

University of Milano-Bicocca

Ph.D. in Materials Science

SILICA-BASED FUNCTIONAL MATERIALS

Charge transport in nanostructured $\text{SnO}_2\text{:SiO}_2$ thin films.

Second Harmonic Generation

in niobium potassium silicate glasses.

Tapered silica optical microfibres for gas sensors.

Supervisor: **Prof. Alberto Paleari**

Ph.D. Student:

Roberto Lorenzi

Matr. n° 044234

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Part I

Charge transport in nanostructured $\text{SnO}_2\text{:SiO}_2$ thin films

Chapter 1

Introduction

The design of nanostructured materials with specific physical properties is generally pursued by tuning nanoparticle size, concentration or surface passivation. An important step forward is to realize active systems where nanoparticles are vehicles for controlling, in situ, some specific, tuneable features of a responsive functional material. In this perspective, we have focused on the rational design of a nanostructured glass with electrically tuneable dielectric function obtained by injection and accumulation of charge on embedded conductive nanocrystals. This enables to achieve electrically controlled switching of semiconducting nanophases to charged polarisable states, which could lead to smart, field enhancement applications in nanophotonics and plasmonics. Nanostructured materials are widely investigated due to their applicative potential for a wide set of technologies, spanning from advanced photonics to quantum computing and bio-medical imaging, and as an important class of model systems for the study of physical properties controlled by nanoparticle size and concentration, such as quantum confinement effects in quantum dots[1]-[3], charge transport mechanisms determined by intrinsic and boundary conductivity[4]-[6], and local field enhancement effects caused by polarization of conductive nanoparticles[7]-[10]. In most cases, the optical, electrical and dielectric properties of

a nanocomposite material can be considered and, indeed, are usually assumed to be determined by the chemical and structural features of the nanophase and the host[11], as well as by their reciprocal and sometime synergetic relationship[12]-[14]. However, a different and challenging approach would be to realize nanostructured systems in which the material properties (functional and/or structural) can be modified in situ by exploiting the response of the nanophase to external stimuli. An example of this is the electric control of magnetic states of semiconductor nanostructures that is currently object of investigation for potential application in spin-based technologies. Similarly, the electric control of the charged states of suitable ensembles of semiconducting nanoparticles in dielectric hosts might be a promising strategy for the achievement of variable-response dielectrics, which is are expected to have an to impact in several areas besides microelectronics, on account of the possibility of local field intensification in fluorescent, electroluminescent light emitting or non-linear optical materials as well as electrical drive of active photonic structures. Indeed, nanoparticle charging processes are a matter of investigation intensively studied in Metal-Oxide-Semiconductor (MOS) systems with ultra-thin layers of metal or semiconducting nanoparticle nanostructures at tunnelling distance from the substrate, which may have for applications in new memory devices[15]-[20].

In this work we study the feasibility of electrically driven responsive nanomaterials focussing on silica films with SnO_2 nanoparticles thermally grown with designed size-dispersion and interphase features. In this model system, the dielectric function of the glassceramic material is externally tuned as a result of nanoparticles charging processes mediated by nanoparticle-to-nanoparticle electron transport in a tree-like percolating network. We analyse the principles of this phenomenon and describe our material at the nanometer scale, giving the details of the new synthesis strategy we developed for producing nanostructured films with highly controlled nanoparticles features. Finally, we report charge transport and capacitance data that demonstrate the role of the nanophase and confirm the polarization effect enabled by tree-like percolating mechanisms.

Chapter 2

Materials and methods

2.1 Material synthesis

Tin-doped silica nanostructured glassceramics have been produced by sol-gel technique. Generally, preparation methods employing tin precursor molecules based on tin alkoxides or tin chloride and nitrate can be easily give rise to segregation or incomplete hydrolysis during the sol gel reaction. These precursor molecules are suitable for the synthesis of SnO_2 fine powders for catalysis application, and can be used in the synthesis of SnO_2 - SiO_2 mixed oxides without stringent requirements on phase homogeneity and crystal-size distribution. In the latter case, largely inhomogeneous SnO_2 clustering occurs with a broad distribution of cluster size resulting in the formation of a material with poor optical quality or even a completely opaque white material unsuitable for optical applications.

Over the last few years, the group studied the structural and optical properties of heavy Sn-doped silica prepared by solgel method, showing that high doping levels could be achieved, despite the low solubility of tin in silica glass, similarly to an oversaturated system. Starting from such a system, sub-micrometer SnO_2 clustering was induced by increasing the synthesis temperature and the Sn content above a critical value, giving

transparent, glass-ceramics, bulk samples.

The main step consists in obtaining a starting low-density skeleton from the hydrolysis of organic molecular precursor of silicon and tin. During this step, tin segregation must be carefully avoided to enable a controlled thermally activated nucleation of the SnO_2 nano-phase during the slow condensation treatment from room temperature up to about 1000 °C. Following this strategy several samples both bulk and film, of undoped, Er doped and Tb doped tin-silicate glassceramics, as well as pure silica reference material. The tin content varied from 0 to 30 %mol. Tin silicate bulk samples have been fabricated by co-gelling tetraethoxysilane $\text{Si}(\text{OCH}_2\text{CH}_3)_4$ (TEOS), dibutyl tin diacetate $\text{Sn}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3)_2(\text{OOCCH}_3)_2$ (DBTDA) in pure ethanol, as a solvent, by adding H_2O (TEOS/ H_2O 1:8 molar ratio, TEOS/ethanol 1:3 volume ratio, with tin precursor in the required molar ratio with respect to TEOS). Gelation was achieved leaving the sealed box containing the solution in a thermostatic chamber at 35°C for a time between 2 hours and 2 weeks. Evaporation times of 2 weeks are required to manufacture bulk samples. In the case of nanostructured films, sols are produced starting from tetramethoxysilane $\text{Si}(\text{OCH}_3)_4$ (TMOS) and DBTDA in tetrahydrofurane (THF), but other solvents, silicon precursor and tin precursor are suitable as well. In order to obtain films with thickness comprise between 50-1000 nm, the colloidal properties of the sol can be usefully modified by adding compounds of silicon with both leaving (hydrolysable) and non-hydrolysable (as alkyl group) ligands. In this process the well known tin based silicon cure agent (DBTDA was employed as dopant in the sol-gel reaction as the precursor of tin oxide nanoclusters. Due to the catalytic effect of this molecular precursor on the sol gel reaction to give the gel product, sol for spinning purposes has necessity to be highly diluted, often giving too thin films unsuitable for photonic applications. In our scheme, the effective linking properties are balanced by a sort of chain terminators. Molecules used for this purpose are: ethyl trimethyl silyl acetate $(\text{CH}_3)_3\text{SiCH}_2\text{CO}_2\text{C}_2\text{H}_5$ (TMSA) and trimethyl methoxy silane $\text{CH}_3\text{OSi}(\text{CH}_3)_3$ (TMMS). These chemicals act as chain ter-

minators and operate reducing the networking and the colloid dimension. The effect on the sol properties is remarkable, and the stability and concentration of chemicals can be improved and thicker films can be obtained.

Rare earth (RE) nitrates or complexes were also added to produce RE-doped glass-ceramics; Er, Ce, Eu and Tb precursors were used, obtaining 200-5000 p.p.m. doping. After 5 or 6 days in thermostatic chamber to allow reaction of hydrolysis and condensation, these sols were deposited on p-type silicon substrate or transparent fused quartz by the spin coating technique. The obtained film were then sintered in controlled atmosphere from room temperature to about 1000° C. As a result of the treatment organic residuals are removed, porosity collapses, the network densifies and finally the phase separation of tin (IV) oxide is succesfully induced. A first stage between room temperature and 400°C, heating rate 5 °C/h, is kept under low partial pressure of oxygen (0.3-3.5% in inert gas, such as Ar) to avoid an excessive shock to the partially organic network of these films. At higher temperature, oxygen may be increased in order to adjust the phase-separation parameters and to obtain different nanophase features as concerns nanoparticle size dispersion and stoichiometry of the nanoparticle/glass interface. However, too high oxygen partial pressure during thermal treatments causes the formation and growth of thermal oxide at the surface between substrate and deposited film. The heating rate during the second step of the densification and phase separation processes may range between 3 to 10° C/h.

