have been performed modifying the alignment properties of commercial DNA in order to stabilize the layer and change its alignment properties. DNA sodium salt (DNA\_SS) and modified DNA - complexing it with a cationic surfactant used in this research was fabricated from the waste product of the salmon-fishing industry.

The precipitation of DNA with a cationic surfactant complex - hexadecyltrimethylammonium chloride (CTMA) make it soluble in organic solvents and additionally appears to be a stable material at high temperatures (up to 200°C) with no visible degradation of film. The DNA+CTMA solution preparation was done based on the procedure mentioned in Ref [6].

The DNA based biopolymer has been used to orient different types of LC molecules. LC mixture used: two commercial mixtures (MLC 6608 and MLC 13000 from Merck) and also a new experimental chiral nematic mixture (1823A with 3% of the chiral dopant) provided by Military University of Technology (MUT).

The electrooptical performance of various LC types with film of aligned double-stranded helical DNA are presented below at Fig.1.



Figure 1. Grey scale transmission of LC mixture. (a) Homogenous aligned cell obtained using MLC 13000 and DNA\_SS as alignment layer (b) Vertically aligned cell obtained using MLC 6608 and DNA+CTMA as alignment layer.

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### **Particles at Nematic Liquid Crystal Interfaces**

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Liquid crystal (LC) colloidal dispersions have been shown to promote complex ordered organizations due to the local distortion of the host by the particles and the resulting long-range elastic interactions mediated by the Frank elasticity. The key components responsible for these colloidal patterns have been well understood at the micron scale and are now increasingly studied at the sub-micron scale. One of the main challenges in order to design useful colloidal dispersions in a nematic however remains the fine control of the multipolar elastic interactions. The attractive components are indeed usually sufficiently strong to lead to a rapid aggregation of dispersed particles. We will first discuss some strategies to prevent this phenomenon in bulk.

We will also discuss the case of particles trapped at liquid crystal interfaces where the elastic interactions are strongly modified by the confinement [1,2] but also might compete with capillary interactions, as we detailed recently [3]. When confined at LC interfaces, spherical particles with homeotropic anchoring interact with repulsive interactions only, then forming regular arrays with large lattice parameters. When they are confined in a thin nematic film the colloidal behaviour is much more complex depending on the boundary conditions at the interfaces. For example we have shown that the capillary attraction expected for particles confined in thin films with hybrid anchorings is counteracted by the nematic texture and the presence of topological defects.

<sup>[1]</sup> M.A. Gharbi, M. Nobili, M. In, G. Prévot, P. Galatola, J.-B. Fournier, and Ch. Blanc, "Behavior of colloidal particles at an air/nematic liquid crystal interface", Soft Matter, 7, 1467-1471, (2011).

<sup>[2]</sup> M. A. Gharbi, M. Nobili, Ch. Blanc, "Use of topological defects as templates to direct assembly of colloidal particles at nematic interfaces", J. Colloid. Interface Science, 417,250 (2014).

<sup>[3]</sup> Jeridi Haifa, Gharbi M. A., Othman Tahar, and Blanc C., "Capillary-induced giant elastic dipoles in thin nematic films", PNAS, 112, 14771–14776 (2015).

## Measurement of spontaneous polarization in novel types of polar liquid crystal materials

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In the last few decades, organic chemistry provided many types of new molecules with different structures showing amazing, more complicated liquid crystal structures providing extraordinary properties not only for understanding in basic research, but also for future, mainly optical applications, because of their possible superior features, like faster switching time, better optical quality, lower power consumption, or bistability. Polar liquid crystals are candidates of being new materials for technological advancement, since their large spontaneous polarization offers a much stronger type of interaction with electric field than the dielectric anisotropy in the case of nematics. The goal of a Short Term Scientific Mission (STSM), the results of which are to be presented, is connected to the determination of this important material parameter, the spontaneous polarization, in newly synthesized, novel types of polar liquid crystal materials by measuring the current response to triangle shaped voltage signals (see Figure 1). The main objectives of the STSM were: (1) to create a fully automatized measuring system that outputs the precise value of spontaneous polarization as a function of temperature using Labview; (2) to test and validate the new setup and software using well known standard materials; (3) to use the system and perform the temperature-dependent measurements of the spontaneous polarization [1] in novel types of polar liquid crystal compounds, prepared in the host institution within the COST project. The results connected to all the above points will be presented.



Figure 1 A typical ferroelectric current response of the compound DL12/8, to a triangular voltage signal. The apparent peaks are due to the spontaneous polarization of the material.

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## Aggregation dynamics of elongated particles confined at liquid surfaces or in nematic phases, a numerical model development

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Designing stable liquid crystal (LC) composites is one of the main tasks pursued by several members of the IC1208 Cost action. Liquid crystal composites are however colloidal dispersions which have very specific properties compared to the usual colloidal dispersions in simple liquids. LC matrices give indeed rise to long-range attractive multipolar interactions between colloidal dispersions [1]. Strong dipolar interactions are mainly observed at large scale, but even at the nanometer scale the interactions between two nanoparticles are quadrupolar, weaker but often sufficient to yield aggregates in many systems [1]. Aggregation phenomena under such multipolar interactions are still not fully understood, so to get a deeper understanding we have considered a 2D model system describing the classical dynamics of elongated particles at a liquid interface.