2.2 Material structure

A crucial prerequisite for achieving fulfilling optoelectronic properties in planar geometries via nanostructured materials is the ability to fabricate planar structures with thickness up to several hundred nanometers, with higly controlled nanoarchitecture, especially with respect to nanoparticles size, concentration, reciprocal spatial arrangement and sur-

face passivation. A large fraction of the current research on nanostructured materials is focussed on the synthesis of nanoparticles with highly reduced size dispersion and homogeneous spatial arrangement (often in single layer geometry) so as to maximize the exploitation of size-dependent quantum properties[27]. A size dispersed distribution of nanoparticles can be obtained by techniques of nanophase growth in glass matrices, provided that methods are found to assure a sufficient control of the dispersion parameters. Thermally activated growth of SnO_2 nanocrystals in silica from sol-gel synthesis fulfils these requirements[28]-[29] and can be suitably implemented for the fabrication of planar structures with thicknesses of several hundreds nanometers in a single deposition step. In the $\text{SnO}_2\text{:SiO}_2$ system, several parameters influence the nanophase and its morphology, especially because the nanoparticles growth is thermally activated and affected by the presence of heterogeneous nucleation centres, such as dopant ions and point defects. Specifically, we found that the mean nanoparticle size in bulk samples can be increased by increasing the maximum treatment temperature in the range of the critical temperature of nanophase segregation (about $900 \pm 100^\circ\text{C}$ [30]), or by reducing the oxygen partial pressure during nucleation[29]. Other factors modify the nucleation features of the nanophase, such as co-doping with rare earth ions, which increases the fraction of small nanoparticles[31] and passivates the nanophase/matrix interphase[28]. Synthesis parameters also affect the nanoparticle-host interphase, with important consequences for the electric and dielectric properties. In particular, thermal treatments in low oxygen partial pressure, with rare earths doping or a fast heating rate, promote the formation of a nanoparticle shell with a stoichiometric other than SnO_2 as support by several results[28],[30]-[32]. The effects of these parameters on bulk samples are summarized in fig. 2.1. According to these evidences, we prepared several nanostructured $\text{SnO}_2\text{:SiO}_2$ films (thickness ~ 600 nm, nanoparticle concentration of the order of 10^{18} cm^{-3}) on p-type silicon substrate, for which the nanophase features were varied by changing the synthesis conditions. Fig. 2.2 shows SEM images of the film. Four different region can be observed: silicon substrate

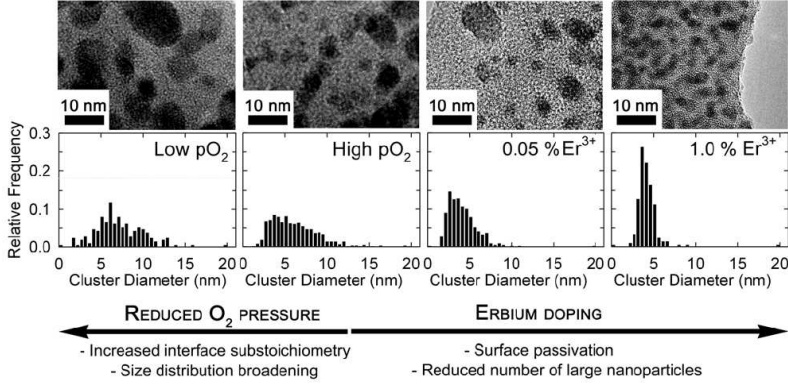


Figure 2.1: TEM analysis of the structural effects induced in nanostructured bulk samples $\text{SnO}_2\text{:SiO}_2$ (10% mol of SnO_2) by the reduction of oxygen partial pressure during the thermally-activated growth of the nanophase and by erbium-doping of the material. Upper panel: Representative TEM images at equal magnification, showing the different size distribution of SnO_2 nanoparticles embedded in the amorphous silica matrix. Bottom panel: Statistical distributions of SnO_2 cluster size in the investigated samples.

(black), thermal grown silicon dioxide (white/grey), nanostructured silica (dark grey) and, in certain cases, tiny whiskers on the top surface of the sample. In these case the grass lawn like effect was attributed to the formation of crystals on the surface of films due to segregation and consequent crystal growth along the c-axes. EDS analysis showed that they were crystals of SnO_2 . Thus, sample were studied both with (as is) and without (cleaned) tiny crystals. Cassiterite whiskers were mechanically removed with a cotton bud. Film thicknesses were measured by m-lines guided mode measurement. Table 2.1 summarizes the synthesis condition and thicknesses of the sample characterized in this work. Evidence of tin segregation in form of cassiterite nanocrystals in silica doped thin film have been found by UV-vis optical spectroscopy (see Fig. 2.3).

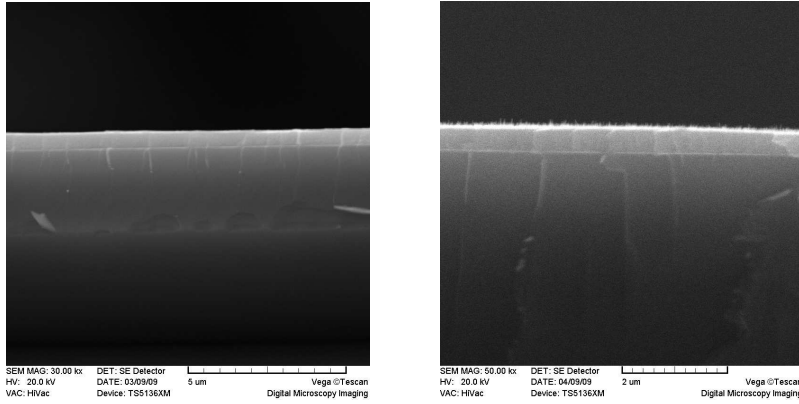


Figure 2.2: SEM images of thin films. In the image from bottom to top it is possible to observe: silicon substrate, high temperature oxide layer (~ 20 nm), nanostructured silica ($\sim 0.7 \mu\text{m}$) with (right panel - 1022axis) or without (left panel - 1032axis) tiny crystals of cassiterite on its surface.

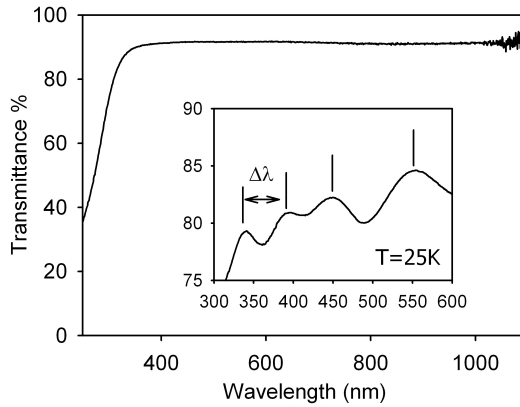


Figure 2.3: Optical transmittivity of thin film grown on silica substrate. Inset: Low temperature optical transmittivity showing thin film interference.

Several films have been grown on transparent substrate (pure silica) and sintered with the same conditions used for films grown on silicon substrate. Optical absorption measurements carried out on these film (see fig. 2.4) showed an indirect band gap at around 3.3-3.6 eV consistent with tin dioxide precipitation.

Sample	%Sn	Atm. ^a	Rate ^b	Thickness (μm)	Area (mm) ^c
S813asis	9	Hi	Fast	0.74	4.00x10.00
S813clean	9	Hi	Fast	0.74	4.00x10.00
S821asis	13	Hi	Fast	0.64	5.00x3.82
S821clean	13	Hi	Fast	0.64	3.90x5.12
S1032asis	30	Hi	Fast	0.42	5.20x4.10
S1032clean	30	Hi	Fast	0.42	5.40x3.32
S813Rasis	9	Low	Fast	0.68	4.22x3.52
S813Rclean	9	Low	Fast	0.68	4.90x3.12
S821asis	13	Low	Fast	0.60	4.22x5.16
S821clean	13	Low	Fast	0.60	3.65x5.00
S1022asis	30	Low	Fast	0.45	4.12x7.46
S1022clean	30	Low	Fast	0.45	3.46x4.12
S1032Rasis	30	VHi	Fast	0.40	4.3x5.62
S1032Rclean	30	VHi	Fast	0.40	5.66x4.06
S551	0	Low	Slow	0.55	5.00x7.00
S233	8	Low	Slow	0.575	8.74x6.9*
S263	15	Low	Slow	0.75	6.24x6.92*
S269	20	Low	Slow	0.74	5.60x6.12*
SE3	15/Er 0.5	Low	Slow	0.55	10.00x5.00
S531	10	Hi	Slow	0.55	10.00x4.00
S1T1.0	8/Tb 0.03	Low	Slow	0.425	19.00x7.50
S2T2.1	20/Tb 0.1	Low	Slow	0.425	10.50x13.20
S2T1.0	20/Tb 0.03	Low	Slow	0.42	17.20x8.00
S2T1.2	20/Tb 0.03	Low	Slow	0.4	12.80x9.90

Table 2.1: Synthesis condition of samples under study.

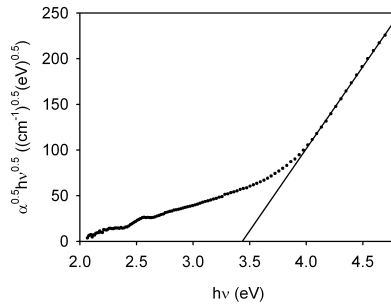
^aLow: O₂ ~0.3%, Hi: O₂ ~2%, VHi: O₂ ~3%^bFast: >7°C/h, Slow: <7°C/h^c3 nm Al + 10 nm Au, except * 3 nm Ti + 10 nm Au

Figure 2.4: Optical band gap analysis of a nanostructured thin film grown on transparent substrate.

Moreover the observed absorbance (Fig. 2.5) scales with nominal tin concentration and slightly depends on the sintering atmosphere reflecting a modification in the system, such as different matrix/nanocrystal interphase.

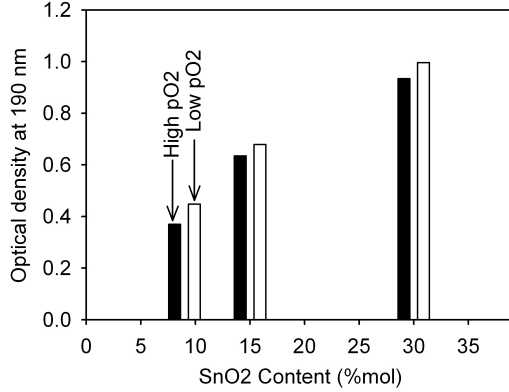


Figure 2.5: Optical absorption at 190 nm as a function of nominal tin content and for different sintering atmospheres: low (white bars) and high (black bars) oxygen partial pressure.

Low temperature optical absorption (~ 25 K, inset in Fig. 2.3) shows interference phenomena with film thickness comparable with refractometric measurement. In fact assuming a Fabry-Perot interference the spacing between adjacent maxima (or minima) depends on the optical path along the thin film:

$$\Delta\lambda = \frac{\lambda^2}{2 \cdot n \cdot l} \Rightarrow l \sim \frac{\lambda^2}{2 \cdot n \cdot \Delta\lambda} = \frac{(335 \text{ nm})^2}{2 \cdot 1.5 \cdot 55 \text{ nm}} = 680 \text{ nm} \quad (2.1)$$

where l is the film thickness, λ is the wavelength of observed maxima (or minima), n the refractive index of the film and $\Delta\lambda$ the spacing between maxima (or minima). Equation 2.1 is a rough approximation with data extrapolated from fig. 2.3. The obtained value of 680 nm is consistent with the measured value of 700 nm from m-line measurements. Finally, thin metal layers of Au, Al, Ti or Ca were sputtered on the films as gate electrodes, while the substrate were connected by conductive silver paint to a copper bar after HF

attack of silicon surface.

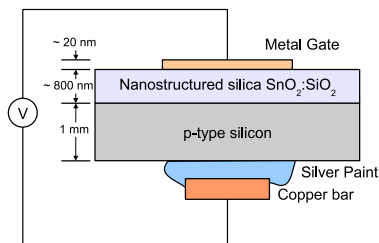


Figure 2.6: Sketch of thin film device.

2.3 Charge transport measurements

Electric measurements were carried out either by applying a static electric field between the metal gate and the silicon substrate and measuring the current in stationary regime by a high sensitive amperometer or by extracting the conductance from complex impedance measurements under external electric bias. The two methods yielded to congruent results; slight differences (see fig. 2.7) are ascribable to AC modulation used in impedance measurements.

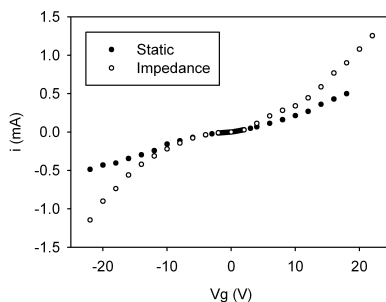


Figure 2.7: i - V curves measured by impedance spectroscopy (empty circle) and in stationary regime with a microamperometer (filled circle).

Conductivity was also studied as function of temperature: two different experimental approaches were chosen. The first was adopted in order to study the electric behaviour

on a large scale of temperatures. Thus samples were placed in a furnace and data were collected both with impedance and static set-up from room temperature to 550 K every 50 K. In the other experimental set up the measurements were focussed on resistance as function of temperature in a short range close to room temperature from $\sim 10^\circ\text{C}$ to $\sim 80^\circ\text{C}$. Temperature was measured with a thermocouple and increased by mean of a Peltier cell mounted on a copper bar whose extremity was immersed in ice as thermal bath. Current was measured with a picoamperometer using a calibrated voltage supplier (+ or - 5V) as d.d.p. source.

2.4 Capacitive measurements

Capacitive measurements were taken with a precision LCR meter (HP 4284A). Care was taken for correction measurement evaluating both short and open circuit response. A Metal Oxide Semiconductor (MOS) capacitor with well known thickness and metalization area (furnished by STM microelectronics) was used as reference material. Capacitances of nanostructured samples were compared with the expected geometrical value C_{geom} defined as the capacitance of two plane parallel conductive plates of area A and with a separation d :

$$C_{geom} = \varepsilon_0 \varepsilon_r \frac{A}{d} \quad (2.2)$$

where $\varepsilon_0 = 8.85 \cdot 10^{-12} \text{F/m}$ is the vacuum permittivity, ε_r the relative permittivity of the dielectric. For nanostructured films with tin volume fraction ξ the relative permittivity was evaluated, within the formalism of the effective medium approximation, as the weighted average of component permittivities:

$$\epsilon_r = \xi \cdot (\epsilon_r^{SnO_2}) + (1 - \xi) \cdot (\epsilon_r^{SiO_2}) \quad (2.3)$$

assuming $\varepsilon_r^{SiO_2} = 3.75$ and $\varepsilon_r^{SnO_2} = 11.24$.

Chapter 3

Results and discussion

3.1 Percolation Theory

Electrical behaviour will be discussed within the theoretical frame of the so-called percolation theory. Charge transport in nanostructured composites can take place via percolative nanoparticle-to-nanoparticle hopping processes[23] if the concentration p of “conductive links”, i.e. the fraction of nanoparticles between which charge carriers can hop[24], is equal to or larger than a critical value p_c , called the percolation threshold. For p not excessively larger than p_c , non-connected islands of conductive links can still survive. However, the number of non-connected islands rapidly decreases when p increases. Similar p -dependence also pertains to the concentration of dead-end lines, which constitute the dendritic fraction of the connected network. Dead ends are network fringes that do not contribute to the conduction through the trunk of the main network because only one link connects a dead end to the trunk. As a result, charge transport in a sandwich-structure device incorporating a nanostructured film occurs exclusively through the trunk, whereas charges can be accumulated in dead ends if the Coulombic repulsive potential resulting from the process is not excessively large. The idea, developed during this thesis, of

chargeable nanostructured dielectrics is based precisely on the possibility of exploiting the connected, but not-conductive, fraction of a percolative random network, which enables the simultaneous occurrence of charge accumulation in dead ends and charge percolation through the conductive trunk (see Fig. 3.1).

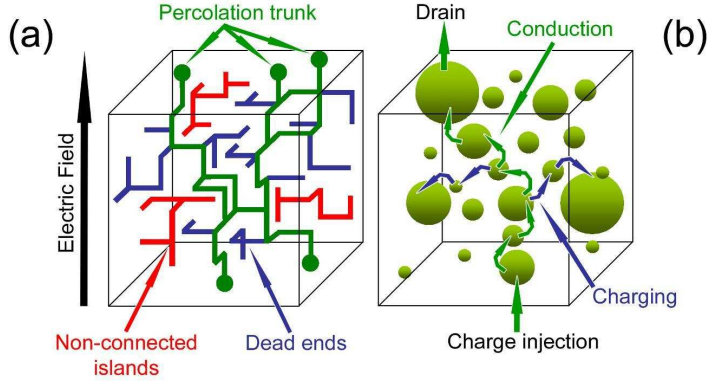


Figure 3.1: Schematic representation of the electric conduction and charging processes in a 3D tree-like percolating network. (a) Representation of percolation trunk (green) and dead-end crown (blue) in a 3D cubic network of conducting links. Non connected domains are depicted in red. (b) Schematics of charge transport processes, comprising both conduction and charging, in a 3D disordered distribution of nanoparticles embedded in an insulating matrix.

Although this parameter is, in general, not easily accessible, numerical analysis of simple systems indicates that the number of sites in dead ends is comparable to that in the trunk only for a restricted range of p -values just above the percolation threshold p_c [25]. In the case of a glass with embedded chargeable nanoparticles, such as the systems investigate here, the 3D percolative structure is essentially determined by the spatial arrangement of the nanoparticles. In particular, the local differences in the charge transport between adjacent sites are greatly dependent on the distribution of nanoparticle distances, D (characterized by a mean value, $\langle D \rangle$, and a spread, σ_D)[26]. At fixed $\langle D \rangle$ the smaller distribution the distribution width σ_D , the larger the probability of finding first-neighbour nanoparticles close enough to yield a conductive link. Since D can approximately range

within the limits determined by the mean volume per nanoparticle, ρ^{-1} , where ρ is the nanoparticle concentration, the spread of interparticle distances is approximately of the same order of $\rho^{-\frac{1}{3}}$, which in turn depends on the size distribution dn/dr :

$$\sigma_D \approx \rho^{-\frac{1}{3}} = \left[\xi^{-1} \int_0^\infty \nu(r) \frac{dn}{dr} dr \right]^{\frac{1}{3}} \quad (3.1)$$

where $\nu(r)$ is the volume of a nanoparticle with radius r and ξ is the volume fraction of the nanophase. In the simple case of Gaussian distribution centred at r , with standard deviation σ_r , we obtain a relation between σ_D and σ_r of the form $\sigma_D^3 = \xi^{-1}(a\langle r \rangle^3 + b\langle r \rangle \sigma_r^2)$, where a and b are numerical constants of the order of the unity. As a result, a broad distribution of inter-particle distances may be the key-factor for obtaining a conducting system just above the percolation threshold, which is the ideal condition for achieving charge percolation together with chargeable dead ends.