When elongated particles are trapped at a liquid interface they distort it and then interact via quadrupolar capillary interactions. Furthermore the interactions between a group of already aggregated particles and a single one located at a large distance strongly depend on the spatial arrangement of the aggregated particles. This phenomenon is further complicated by the presence of possible direct solid-solid interactions, which would arise when the particles enter into contact and possibly freeze the aggregate shapes. Currently we are focusing on modeling the above described aggregation phenomena by developing a numerical code that is sufficiently accurate in order to catch the many-body interactions mentioned above in a simple way. Once this is achieved extensive comparison with experiments will be possible and the model system may be used to address open questions arising from the experiments. Our model is based on the 2D solution of the Young-Laplace equation to gain the forces acting on the particles, then moving each particle individually by solving the Newton equations based on classical discreet element methods. In this presentation I would like to give an insight into the current state of the development of the numerical model and our future objectives.

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# Special features of electro-optics of composites with liquid crystal

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The review paper considers the basic features of structuring the composite liquid crystalline media and their classification with regard to the percentage of liquid crystal (LC) and polymer. We have carried out the comparison of properties of such media with the homogeneous LC media. We have also analyzed the possibilities of using such media in the opto-electronic devices. It was shown that for the low (less than 10%) concentration of monomer in the composite medium its polymerization produces the grid with the thin walls. This grid splits the LC volume into separate domains with the uniform orientation in the volume. The layer elasticity grows up; the relaxation time reduces. However, the devices with such composites are usually working with the polarized light and employ approximately the same principles as the devices, filled by the pure LC media. However, the splitting of the LC volume into the relatively independent domains makes it possible to design the polarization-independent devices, employing the scattering effects. The increase of the relative content of monomer makes it possible to create the porous matrix, containing the mutually isolated drops of LC. There are two sorts of such devices. In the first case the switched-off device scatters the light of any polarization, and application of the electric field makes them transparent. In the second case, known as the reverse mode devices, the use of special technology makes it possible to switch the properties of switched-off and switched-on devices. Main advantages of the composite media are the polarization independent behavior, mechanical strength and short relaxation time, while main disadvantages are the higher energy consumption, relatively strong non-polarized losses and much lower contrast. In the paper we consider the approaches to the contrast increase. Finally, we consider the possibilities of comprising the composite media with the biaxial LC media.

## Spontaneous Mirror-Symmetry Breaking in Different non-Chiral Liquid Crystalline Systems.

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Spontaneous Mirror-Symmetry and appearance of chiral self-assembled superstructures in non-chiral systems represents a fascinating field of contemporary research with potential applications. For long time the formation of helical superstructure was associated with enantiomeric chiral molecules. Later on Pasteur showed that that the racemic mixtures of chiral molecules can resolve spontaneously into two chiral forms. Such deracemization or symmetry breaking in racemic mixtures was observed during crystallization. In recent years interest in mirror-symmetry breaking extended to soft matter systems.

Recently mirror-symmetry breaking was observed even in non-chiral systems. Special progress in this field was made in achiral liquid crystalline phases formed by bent-core molecules which form two types of chiral conglomerates with opposite sign of spontaneous polarization [1] and very short pitch helical superstructures [2] which show fast electrooptic response and V-shape switching shown in Figure 1.



Figure 1. Oscilloscope screenshots of (a) linear ( $\alpha$ = $\theta$ ) and (b) quadratic (V-shape) ( $\alpha$ =0) electro-optical response of 8µm planar LC cell at 105 °C

Later on mirror-symmetry breaking was observed in bent-shaped (or twist-bent) nematic dimers [3], which also form short pitch helices [4]. Finally the chiral separation was reported even in achiral isotropic liquids [5]. Herein we report recent results on symmetry breaking in different LC systems: bent-core smectics; twist-bent nematics; and even in de Vries SmA phase. The physical reasons for the symmetry breaking in these systems will be discussed.

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### Angular Plasmon Response of Gold Nanoparticles Arrays: Approaching the Rayleigh Limit

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### Introduction

The behaviour of a diffraction grating is governed by the so-called grating equation that is a simple relationship between incidence  $\theta_{inc}$  and diffracted  $\theta_{diff}$  angles, wavelength of the impinging light  $\lambda$  and grating pitch  $\Lambda$ .

Under certain conditions, typically when  $\lambda >> \Lambda$ , no radiative diffracted orders exist but only evanescent ones, and the system is defined as a sub-wavelength grating (SWG) [1]. In case a SWG is made of metallic stripes or nanoparticles, a peculiar behaviour emerges where the presence of the grating influences spectral position and shape of the excited plasmon modes.

In this work, we have designed and fabricated an array of Au nano-cylinders to operate in SWG configuration. The grating has been characterized by performing angular resolved extinction measurements. These angle measurements allow the progressive analysis of several plasmon modes that have been excited. A complete analysis of these excited plasmon modes and their origin has been possible by comparing obtained experimental results with theory. Numerical simulations have been performed on both isolated particles and arrays and confirm both the observed behaviour and proposed interpretation.