3.2 Electric Transport

Current voltage measurements have been conducted on all the samples from -40 to +40 V as gate voltages, two different behaviours have been observed. Data in fig. 3.2 summarizes the two class of samples.

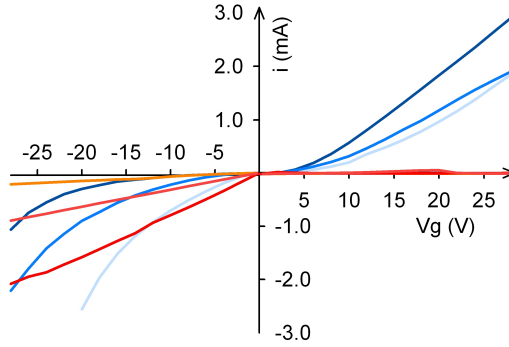


Figure 3.2: Electric response of $\text{SnO}_2\text{:SiO}_2$ nanostructured thin films. Representative i - V curves for rectifying (warm colours) and non rectifying film (cold colours)

Samples with rectifying electric response are obtained by reducing the oxygen partial pressure during the synthesis, by doping the material with erbium ions (or other rare earth ions), or by changing the heating rate (warm colours in fig. 3.2). In all these cases, significant electric transport is observed for negative bias only. By contrast, symmetric responses (cold colours in fig. 3.2) are observed for film produced in higher oxygen partial pressure or after low heating-rate thermal treatments. Thus the observed electric responses cover a broad range of currents ranging more than three order of magnitude from few μA to several mA.

Further differences is the temperature dependence at negative gate voltages (Fig. 3.3, upper panel): conductivity decreases for the rectifying films with increasing temperature, whereas the opposite is observed for un-rectifying ones.

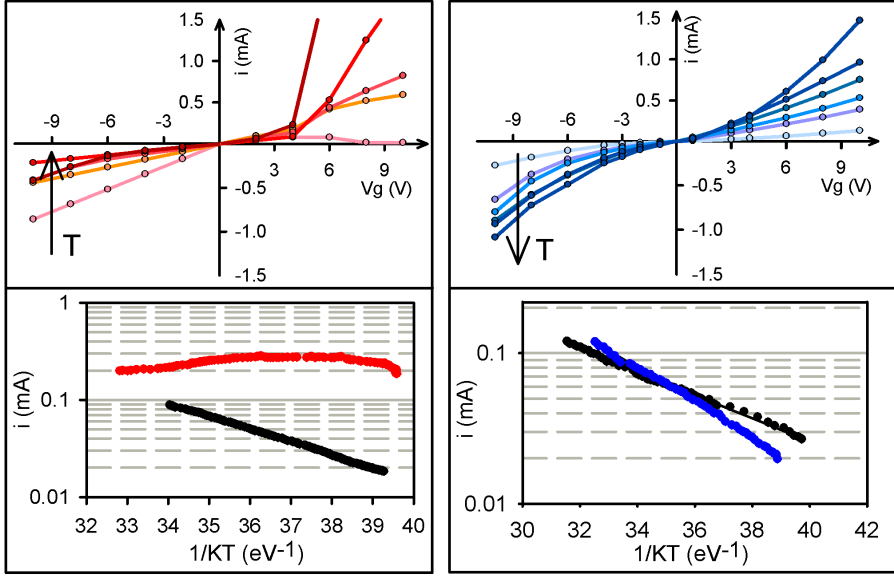


Figure 3.3: Upper panel: temperature dependence of i - V response. Lower panel: Arrhenius plot of current vs $1/kT$ for negative (coloured) and positive bias (black).

As regard currents registered for positive gate bias the behaviour is similar in both cases: currents increase with temperature. Let us consider the current density J as a product of several terms:

$$\vec{J} = e \cdot n \cdot \vec{v}_d = e \cdot n \cdot \mu \vec{E} \quad (3.2)$$

where e is the charge of the individual particle (in the case of electron or holes e is the elementary charge, $e = 1.6 \cdot 10^{-19} C$), n is the density per volume of the particles and $\vec{v}_d$ the drift velocity of particles proportional to the charge mobility μ and the applied electrostatic field $\vec{E}$. It is well known that for semiconductors, due to impurity ionization, the amount of available charge carriers (and current density) increases with temperature, as observed for positive gate voltages in all the systems under study. Moreover the observed experimental data are, in general, more reproducible and stable for samples with symmetric response. It is worth noting that data in Fig. 3.3 (upper panel) spread over a broad range of temperatures from room temperature up to 300 °C. A detailed analysis of

temperature dependence has been carried out on a shorter range of temperatures (10-80 °C) and summarized in Fig. 3.3 (lower panel). The charge transport phenomenology in Fig. 3.2 and 3.3 can be rationalized by analysing the energy level structure of the composite system (see fig. 3.4) for SiO_2 , SnO_2 , and SnO -like non-stoichiometric interphase in the approximation of negligible band bending effects.

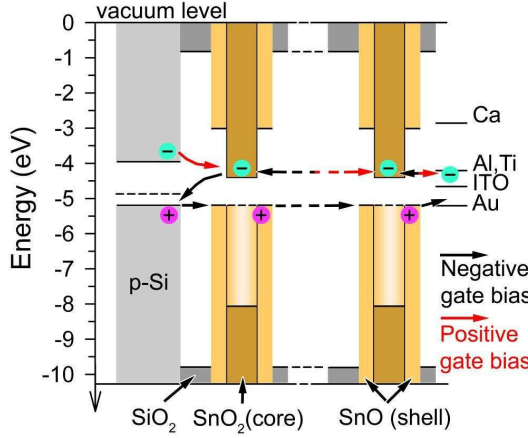
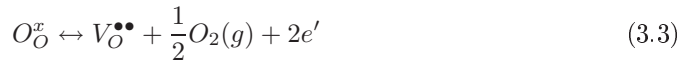


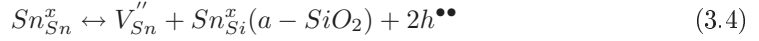
Figure 3.4: Energy band scheme of nanostructured film. Possible charge transport for electrons (blue circles) and holes (pink circles) are indicated for negative (black arrows) and positive (red arrows) bias.

The work functions of some metal electrodes are also reported[33]-[37]. The nanoparticle/host interphase, whose relative contribution to the nanophase depends on the synthesis parameters, is a SnO -like phase[28] with electric properties that differ from SnO_2 . SnO_2 is a wide band gap semiconductor ($E_g=3.6$ eV) with n-type character due to oxygen vacancy defects[29]-[35], in Kröger-Vinks notation:



whereas SnO is a semiconductor with energy gap of 2.3 eV and p-type character[36] due

to Sn vacancies that probably migrates toward silica matrix forming substituted silica:



At negative voltages, holes can be injected from silicon into the valence band of SnO and contribute to the electric current due to the electrons injected from the metal electrode into the conduction band of SnO₂. When positive bias is instead applied at the gate, charge transport can only be sustained by electrons injected from p-type silicon substrate into the conduction band of SnO₂ and the related shallow electron levels. This process is expected to be hindered by a particular thick substoichiometric nanoparticle shell. Accordingly, we register rectifying response in sample synthesized in conditions that induce oxygen substoichiometric or erbium- modified interphases. In these cases, the electric characteristic at negative bias is determined by hole injection from p-type Si substrate into SnO-shell like interphase. es

We note that injection process from electrodes and the conduction mechanism among nanoparticles requires non-null activation energies, which give rise to thermally activated contributions to the conductivity. The electric response at positive gate biases, as well as negative bias in the case of non rectifying films, reflects this kind of conduction regime with a typical Arrhenius plot behaviour ($\ln[i]$ vs. $1/k_bT$, where $k_B = 8.62 \cdot 10^{-5} \text{ eV/K}$ is the Boltzmann's constant). Moreover for film growth with the same sintering condition the activation energy E_a (i.e. the opposite of Arrhenius curve slope, see Eq. 3.5) scales with nanophase content:

$$i = i_0 \exp\left[-\frac{E_a}{k_bT}\right] \Rightarrow \ln[i] = const - \frac{E_a}{k_bT} \quad (3.5)$$

In particular, lower tin content corresponds to higher barrier indicating a hopping process between nanoparticle, however such hopping is not tunneling driven. Tunneling processes have been studied and follow the Nordheim-Fowler (NF) formalism, in which the current

density J is described by:

$$\begin{aligned}
 J &= C \cdot E^2 e^{-\frac{\beta}{E}} \\
 C &= \frac{e^3 m_0}{16\pi^2 \hbar m_{eff} \phi} \\
 \beta &= \frac{4\sqrt{2m_{eff}}}{3e\hbar} \phi^{\frac{3}{2}}
 \end{aligned} \tag{3.6}$$

where e is the elementary charge, m_0 , m_{eff} are the electron mass in free space in the semiconductor, and ϕ is the effective potential barrier. Since β is a positive constant it is possible to check possible tunnel effect by plotting $\ln[J/E^2]$ vs. $1/E$ and evaluating the negative slope of the curves (see fig. 3.5).

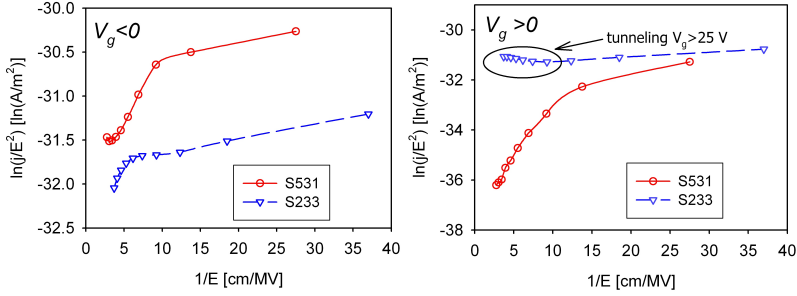


Figure 3.5: Fowler Nordheim plot for negative (left panel) and positive bias (right panel), tunneling may occur for high voltages at positive bias.

However, in our system the slope of curve in the Fowler-Nordheim plot are positive, except for high voltages. Instead we observed Schottky (or Poole-Frenkel) effect. In these cases the current density is determined by the effective Coulomb potential that is necessary to overcome to have charge flow. Assuming Schottky effect the current density-electric field dependence for a film of thickness d has the following form:

$$\begin{aligned}
 J &\propto E \exp[(\beta\sqrt{E} - \phi)/k_b T] \\
 \beta &= \frac{1}{2} \left(\frac{e^3}{\pi \epsilon_0 \epsilon_r d} \right)
 \end{aligned} \tag{3.7}$$

In these cases, the response is not ohmic and we observe a linear dependence of $\ln(j)$ vs. $\sqrt{E}$ (see Fig. 3.6), charge transport is mediated by a Schottky-like mechanism with an expected relevant role of metal work function ϕ .

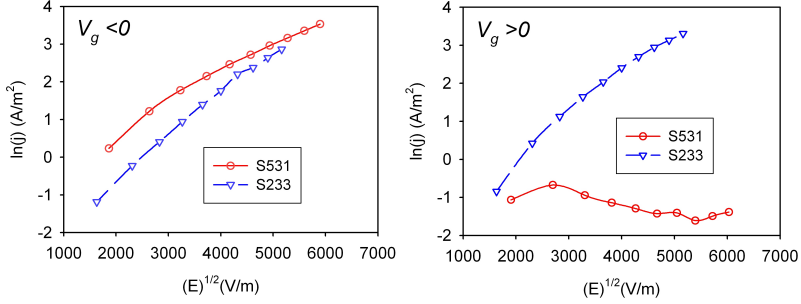


Figure 3.6: Schottky plot for negative (left panel) and positive (right panel) of nanostructured film.

Accordingly, we register more than one order of magnitude larger currents with calcium electrodes with respect to aluminum, gold and titanium, which instead show only small differences between each other. This is interesting because the large Au work function locates its Fermi level below the electron levels of SnO_2 and SnO phases, which should drastically reduce the efficiency of electron injection with respect to an Al gate. This suggests that, apart from devices with Ca gates, the conduction at negative voltage is governed by p-type electric transport sustained by holes injected from silicon substrate and mediated by SnO shells around the SnO_2 nanoparticles. When the fraction of the conductive path with metal-like character - which is that related to SnO interphase - is dominant, the thermal coefficient of resistivity may become positive. This change of sign of the thermal coefficient of resistivity is similar to that observed in granular metal oxides as a function of the stoichiometry of the grain boundaries. It is worth noting that in this regime we observe Ohmic i - V curves. Hole conduction within the nanostructured films is indeed consistent with the observed charging properties of these materials in C - V measurements at negative bias voltage.

3.3 Dielectric Response

Although all investigated films show conductive behaviour due to nanoparticle-mediated charge transport, films grown with low oxygen pressure or co-doped with rare earth ions also display a large capacitance contribution at negative gate voltages (curves in warm colours in Fig. 3.7).

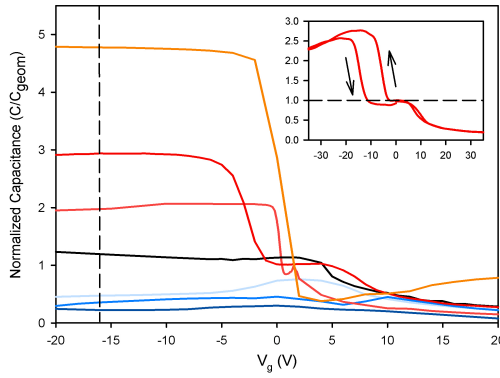


Figure 3.7: C-V plots for nanostructured thin films. Film capacitance is displayed after normalization to the geometrical capacitance. Chargeable systems shows dielectric response >1 (warm colours); conductive non-chargeable systems show negligible capacitance (cold colours). Inset: anticlockwise capacitance hysteresis compatible with hole trapping.

These synthesis conditions favour a broad distribution in nanoparticle size (see Fig. 2.1) and nanoparticle with hole-type free conduction. The resulting films show rectifying electring response (see Fig. 3.2) and MOS-like C-V characteristics, with largely enhanced capacity with respect to the pure oxide. By contranst, the capacitance of films with symmetric electric response (curves in cold colours in Fig. 3.7) approaches its maximum value near null gate voltage, at which the barrier for hopping contrasts charge transport through the film, then becoming negligible at higher gate voltages. A clear indication that an enhanced capacitive response at negative gate bias largely correlates to a metal-

like conduction is provided by the analysis of transport and capacitance data. Fig 3.8 reports the normalized capacitance as a function of the thermal behaviour of the charge transport process, as reflected by the slope of the Arrhenius plot of current vs. $1/k_bT$ in non rectifying films (Fig. 3.3) and by the upper value of the semi logarithmic current vs. $1/k_bT$ plot for films with nonlinear dependence on the temperature (see Fig. 3.3).

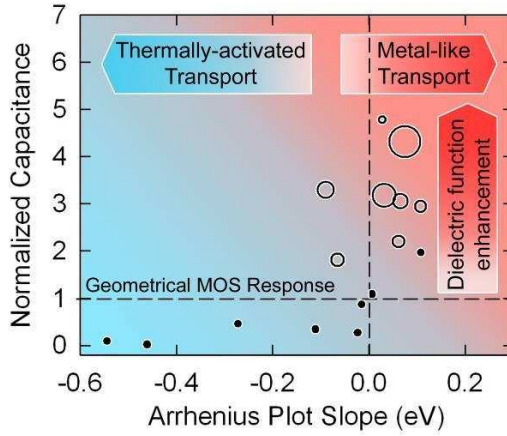


Figure 3.8: Correlation between enhanced dielectric responses and metal-like conduction features at negative gate voltage. Capacitance at -16V is reported on y-axis after geometrical normalization, while x-axis reports the slope of the Arrhenius plot of current vs. $1/kT$. The value is the angular coefficient of the linear regression of data in non-rectifying films, whereas it is the upper slope value for films with non-linear current vs. temperature dependence.

Since the slope of the Arrhenius plot is strictly related to the thermal coefficient of resistivity, the data in Fig. 3.8 suggest that increasing metal-like contributions to the charge transport process (from largely negative to positive slope values) finally cause the transition toward systems with electrically enhanced capacitance. It is remarkable that the observed C-V response is largely different, quantitatively, to what expected. In fact, upon switching between positive and negative gate bias, the capacitance undergoes a progressive increase with an initial smooth step from depletion condition of a MOS (in the pF range) toward the expected capacitance value of the oxide (Eq. 2.3), as in the case of MOS in the accumulation regime. Nevertheless, MOS-like nanostructured films

show a surprising further increase of capacitance at negative bias, which leads to a second steep step, up to C-values that are 5 times larger than expected (curve in warm colours in Fig. 3.7). It is worth noting that, concomitant to the capacitance enhancement, the film conductance is not null but instead increases with the negative voltage (i-V data in Fig. 3.2). Electrodes are not blocked and the films are able to sustain a constant current at any applied voltage which indicates the occurrence of a charging process concomitant to charge transport supplied by hole injection from the substrate. A hole charging process in a fraction of the nanoparticle population (corresponding to dead ends) is consistent with the increase of capacitance and can quantitatively account for the enhancement factor observed in the experiments. As in the case of a dielectric host with embedded metal particles, charged conductive shells make the voltage drop across a layer of nanoparticles negligible if the amount of the charge accumulated in the layer is comparable to the charge Q accumulated on the electrodes. Taking $\xi = 0.1$, $\langle r \rangle = 2.5$ nm, a layer thickness of the order of the nanoparticle size (about 5 nm), and a nanoparticle concentration of about 10^{12} cm $^{-2}$, we can estimate Q from $Q = C_0 \Delta V$, with $C_0 = 3.5$ nF being the capacitance before charging. The obtained values range between 3.5 and $7 \cdot 10^8$ C when ΔV changes from -10 to -20 V, which corresponds to a surface density of $4\text{-}8 \cdot 10^8$ |e|/cm 2 . This amount of charge corresponds to an excess of one hole per nanoparticle in no more than 50% of the nanoparticle population. Such a fraction is however rather large, in terms of crown-to-trunk ratio in a percolative network, and points to a condition really just above the percolation threshold, which is consistent with the observed critical role of nanoparticle size dispersion in the charging process. With regard to the effect on the capacitance, we note that if charging a single layer of nanoparticle remove the voltage drop across a portion of the film that approximately corresponds to the nanoparticle diameter, it also causes an increase in the effective capacitance, which we can estimate using $\Delta C = C_0(L/(L-\delta)-1)$, where δ is the thickness of the charged nanoparticle layer and L is the film thickness. According to this expression, $\Delta C/C_0 < 1\%$ for a single layer of nanoparticles. This is