### **Results and Discussion**

A 2D array of gold monomers was deposited by electron beam lithography on an ITO (Indium Tin Oxide, 30nm thick) coated glass. The array consists of Au nano-cylinders (200nm diameter, 50nm height) with a (center-to-center) pitch  $\Lambda_x = \Lambda_y = 300$ nm. Figure 1a shows a SEM picture of the fabricated sample. A confocal transmission set-up, with angle resolved measurement possibility, was used for the optical characterization of the sample. An illumination part, a sample holder and a collection part compose the set-up. All the parts are mounted on a rotating stage to allow the maximum flexibility during measurements (Figure 1b).

More interestingly, a new mode, different than both dipolar and quadrupolar ones, can be noticed in the spectra at  $\lambda \sim 570$ nm (**Figure 2b**). This peak is already visible at  $\theta_{inc}=25^{\circ}$  and can be attributed to a vertical out-of-plane mode corresponding to the excitation of a plasmon oscillation in the direction along the height of the nano-cylinders. Indeed, it is reliable to consider that, in the TM mode only, the exciting field has a  $sin\theta_{inc}$  component that is exactly parallel to this direction. Moreover, from the graphs it is visible that the amplitude of this mode is directly proportional to the incidence angle that matches well with the monotonously increasing behaviour of  $sin\theta_{inc}$  in this angular interval. Both these arguments suggest that the observed mode is exactly the vertical one. In our knowledge,

this is the first time that this mode has been observed while performing this kind of measurement.



Figure 1: (a) SEM image of the grating of Au NPs, the scale bar is  $1\mu m$ . The experimental set up is presented in (b).



Figure 2: Extinction measurements resolved in angle in TE (a) and TM (b) polarization.

### **Conclusions and/or Outlook**

In this work, angular resolved extinction measurements have been performed on a 2D sub-wavelength grating made of an array of Au nano-cylinders. Exploiting this experimental approach, several plasmon modes have been excited that are usually not observed at normal incidence. The appearance and behaviour of these modes is strongly related to the incidence angle. In particular, by increasing the angle, a red-shift of the dipolar peak is observed that has been interpreted by using a semi-quantitative approach. Numerical simulations have been performed on both isolated particles and arrays and confirm both the observed behaviour and proposed interpretation.

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# Electro- and magneto-optical studies of colloidal suspensions of anisometric particles

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The optical answer for an external electric or magnetic field in nanorod suspensions was extensively studied in the past years by the host institution in Magdeburg [1, 2]. Phase separation in electric fields and homogenisation dynamics was studied [2]. Recently, they explored the magnetic field induced birefringence of the nanorod suspensions doped with magnetic nanoparticles, and found that the birefringence saturates at above 500 mT, and its final value is proportional to the concentrations of nonmagnetic nanorods and magnetic particles.

During my Short Term Scientific Mission (STSM) between 6<sup>th</sup> September and 4<sup>th</sup> October 2015, I investigated the magnetic properties of the same nanorod suspensions (called Novoperm Carmine) without magnetic nanoparticles, and started similar measurements on a new type of anisometric nanoparticles called Permanent Rubin.

The pure Novoperm Carmine samples showed an increase in the birefringence on increasing the magnetic field. For the pure Permanent Rubin suspensions however, the opposite sign was observed. In this case the change in the birefringence was significantly larger, and the magneto-optical effect was clearly visible. The Permanent Rubin suspensions were also doped with magnetic nanoparticles. For this material, the final value of the birefringence was reached at a lower magnetic field, and this value was not proportional to the magnetic nanoparticle concentration.

The pattern formation was also investigated for the (pure) Permanent Rubin suspensions under AC electric field, as shown on Figure 1. Compared to the Permanent Rubine, this sample showed a new pattern at intermediate amplitudes. The phase diagram was recovered for a wide range of frequency and amplitude values.



Figure 1: The observed optical patterns for the Permanent Rubin sample, applying an AC electric field of a constant 200 Hz frequency and an increasing amplitude (2.4, 4.08, 5.76, 8.4 and 14.4 V/µm, from left to right).

Some of these results were already presented on a poster at the meeting called "3. Kolloquium des SPP 1681" in October 2015 in Benediktbeuern, Germany.

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## **Terahertz Characterization of metamaterial**

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In the last decade, the research interest on the scientific field of terahertz (THz) technology has drastically increased trying to fill the so-called THz gap. The reason of this wide interest is being related to the particular properties of material in this spectral frequency region that provide a variety of application and opportunities in various field [1]. The properties of liquid crystals, already used specially in optical regime, were used to fabricate terahertz switchable device. Novel liquid crystal with high birefringence and low absorption are synthetized [2] in order to reduce the thickness of the device and hence the loss.

Based on theoretical simulations performed in our research group [3], I fabricated a THz electrically tuneable fishnet metamaterial device, the latter is composed of nine chips with different patch size, W, and interconnecting stripe width, w.



Figure 1: Fishnet Metamaterial unit cell

Figure 1 shows the unit cell of the proposed device that was infiltrated with dual frequency liquid crystal (DF-LC) provided by Prof. Dabrowski's research group (Military University of Warsaw). A DF-LC is a special liquid crystal where its parallel dielectric constant depend on the frequency of the applied voltage. In particular, at low frequency, 1KHz in our case, the  $\Delta \varepsilon$  is positive while at high frequency, 50KHz, is negative. This liquid crystal allows us to rotate the director by changing the apply voltage frequency. In the simulations the parameters of a nematic LC with high birefringence were used instead of the one of DF-LC. Unfortunately, for all the chips, by changing the frequency I cannot observe a large shift of the resonance as expected from the simulations: because the device does not have an alignment layer, we only exploit a fraction of the total birefringence. However, the resonance peaks are in the expected position, their position moves by changing the patch size and interconnecting stripe width parameters as expected from the simulations.

In conclusion, the results obtained during my STSM give us confidence that we are following a correct route to the fabrication of a tuneable THz device operating in the THz frequency range.

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# Plasmon-exciton interaction study carried out on elastomeric template covered with Gold Nanoparticles and **Rhodamine-6g**<sup>[1]</sup> <u>U. Cataldi</u><sup>1</sup>, G. Strangi<sup>2</sup>, J. Bierwagen<sup>1</sup>, T. Buergi<sup>1</sup>

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A tunable plasmon-fluorescent elastic pad was realized using a Polydimethylsiloxane (PDMS) template covered with gold-nanoparticles (GNPs) and Rhodamine 6g. By increasing the size of particles, through chemical growth processes, and by applying mechanical strain, we found a red-shift of plasmon resonance and increasing of fluorescence by applying mechanical strain.



Figure1: Absorption and fluorescence spectra at rest and under stretching with gold GNPs not grown (a) and after 9 cycles of growth (b); Lifetime acquisition under stretching with GNPs not grown (c) and after 9 cycles of growth (d); Behaviour of peak areas of fluorescence during the growth of GNPs and under mechanical strain (e).

[1] submitted

# April 15, Friday

## Non-Volatile Resistive Switching Memories based on Nanoscale Hybrid Materials

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We report our recent results on the fabrication and electronic characterization of two types of hybrid nonvolatile resistive memories. The first resistive memory, shown schematically in Fig.1a, consists of vertically aligned ZnO nanorods embedded in a polymer PMMA material. The ZnO nanorods are grown using a novel ultra-fast microwave heating method, which permits growth of the nanorod layer in just a few minutes. The nanorods are approximately 500 nm in length with diameters of 40-50 nm. Typical current voltage sweeps made on the devices are shown in Fig. 1b. The resistive memory exhibits reliable and reproducible bipolar resistive switching at low switching voltage and with low power usage and do not need a forming step to initiate switching in the devices. We attribute these properties to a combination of the high aspect ratio of the nanorods and the inclusion of the insulating polymer material in the device structure [1]. Devices made without the PMMA layer in contrast exhibit unpredictable changes in current during a single I-V sweep and have erratic changes in the Set and Reset voltages. The second type of device we report on is instead based on metal nanoparticles. These are distributed randomly throughout a PMMA layer which is sandwiched between gold crossbar electrodes. These devices exhibit optimal switching at surprisingly low nanoparticle concentrations. Similar to the nanorod based devices the nanoparticle resistive memories have low Set and Reset voltages and do not need a forming step for initialization. The nanoparticle approach however has the advantage that much higher resistance on/off ratios can be achieved. The fabrication of both types of devices is extremely easy and fast and uses simple inexpensive equipment with patterning possible over large areas, characteristics that make them well suited for use in low cost memory applications.



Figure 1 (a) Crossbar memristor device based on vertically aligned ZnO nanorods embedded in PMMA. (b) Typical current voltage characteristics for the device in (a) showing a pinched hysteresis loop and low voltage switching.

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## Development of Love wave mode device for glucose detection

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Acoustic wave devices are currently used for telecommunication and sensor applications. Recent investigation proved that such devices can be used as biosensors not only in air but also in liquid environments. One of the acoustic wave sensors is a Love wave delay line device which incorporates piezoelectric layer, metallised interdigital transducers (IDT's) and piezoelectric guiding layer deposited on top of the structure. This guiding layer confines a shear horizontal wave created by the IDTs. The guiding layer of the stack has to be of optimum thickness in order to achieve high sensitivities. The sensitivities of such devices also frequency dependent, meaning that the device operating at higher frequencies will exhibit higher sensitivities. This work targets the glucose detection device which could be produced by standard photolithography techniques.

In this work a 3D-finitite element modelling (FEM) using COMSOL and analytical calculation has been used to perform the optimisation of the Love wave delay line device. Analytical calculations were based on the dispersion equation for anisotropic piezoelectric substrate. Using these simulation tools key device parameters such as electrode width, guiding layer thickness, number of electrodes and have been defined.

A 3D FEM simulation tool permits an incorporation of various thickness layers to be deposited on top of a guiding layer in between the transducers. In such way the phase change can be monitored and the device phase mass sensitivities can be estimated. Simulation of Love wave device predicts high enough phase mass sensitivities needed for the direct detection of glucose on the functionalized Love wave mode device surface.

The specificity of Love wave device is defined by the type and chemistry of the immobilised layer. For the glucose detection application it was developed a protocol where Concanavalin A (ConA) is immobilised on the surface of quartz (SiO<sub>2</sub>). Accordingly, the surface after treatment was modified with the hydroxyl groups prior to silanisation process, and ConA was immobilised via the stable amide bonds between amine group and the carboxyl group functional silane.