the reason why no relevant capacitance enhancement has ever been reported in studies of memory devices based on 2D nanoparticles layer. By contrast, in our system, we need to consider a 3D multilayered structure and an effective thickness of the polarisable region occupied by layers of polarisable dead ends. This effective thickness can be simplified as $\delta[L/(\delta + \eta)]$, where the factor in square brackets is the number of polarisable layers in the film, as roughly modelled by the ratio between the total film thickness, L , and the sum of single-layer mean thickness, δ , and mean inter-layer distance, η . As a result, in a 3D multilayered structure of dead ends we expect a capacitance enhancement of $\Delta C/C_0 \sim \delta/\eta$. By substituting δ and η with the mean nanoparticle size d and the mean interparticle distance D we obtain $\Delta C/C_0 \sim 1$ (since d and D are comparable, as we can gather from TEM analysed by Eq. 2.1), which corresponds to an increase of a factor 2 and is consistent with our experimental results for some of the investigated films (Fig. 3.7). However, in several other cases, the increase of the effective dielectric function is significantly larger, up to a factor 5. This suggests that, in terms of the conductive and charging properties, the networks of chargeable dead ends is, in fact, sensibly more complicated than a simple layered-structures of charged nanoparticles. In these more complex architectures, the effective δ is likely to be determined by the thickness of the polarisable domains extending over few nanoparticles that share the excess of free charge injected into the dead ends, In this case we may expect δ/η sensibly larger than one, as suggested by experimental evidences. Interestingly, upon increasing the voltage from -20 to -40 V, the capacitance slightly decreases and, in some cases, shows an hysteretic behaviour. The decrease of C is expected to be a limiting effect to the charging process dictated by both the limit to the concentration of dead ends in the nanoparticle network and the effect of increasing bias in unblocking some dead ends with a consequent partial discharging of the system. The hysteresis manifests the charge trapping in the dead-ends for bias voltages progressively decreasing below the threshold values above which dead end become unblocked. This mechanism regards the fraction of nanoparticles that require

higher energy for the hopping mechanism and that are charged at a higher bias in the forward charging process.

Chapter 4

Conclusion

In summary, we have demonstrated the feasibility of a simultaneous chargeable and conductive system based on semiconducting nanoparticles in a dielectric medium. The observed increase in the dielectric function, with respect to mean-field effects, is consistent with a polarization process of electrically charged nanocrystals. The quantitative analysis of the nanoparticle charging processes supports the co-existence of charge transport through the nanostructured material and nanoparticle dielectric polarization. This achievement represents a first step towards a new type of functional silicon-compatible nanostructured materials for electrically-responsive systems with switchable plasmonic properties. Moreover, the high conductivity observed for negative bias in non-rectifying film is ascribable to percolative motion of both electrons and holes, this premise is the key point for new functional materials for light emitting diode application, in which the p-n junction is located at the nanophase itself. Preliminary results of electroluminescence carried on these materials have demonstrated that $\text{SnO}_2\text{:SiO}_2$ thin film are able to emit ultraviolet light, accordingly to the SnO_2 energy gap. However, further investigation, in particular on the observed cavity modes, are needed in order to explain the observed phenomena.

Part II

Second Harmonic Generation in potassium niobium silicate glasses

Chapter 5

Introduction

Second Harmonic Generation (SHG) in transparent glasses and glass ceramics has received much interest in the last years in the area of photonics. Since such materials combine good mechanical and optical properties with non-linear behavior they could open the way to innovative applications in solid state laser, waveguides, electro-optics, tunable fiber gratings and so on. In fact amorphous and nano- or micro- crystalline materials respect to single crystals (currently the main solution for non linear application) have better workability and lower production costs. However SHG in any type of material is possible if and only if the medium itself lacks inversion symmetry. Such condition always occurs in piezoelectric and ferroelectric crystals such as mono potassium carbonate, lithium niobate, perovskites, quartz. On the other hand the isotropy of glasses forbids any 'even' non linear process. In 1991 Myers et al.[58] found a simple and reproducible way to induce a permanent second order non linearity in silica glasses. This processes, known as thermal poling, relies on the creation of a large electrostatic field inside the glass when heated (~ 300 °C), with a large voltage applied (several kV) and then cooled down to room temperature with voltage still applied. The second-order non linearity is induced through a third-order non linear process $\chi^{(2)} = 3\chi^{(3)}E_{DC}$. The static electric

field inside the glass is reached mainly by a depletion layer caused by the migration of alkali ions (rarely from the preferred reorientation of defect matrix and OH groups) toward the anode, hence a thin charged layer breaks the inversion symmetry allowing the second-order nonlinear processes. Up to now several variants of thermal poling have been employed to induce non linear processes in glasses: corona poling, UV-poling, electron-beam poling, all-optical poling but, so far, none of these techniques have been proved to produce nonlinearities as stable as in thermal poling[44]-[51]. What seems to be a limit for silica glasses is that the nonlinearity values achieved in bulk glasses ($\sim 1\text{pm/V}$) are more than one order of magnitude lower than the $\chi^{(2)}$ values in other nonlinear material such as LiNbO_3 (-33 pm/V). For this reason, during last years, numerous studies have been devoted to glasses with various compositions such as lead silicate, titanium silicate, lithium niobium tellurite, potassium cesium niobium silicate, niobium borophosphate, lanthanum borate and others. In these cases beyond the depletion layer the SHG is achieved by recrystallization of the glass in form of active nano- and micro- crystalline domains.

Aim of this work is to study activation mechanism and characteristics of second harmonic generation in potassium niobium silicate glasses, after thermal poling treatments.

Chapter 6

Materials and methods

6.1 Materials

Niobium potassium silicate glasses with various composition have been prepared at the University Federico II of Naples - Italy by a melt-quenched method. Glasses were prepared from reagent grade precursor: KNO_3 (or K_2CO_3), Nb_2O_5 , and SiO_2 . The right amount of starting reagents were weighted to obtained 300 g of glass, powders were then mixed and melted in a platinum crucible for 1.5 h at 1530-1560 °C. The melt were quenched by pouring out the melt into another crucible and then annealing for 1 h at temperatures close to glass transition temperature T_G as determined by Differential Thermal Analysis taking the inflection point at the slope change. Flat bubble-free glass samples of about 10mm X 10 mm and 1-4 mm thickness were fabricated. In order to obtain samples with plane, parallel optical surface suitable for non linear optical measurements glasses were mechanical polished with a professional lapping machine (Logitech 1-PM51). Tab. 6.1 reports the composition of the samples under study, it can be expressed by the general formula $x\text{K}_2\text{O} \cdot x\text{Nb}_2\text{O}_5 \cdot (1-2x)\text{SiO}_2$.

sample	composition (mol%)			$T_G(^{\circ}\text{C})$
	K ₂ O	Nb ₂ O ₅	SiO ₂	
KNS 202555	20	25	55	not detected
KNS 232750	23	27	50	684
KNS 252550	25	25	50	688
KNS 303040	30	30	40	634

Table 6.1: Glass composition and glass transition temperatures of the studied glasses.

Refractive indices and optical transmittance were investigated before poling treatments. Since a precise determination of the optical dispersion in the material is crucial for nonlinear optical characterization the refractive index $n(\lambda)$ was measured at five different wavelengths (633, 825, 1061, 1312, and 1533 nm) using a prism coupler refractometer Metricon 2010. Table 6.2 and figure 6.1 resume the measured refractive indices of the samples under study.

sample	measured $n(\lambda)$				
	633 nm	825 nm	1061 nm	1312 nm	1533 nm
KNS 202555	1.7801	1.7641	1.7548	1.7487	1.7449
KNS 232750	1.7886	1.7728	1.7633	1.7573	1.7538
KNS 252550	1.7805	1.7488	1.7403	1.7334	1.7296
KNS 303040	1.79250	1.7763	1.7672	1.7614	1.7577

Table 6.2: Measured refractive indices of the studied glasses

The n -value at 532 and 1064 nm (respectively the fundamental and second harmonic) was evaluated by fitting the measured values with a three parameters Sellmeier equation and extrapolating the relative values:

$$n^2(\lambda(\mu\text{m})) = a + \frac{b}{\lambda^2 - 0.35^2} + \frac{c}{\lambda^2 - 1.8^2} \quad (6.1)$$

Table 6.3 reports the results of the fit and the extrapolated values of refractive indices for all samples.

sample	fitting parameters			calculated values	
	a	b	c	2ω (532nm)	ω (1064 nm)
KNS 202555	2.957	0.1026	-0.0301	1.79366	1.75445
KNS 232750	2.981	0.1038	-0.0370	1.80228	1.76303
KNS 252550	2.663	0.1894	-0.340	1.80305	1.73791
KNS 303040	2.990	0.1046	-0.044	1.80612	1.76684

Table 6.3: Fitting parameters for the Sellmeier (eq. 6.1) and extrapolated values for fundamental frequency and second harmonic.