The functional assessment of immobilised ConA on  $SiO_2$  by fluorescence method confirmed that the immobilised ConA has the ability to bind the glucose. The structural assessment using atomic force microscope (AFM) were performed and has also proved that a layer of globular molecules has covered the surface of quartz after immobilisation.



Figure 1: Schematics diagram of Love wave device

### Transparent thin film bulk acoustic wave resonators

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Transparent electronics have interesting applications in the field of electronic consumables. Wearable devices, intelligent windows or new concepts of smartphones and screens could certainly benefit from the integration of fully transparent devices on different substrates. Film bulk acoustic wave resonators (FBARs) have demonstrated their usefulness in different areas, from communication filters [1] to high sensitivity sensors [2]. Modifications in their fabrication process to make them fully transparent while maintaining a good performance could lead to a new generation of devices.

In this work we present fully transparent FBARs with a solidly mounted resonator (SMR) structure. A 0.6 mm-thick Corning Glass<sup>®</sup> was used as substrate. The acoustic reflector was made of 7 alternated layers of SiO<sub>2</sub> and Ta<sub>2</sub>O<sub>5</sub>. A 250 nm-thick layer of sputtered Indium Tin Oxide (ITO) was used for both the top and bottom electrode. Alu-



Fig. 1: Frequency response of the transparent resonator (a) and photograph of a sample containing a set of transparent devices placed on top of a retro-illuminated display (b).

minum nitride (AlN) was the chosen piezoelectric material, which also presents a high optical transmittance. To improve the response of the devices, in some samples a 100 nm-thick capping layer of room-temperature growth AlN was used to prevent the direct contact of the active layer with the ITO electrode.

The SMRs displayed a resonant frequency  $f_r \approx 1840$  MHz, a quality factor Q around 100, and an electromechanical coupling coefficient  $k^2$  up to 4% while keeping a good transparency when placed on a retro-illuminated display, as shown in figure 1. Even though the performance of the devices should be improved, these results are a promising first step in the integration of fully transparent BAW resonators.

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## Pure and doped piezoelectric aluminium nitride thin films and their applications in MEMS devices

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The group III–V material aluminium nitride (AlN) is frequently used in micro and nano electromechanical devices and systems (MEMS/NEMS) due to its compatibility with CMOS technology [1]. In addition, AlN features high thermal and electrical stability, but only moderate piezoelectric coefficients [2]. Given the current trend towards continuous miniaturization of MEMS devices, a decrease of the film thickness of the active AlN thin film is required while keeping at the same time the piezoelectric properties as high as possible.

The piezoelectric coefficient  $d_{33}$  is increased by about 20% by introducing an inverse sputter etching step of the silicon substrate prior to thin film deposition. This effect is attributed to the forming of an amorphous silicon interface layer by the ion bombardment and thus the introduction of a large number of structural defects as well as the removal of the silicon crystal information [3]. In order to increase the potential of AlN based MEMS even further, both piezoelectric coefficients  $d_{33}$  and  $d_{31}$  are increased significantly by doping of AlN with high concentrations of scandium [4]. The synthetization of  $Sc_xAl_{1-x}N$  is done on wafer level for a fixed value of x = 27% using reactive dc magnetron sputtering of an alloyed  $Sc_{0.3}Al_{0.7}$  target. Variation of deposition parameters allows the deposited thin films. The piezoelectric properties are measured both averaged over a large number of grains by laser Doppler vibrometry (LDV) in combination with finite element analysis as well as locally using piezo force microscopy (PFM).



Figure 1: ScAlN based vibrational energy harvester.

Figure 2: Q-factor of roof tile-shaped modes in deionized water.

Figure 1 shows a vibrational energy harvester, which was characterized using external acoustic excitation. The device has been manufactured with pure AlN as well as  $Sc_xAl_{1-x}N$  (x = 27%) of lower and higher quality. The output power of the device is between 10 and 25 nW/g<sup>2</sup> normalized to earth's acceleration g. The device based on high quality  $Sc_{0.27}Al_{0.73}N$  showed an increase in output power of approximately 100% compared to pure AlN, which correlates well with the measured increase in the piezoelectric coefficients, given an increase in dielectric constant from ~10 to ~15 for pure AlN and  $Sc_xAl_{1-x}N$  (x = 27%), respectively.

Figure 2 shows the quality factors of MEMS resonators based on pure AlN thin films similar to Figure 1 in deionized water for different orders of root tile-shaped modes [5]. These resonators feature optimized electrode designs, tailored to each mode shape individually, and show extremely high quality factors in water compared to literature. This excellent performance makes this new type of resonance mode an ideal candidate for liquid monitoring applications in portable systems or "on board" technical systems, such as automobiles or aircrafts.

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### Low-loss flexible terahertz polarizers with high extinction ratio

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Wire-grid polarizers constitute a traditional component for the control of polarization in free-space devices that operate in a broad part of the electromagnetic spectrum. Here, we present the design and fabrication of an aluminum-based THz wire grid polarizer, demonstrated on a sub-wavelength thin flexible and conformal foil of the cyclo-olefin Zeonor polymer [1]. The device is characterized by means of THz time-domain spectroscopy, performed on both flat and curved configurations. A high extinction ratio between 40 and 45 dB in the 0.3-1 THz range and in excess of 30 dB up to 2.5 THz is demonstrated. The insertion losses are lower than 1 dB and almost exclusively stem from moderate Fabry-Perót reflections, which disappear at discrete frequencies. The polarizer can be easily fabricated with low-cost techniques such as roll-to-roll and/or large-area electronics processes and promises to open the way for a new class of flexible and conformal THz device, for use in applications such as secure short-range communications, defense and security [2], or explosive and drug detection [3].



Figure 1: a) Comparison of experimental measurements and numerical results of the ER and IL for the THz WGP with a pitch of 10 µm and a filling ratio of 68% for normal incidence. b) Experimental investigation of the ER and IL for the THz WGP in two bending configurations.

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## A New Design Method for The Improvement of FBAR Quality Factor at Anti-resonance Frequency

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Bulk acoustic wave (BAW) filters offer higher selectivity, lower loss, smaller size, less sensitivity to temperature change, better power capability and good compatibility with standard IC technology at RF range above 2GHz compared to conventional filters. They are therefore well suited for satellite and mobile telecommunication applications. Because of these reasons, thin Film Bulk Acoustic Resonator (FBAR), a member of BAW family, becomes a promising candidate for future filter technology. Applications such as 3G or 4G/LTE require highly selective filters in order to prevent signal path interference. It means the filter must possess very steep skirts and low loss, which poses an urgent demand for excessively high quality (Q) factors for its core FBAR elements. To fulfill such demand, the resonator needs to be further optimized to provide better Q factors.

This work focuses on the optimization of 2 GHz-ranged FBARs for filter applications. The idea is that if the resonator geometry is carefully modified, by adding to its periphery a so-called frame structure, laterally leaking Lamb waves can be prevented (Fig.1). In this way, energy loss is reduced and Q factors consequently increase. The power of this frame design lies in its working principle as a lateral Bragg reflector. This reflector is not a traditional one for it is able to reflect two Lamb modes with two different wavelengths at the same time. This design is targeted for increasing the Q factor at anti-resonance frequency ( $f_a$ ) at which the resonator is more vulnerable to Lamb waves. At fa, there exist at least four Lamb modes, two lowest order symmetric (S0, S1) and two lowest order anti-symmetric (A0, A1) modes. In order to determine which modes need to be reflected at the periphery, i.e. they cause more loss to the system, mode power analysis based on Poynting theorem is carried out. The simulation results show a significant improvement in Q value at  $f_a$  (QzB values in Fig.1) and a slightly increase in Q value at resonance frequency ( $f_s$ ) for the optimized resonator compared to the traditional FBAR with no frame.

The method, although has obvious advantage in providing better Q factors, comes with a rate. The trapped Lamb waves definitely cause a generation of more unwanted lateral resonances which parasite on the resonator electrical characteristic. This phenomenon is more pronounced at resonance frequency. As a result, stronger ripples appear in the filter passband making it less even, especially at the region near its left-handed skirt. The disadvantage can be overcome by apodizing the shape of the FBAR top electrode in a way that no parallel edges can coexist to avoid the same lateral resonance path length.



Fig. 1. 2D schematics and frequency responses of a traditional FBAR (a) and a frame-designed FBAR (b)

## Recent developments in the synthesis and microstructure of multiferroic materials based on BiFeO<sub>3</sub>

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The purpose of this contribution is to present the most relevant results of one of our research lines which is focused on the preparation of magnetoelectric multiferroic materials for Information and Communication Technologies applications. In this kind of materials, the coupling between the ferroelectricity and ferromagnetism provides an extra degree of freedom that enables the control of magnetization through electric fields as well as switching the polarization by magnetic fields. Namely, our work during the last few years has targeted the preparation of materials based on BiFeO<sub>3</sub> which is one of the very few known single-phase multiferroic oxides (i.e. ferroelectricity and ferromagnetism arose within the same phase). This compound has a rhombohedrically distorted perovskite structure and high phase transition temperatures that make possible to use it as a room-temperature multiferroic. However, the synthesis of BiFeO<sub>3</sub> as a pure phase is very tricky and, in practice, the functional response of the BiFeO<sub>3</sub> materials is usually not suitable for practical applications since the leakage current is too high and they show an anti-ferromagnetic response. Doping with certain cations in the A or B positions of the perovskite structure is one of the most commonly resorted strategies in order to avoid these problems and improve the multiferroic response of these materials. We have studied the effect of different donor doping ions finding out Ti<sup>4+</sup> as one of the most promising. HRTEM studies evidence that the Ti-doped BiFeO<sub>3</sub> materials develop a peculiar nanostructure as a result of the titanium tendency to segregate out of the perovskite. This nanostructure consists in crystallographic domains of ~ 50 nm in size in which the titanium ions are mainly located at the interfaces. Moreover, our results demonstrate that the improvements in the ferroelectric and magnetic response of the Ti-doped materials lie in the observed nanostructure: the titanium rich interfaces behave as resistive layers that decrease the macroscopic conductivity of the materials while the existence of crystallographic domains of 50 nm in size gives place to a frustrated anti-ferromagnetism with huge coercive field values.