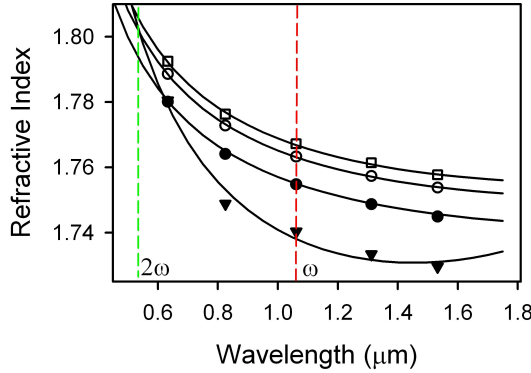


Figure 6.1: Refractive indices (square KNS303040, empty circle KNS232750, filled circle KNS202555, and triangle KNS252550) and Sellmeier (solid line) fitting (eq. 6.1). Dashed lines refer to fundamental frequency and second harmonic.

Transmittance spectra of samples were investigated with a UV-vis spectrophotometer (Cary 900) in the range 190-1100 nm, figure 6.2 shows a representative spectrum of potassium niobium silicate glass.

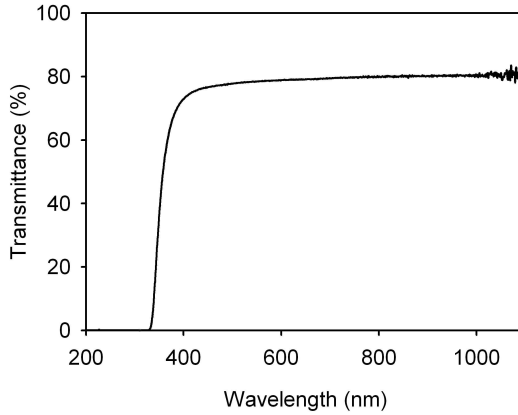


Figure 6.2: Transmittance spectrum of KNS 232750.

Optical grade samples are transparent in the range 400 - 1100 nm and their transmittance spectra are independent of the chemical composition.

6.2 Methods

6.2.1 Thermal Poling Treatments

Thermal poling treatments have been carried out at the Politecnico di Torino. As already mentioned, thermal poling is a method for inducing a second order nonlinearity otherwise forbidden in amorphous materials due to the inversion symmetry of such systems in a macroscopic scale. Thermal poling consists in applying large electrostatic field while the sample is kept in an oven at relative high temperatures. Hence the experimental set up comprises a high voltage supply, a muffle furnace, and temperature and current indicators. In our system the current was measured as a voltage drop at the end of a resistance and recorded during the experiment. In order to avoid thermal runaway and sample breakdown voltage was increased in steps of 200 V up to 1.8 kV. Thermal poling treatments were carried out in air at 500 K.

6.2.2 Maker Fringe Technique

Measurements of the second-order non linearity induced in glass by thermal poling are seldom very precise and are nearly always comparative measurements rather than absolute measurements. An absolute determination of the non linear coefficient requires a precise determination of the spatial and temporal evolution of the fundamental and the generated beam. Since these parameters are difficult, if not impossible, to determine other measurement solutions are preferred. Such difficulties are overcome with a comparative method. In the Maker Fringe Technique (MFT), first developed by Maker et al. in 1962, the nonlinear coefficient and thickness of the active layer of the material under investigation is obtained with respect to a material with known nonlinear properties, e.g. α -quartz. Nowadays, this technique is one of the most widely used methods for the measure of SHG in poled materials. In such experiment the laser beam is focused on the sample and the generated second harmonic is measured as a function of the incident angle. The SH intensity exhibits an oscillating behavior resulting from the interference between the fundamental and second harmonic waves. Due to the dispersion of the material the two waves travel with different velocities and their phase relationship at the output surface of the sample depends on the actual path traveled inside the glass. For a fixed pair of refractive indices (at the fundamental wavelength and second harmonic), the distance between peaks depends only from the thickness of the active layer, while the intensity of the observed pattern depends on the SHG efficiency of the system (see figure 6.3).

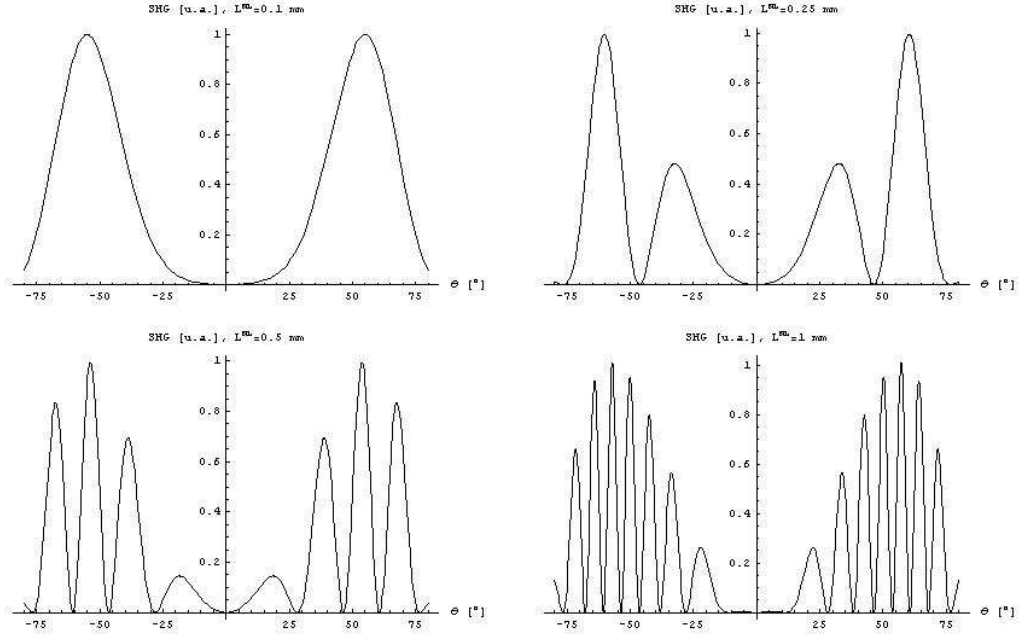


Figure 6.3: Simulated pattern of a Maker Fringe Measurement for a glass with different non linear layer and second order susceptibility.

It is worth noting that for non linear thickness smaller than a critical value (for glasses typically $10 \mu\text{m}$) from Maker Fringe Technique is impossible to infer the extent of the active region, but it's however possible to measure the value of $\chi^{(2)}$.

6.2.2.1 Theory of second harmonic generation

Since second harmonic generation is a non-trivial solution of Maxwell's equation, a background theory is necessary in order to clarify the equation used to fit the MF pattern[66, 82]-[88]. In the following discussion we will assume that samples are perfectly transparent (e.g. non absorbing materials). Let us consider a fundamental laser beam, of fixed power $\mathcal{P}_\omega$, linearly polarized $\vec{E}_\omega$ electric field and wave vector $\vec{k}_\omega$, which is incident on a plane parallel nonlinear sample of thickness L . Let ϑ be the incidence of the light beam on the sample measured between the beam direction and surface normal, allowing for rotation

of the sample around an axis perpendicular to $\vec{k}_\omega$. The following discussion gives the theoretical background of SHG within this experimental configuration. The starting point are the Maxwell's equations in MKS system:

$$\begin{aligned}\nabla \cdot \vec{D}(t) &= \rho & \nabla \cdot \vec{H}(t) &= 0 \\ \nabla \times \vec{E}(t) &= -\frac{\partial \vec{B}(t)}{\partial t} & \nabla \times \vec{H}(t) &= \frac{\partial \vec{D}(t)}{\partial t} + \vec{J}\end{aligned}\tag{6.2}$$

where

$$\begin{aligned}\vec{D}(t) &= \varepsilon_0 \vec{E}(t) + \vec{P}(t) \\ \vec{B}(t) &= \mu_0 \left(\vec{H}(t) + \vec{M}(t) \right) \\ \frac{1}{c^2} &= \varepsilon_0 \mu_0\end{aligned}\tag{6.3}$$

we assume that the medium does not contain free charge ($\rho = 0$) and is a nonmagnetic material ($\vec{M} = 0$). In such conditions eq. 6.2 can be rearranged as follow:

$$\nabla \times \nabla \times \vec{E}(t) = -\frac{1}{c^2} \frac{\partial^2 \vec{E}(t)}{\partial t^2} - \mu_0 \frac{\partial^2 \vec{P}(t)}{\partial t^2}\tag{6.4}$$

or in the frequency domain:

$$\nabla \times \nabla \times \vec{E}(\omega) = -\frac{\omega^2}{c^2} \vec{E}(\omega) + \mu_0 \omega^2 \vec{P}(\omega)\tag{6.5}$$