## Multiferroic diluted magnetic oxides: The influence of iron addition on the functional properties of BaTiO<sub>3</sub> ceramics

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The research field of dilute magnetic oxides (DMO) has a great interest in the last years as attractive materials for spintronics and different magnetoelectric devices [1,2]. In the present study, BaTi<sub>1-x</sub>Fe<sub>x</sub>O<sub>3</sub> ( $0 \le x \le 0.02$ ) ceramics have been synthesized by solid state reaction technique. The structural, microstructural and functional properties of BaTi<sub>1-x</sub>Fe<sub>x</sub>O<sub>3</sub> ceramics were investigated and discussed. X-ray diffraction analysis indicated that higher doping level of Fe, higher sintering temperature and longer sintering time promoted the formation of hexagonal phases in Fe-doped BaTiO<sub>3</sub> ceramics. The composition with  $x=0\div0.015$  presents a tetragonal crystalline symmetry, while a superposition of tetragonal and hexagonal phases was found for x=0.018 and 0.02. SEM analysis indicates a heterogeneous microstructure with a small degree of porosity (relative densities are above 94% for all samples) and a bimodal grain size distribution, consisting of larger grains with an equivalent grain size of ~15-18 µm and of smaller grains of~ 4-8 µm. Dielectric properties in the frequency range (20Hz-2MHz) showed that all the Fe-doped  $BaTiO_3$  ceramics have some anomalies. The dielectric permittivity maximum vs. temperature presents a decrease around the ferroelectric-paraelectric phase transition from  $127^{\circ}$ C for pure BaTiO<sub>3</sub> to ~85°C for x=0.02. Using impedance spectroscopy, we can easily separate the contribution from the grain or grain-boundary. It was observed that by Fe doping, the complex impedance plot indicates more than one semi-circle, demonstrating that ceramics have a local electrical heterogeneity, even they look homogeneous from structural and compositional point of view. The EPR analysis for the composition x=0.005 supports the X-ray diffraction results, since the observed Fe<sup>3+</sup> spectrum corresponds to tetragonal Fe-doped BaTiO<sub>3</sub>. It was found that paramagnetic Fe<sup>3+</sup> ions reside at the Ti lattice sites. The presented results have indicated that the  $BaTi_{1x}Fe_xO_3$  system can be considered as a possible candidate for modern electronics applications and functionalized materials.

Acknowledgements: The collaborations in the frame of COST IC1208 Action are highly acknowledged. This work was financial supported by MEN-UEFISCDI project no. PN-II-PT-PCCA-2013-4-1119.

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## Improvement of electrical and electronic properties, polarization and magnetization of BiFeO<sub>3</sub> by modification of synthesis route and chemical composition

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Bismuth ferrite is a material well known for its potentially remarkable high-temperature multiferroic properties ( $T_{\rm C}$ ~1103 K,  $T_{\rm N}$ ~643 K [1]), but it is still far from being used in devices. Many attempts are being made in overcoming problems with appearance of impurity phases, small specific surface area (powders) and density (ceramics, thin films), large leakage currents and small ferromagnetic response. Structural transitions induced by change of particle/grain size [2] and average size of A-site ion [3], and introduction of magnetic elements [4] were reported to rise electrical resistivity and enabling exhibition of ferroelectric and ferromagnetic properties.

Bismuth ferrite powders were synthesized by chemical methods from solution. Synthesis parameters were modified and their influence on phase composition investigated. Thermal treatments were taken at minimal possible temperatures and times in order to keep crystallites as small as possible. Only auto-combustion synthesized powders with glycine as a fuel was completely crystallized in rhombohedral perovskite lattice without thermal treatment. Substitution of Bi<sup>3+</sup> and Fe<sup>3+</sup> ions with other elements led to higher electrical resistivity of ceramic samples, which is illustrated with impedance measurements for Y<sup>3+</sup> doped BiFeO<sub>3</sub> samples in figure 1. Thanks to improved resistivity, for many of doped samples it was possible to measure ferroelectric hysteresis loop, for which undoped BiFeO<sub>3</sub> was too conductive. Dopants have also prevented excessive grain growth, lowered the energy band gap, facilitating possible visible light activated photocatalytic uses and in some cases introduced enough distortion in magnetic spin structure to arise weak ferromagnetism.



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## Dielectric properties of multiferroic BaTiO<sub>3</sub>/NiFe<sub>2</sub>O<sub>4</sub> multilayer thin films: Interface effects

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With development of modern science a number of new materials with advanced and multifunctional properties expanded possibilities in microchip industry. A novel group of multiferroic materials have found a special application in field of microelectronics due to their unique ability to exhibit more than one ferroic property. The aim of this research was to inspect the dielectric properties of thin films, explore interfacial effects between different phases and its contribution to relative permittivity in range of frequencies and temperatures.

This research, represents characterization of multilayer thin film structures based on ferroelectric BaTiO<sub>3</sub> and ferromagnetic NiFe<sub>2</sub>O<sub>4</sub> phase. The multiferroic thin films were obtained by spin coating of different layers in specific order on platinum coated silicon substrates, finally sintered on 750 °C for 30 min. The thickness of all samples was below 1 $\mu$ m, with defined layered structure, flat and crack-free surface. Interfacial effects have shown complex influence on values of relative permittivity on lower frequencies, characteristic for Maxwell-Wagner relaxation, which is noted to be more pronounced on higher temperatures. Overall, relatively low values of relative permittivity have been recorded due to nanosized microstructure, with no phase transitions in inspected temperature range, up to 200 °C.

## Nano fabrication processes for innovative plasmonic systems

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A new nano-fabrication process for a plasmonic based stress sensor is proposed. The system is made of a regular array of coupled gold nanoparticles onto a flexible substrate (PDMS). A previous attempt with negative resist electron-beam-lithography (EBL) and focused-ionbeam (FIB) showed that it is possible to pattern such a challenging substrate. Unfortunately, a strong inclusion of Ga+ ions has been observed. This residuals, due to the FIB milling process, negatively influence the optical response of the system annulling, de facto, the progresses made with the nano fabrication process. The FIB is a slow, expensive and low throughput technique as well, all these factors limits the spatial extension of the device making it difficult for future applications. In order to solve these problems, a new fabrication approach, based on hard masking and reactive ion etching (RIE), is presented with related experimental difficulties faced.

The second system described here is the fabrication process for novel plasmonic antennas based on metal-dielectric multi-layers. It has been shown that these "confined" hyperbolic materials can exhibit complex optical behaviour. The optical properties of such systems depend on the effective index of the multilayer stack, therefore allowing for a whole new range of optical phenomena to be explored, including the highly sought after epsilon near zero and negative epsilon regimes [1]. Preliminary FEM calculations on specific geometries performed by Dr. J.-S. Bouillard already show evidence of epsilon near zero behaviour. All these systems exhibit great physical properties, as well as possible commercial applications, but their fabrication is long and difficult. To make the devices production easier, some tests with nano imprint lithography (NIL) are going to be carried out soon. The fabrication of molds for the (NIL) has been made in parallel.

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Co-based catalysts for the growth of carbon nanotube forests with controlled chirality

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Bi-metallic nanoparticles are reported to be more catalytically active towards the synthesis of carbon nanotubes by chemical vapour deposition, and are considered one of the possible routes to control nanotube chirality in bulk quantities. Herein, we systematically study different combinations of evaporated films of Co and Nb to grow nanotube forests. Our results show this novel catalyst system is able to nucleate and grow nanotubes at temperatures as low as 380C. This is of utter importance as low temperatures minimise nanoparticle aggregation and further deactivation. Equally important, low temperatures are necessary for nanotube integration into various technologies such as microelectronics and sensors. In-situ photo-emission analysis during catalyst preparation shows that, in the presence of Nb, the Co films restructure into catalytically active nanoparticles at much lower temperatures than the pure Co counterpart. Such results may pave the way to controlling the arrangement of carbon atoms along the longitudinal axe of the tubes.

## Physicochemical and electrooptical properites of new orthoconic ferro- and antiferroelectric liquid crystalline materials

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It is still suggested that antiferroelectric smectic liquid crystals may provide an alternative to nematic liquid crystals commonly used in display, due to their shorter response times and properties promising passive addressing capabilities [1]. Surface stabilized structured (SSAFLC) formed with regular ALFCs exhibit low optical contrast at the electrooptical switching (when placed between crossed polarizers) due to a poor dark state. In orthoconic antiferroelectric liquid crystals (OAFLCs) the molecular tilt of is saturated at the angle  $\theta = 45^{\circ}$ . Such a liquid crystalline medium is optically negative with the optical axis in plane of the smectic layers [2, 3]. At the surface stabilized structure SSOAFLC, for a light beam at an angle of incidence parallel to the smectic planes, act as an optically isotropic medium, providing a perfect black state when placed between crossed polarizers. Structural defects do not deteriorate the dark state which is near perfect. The contrast observed for SSOAFLC depends practically on the quality of used polarizers. Such uniaxial properties are observed only under certain conditions, namely when the cone angle (double molecular tilt -  $2\theta$ ) does not differ from the orthoconic angle by more than 3 degrees. If the cone angle is smaller, a drastic decrease in contrast is observed [1]. Although the OAFLCs solve the contrast problem, the other obstacles for their common applications still remain or even increase. A big asymmetry between  $\tau_{on}$  and  $\tau_{off}$  switching times are observed which are even much bigger than those for nematic materials or than in non orthoconic materials. This effect is strictly connected with the balance between synclinic-ferroelectric (F) and anticlinic-antiferroelectric (AF) state. There are known two methods to limit huge asymmetry of switching times. One is connected with a special driving technique based on a reverse electric field pulse application [4]. Second method to solve problem with metastable F-state in AFLCs is polymer-stabilisation of the orthoconic state [5]. In the present talk, it will be discuses the influence of such methods on physicochemical and electrooptical properties of new antiferroelectric materials, especially with the direct transition from the antiferroelectric to the isotropic phase. For this materials smectic layers change their dimension in minor scale during cooling hence its shrinkage should be very small, see Figure 1 [6]. This shall decreases the number of defects and allows to obtain good dark state even in materials with a tilt angle lower about 3-5° than orthoconic one.



Figure 1. The temperature dependence of the layer spacing (d) and arrangement of smectic layers as well as optical axes in antiferroelectric materials with orthogonal phase below isotropic phase (1b) and with direct transition from isotropic phase to antiferroelectric phase (I).

#### Acknowledgment: This work has been done under grant COST Action IC1208 and grant RMN 737/2015/WAT.

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