For electric field small compared to the atomic electric field ($\sim 3 \cdot 10^8 \text{V/cm}$) the polarization response of the medium is linear to the applied external field:

$$\vec{P}(\omega) = \varepsilon_0 \chi^{(1)} \vec{E}(\omega)\tag{6.6}$$

where $\chi^{(1)}$ is the linear electric susceptibility, a tensor of order two, that for isotropic media is a proportionality factor depending on the index of refraction: $n(\omega) = \Re \sqrt{1 + \chi^{(1)}}$. When the applied external field is of the same order of magnitude as the atomic electric field, the non linear response can not be neglected anymore. In this scenario the polar-

ization can be expressed as the sum of a linear (Eq. 6.6) and a nonlinear contribution $\vec{P}(\omega)^{NL}$:

$$\vec{P}(\omega) = \varepsilon_0 \chi^{(1)} \vec{E}(\omega) + \vec{P}^{NL}(\omega) \quad (6.7)$$

By substituting eq. 6.7 in eq. 6.3, the nonlinear equation describing the wave propagation is obtained:

$$\nabla \times \nabla \times \vec{E}(\omega) = -\frac{\omega^2}{c^2} \epsilon_r \vec{E}(\omega) + \mu_0 \omega^2 \vec{P}^{NL}(\omega) \quad (6.8)$$

where $\epsilon_r = 1 + \chi^{(1)}$ is the linear dielectric tensor. Solutions for SHG of eq. 6.8 consist in a set of two equations one describing the field at fundamental frequency ω and the other one for the component at 2ω . These equations are not independent one each other and are coupled through the nonlinear polarization $\vec{P}(\omega)^{NL}$ by:

$$\begin{cases} \vec{P}^{(2)}(\omega) = \frac{1}{2} \varepsilon_0 \overline{\chi}^{(2)} |\vec{E}_{2\omega} \vec{E}_\omega \\ \vec{P}^{(2)}(2\omega) = \frac{1}{2} \varepsilon_0 \overline{\chi}^{(2)} |\vec{E}_\omega \vec{E}_\omega \end{cases} \quad (6.9)$$

Eq. 6.9 is the starting point to solve the non linear wave equation (Eq. 6.8), however is necessary to introduce some further approximation:

- The solution will be in the form of plane waves propagating in the z direction :

$$\vec{E}_\omega = \vec{E}_{0,\omega}(\hat{x}, \hat{y}, \hat{z}) \cdot e^{i\vec{k} \cdot \vec{r}} = \vec{E}_{0,\omega}(\hat{x}, \hat{y}, \hat{z}) \cdot e^{i\frac{\omega}{c} n_\omega \pm k z} \quad (6.10)$$

- The electric field vector is always orthogonal to the wave vector so the left side of eq. 6.5 can be simplified:

$$\nabla \times \nabla \times \vec{E}(\omega) \Rightarrow -\frac{\partial^2 \vec{E}(\omega)}{\partial z^2} \quad (6.11)$$

Assumption of the Slow Varying Envelope Approximation, this approximation can be justified if the phase and amplitude variations are small over distances of the order of the

wavelength:

$$\left| \frac{\partial^2 \vec{E}_0(\omega)}{\partial z^2} \right| \ll \left| k \frac{\partial \vec{E}_0(\omega)}{\partial z} \right| \quad (6.12)$$

Finally the expression of the derivative of amplitude is derived:

$$\frac{\partial \vec{E}_0(\omega)}{\partial z} = i \frac{\mu_0 \omega^2}{2k} \vec{P}_\omega^{NL} e^{-ikz} \quad (6.13)$$

The final goal of this physical model is to obtain the equation of the output signal of the MFT. Thus we have first to evaluate the case of the ideal model and then apply some correction for the real case. First of all we will examine the boundary conditions of our system. Due to dispersion the two waves traveling in the medium will propagate with slightly different velocities and directions. The two different directions of the pump beam and the generated wave can be evaluated by Snell's law:

$$\begin{aligned} \theta_\omega &= \arcsin\left(\frac{\sin \theta}{n_\omega}\right) \\ \theta_{2\omega} &= \arcsin\left(\frac{\sin \theta}{n_{2\omega}}\right) \end{aligned} \quad (6.14)$$

Eq. 6.13 for fundamental and generated wave becomes:

$$\begin{aligned} \frac{\partial \vec{E}_{0,\omega}}{\partial z'} &= i \frac{\mu_0 \omega^2}{2k_\omega} \vec{P}_\omega^{NL} e^{-ik_\omega z'} \\ \frac{\partial \vec{E}_{0,2\omega}}{\partial z''} &= i \frac{\mu_0 \omega^2}{2k_{2\omega}} \vec{P}_{2\omega}^{NL} e^{-ik_{2\omega} z''} \end{aligned} \quad (6.15)$$

where $\vec{E}_{0,\omega} = \hat{e}_\omega E_{0,\omega}$ and $\vec{E}_{0,2\omega} = \hat{e}_{2\omega} E_{0,2\omega}$ with the versors $\hat{e}_\omega$ and $\hat{e}_{2\omega}$ oriented in the propagation direction of pump and SH beam. Thus, making the scalar product of eq. 6.15 with the versors, the system can be rewritten in a more convenient form:

$$\begin{aligned} \frac{\partial \vec{E}_{0,\omega}}{\partial z'} &= i \frac{\mu_0 \omega^2}{2k_\omega} \hat{e}_\omega \vec{P}_\omega^{NL} e^{-ik_\omega z'} \\ \frac{\partial \vec{E}_{0,2\omega}}{\partial z''} &= i \frac{\mu_0 \omega^2}{2k_{2\omega}} \hat{e}_{2\omega} \vec{P}_{2\omega}^{NL} e^{-ik_{2\omega} z''} \end{aligned} \quad (6.16)$$

The explicit form of the second order nonlinear polarization $\vec{P}^{NL}$ of eq. 6.9 is given by:

$$\begin{cases} \vec{P}_\omega^{(2)} = \varepsilon_0 \bar{\chi}^{(2)} |\hat{e}_{2\omega} \hat{e}_\omega \vec{E}_{0,2\omega}^* \vec{E}_{0,\omega} e^{i(k_{2\omega} \cos(\theta_{2\omega} - \theta_\omega) z' - k_\omega z')} \\ \vec{P}_{2\omega}^{(2)} = \varepsilon_0 \bar{\chi}^{(2)} |\hat{e}_\omega \hat{e}_\omega \vec{E}_{0,\omega}^* \vec{E}_{0,\omega} e^{2i(k_{2\omega} \cos(\theta_{2\omega} - \theta_\omega) z' - k_\omega z'')} \end{cases} \quad (6.17)$$

The spatial derivative of generated harmonic is obtained by substituting Esq. 6.17 into eqs. 6.16:

$$\frac{\partial E_{0,2\omega}}{\partial z''} = i \frac{\mu_0 (2\omega)^2}{2k_{2\omega} c^2} d_{eff}(z'') |E_{0,\omega}|^2 e^{-i\Delta k'' z''} \quad (6.18)$$

where $\Delta k''$ is the projection of the wave vector mismatch along the second harmonic direction:

$$\begin{aligned} \Delta k''(\theta) &= \text{proj}_{\vec{k}_{2\omega}} (\vec{k}_{2\omega} - 2\vec{k}_\omega) = k_{2\omega} - 2k_\omega \cos(\theta_{2\omega} - \theta_\omega) = \\ &= \frac{4\pi}{\lambda} (n_{2\omega} - n_\omega \cos(\theta_{2\omega} - \theta_\omega)) \end{aligned} \quad (6.19)$$

It is more convenient to express the wave vector mismatch in the real space. In this case an important parameter for nonlinear characterization, the so called coherence length, is defined:

$$\Lambda_c = \frac{\pi}{\Delta k} = \frac{\lambda}{4(n_{2\omega} - n_\omega)} \quad (6.20)$$

Eq. 6.18 has been also introduced the effective nonlinear optical coefficient d_{eff} a parameter strictly related to $\chi^{(2)}$. d_{eff} is defined as a scalar parameter rather than a tensor, thus its value depends on the particular geometrical configuration (including polarizations) under study and it is defined as the projection of the nonlinear polarization vector along the direction of the second harmonic electric field:

$$d_{eff} = \text{proj}_{\hat{e}_{2\omega}} (\vec{P}_\omega^{NL}) = \frac{1}{2} [\hat{e}_{2\omega} \cdot \bar{\chi}^{(2)} |\hat{e}_\omega \hat{e}_\omega|] \quad (6.21)$$

where the explicit form of $\vec{P}_\omega^{NL}$ is a three order tensor:

$$\vec{P}_\omega^{NL} = \frac{1}{2} \left[\overline{\overline{\chi}}^{(2)} | \hat{e}_\omega \hat{e}_\omega \right] = \overline{\overline{D}} \cdot \begin{pmatrix} E_x^2 \\ E_y^2 \\ E_z^2 \\ 2E_y E_z \\ 2E_x E_z \\ 2E_x E_y \end{pmatrix} =$$

$$= \begin{pmatrix} d_{11} & d_{12} & d_{13} & d_{14} & d_{15} & d_{16} \\ d_{21} & d_{22} & d_{23} & d_{24} & d_{25} & d_{26} \\ d_{31} & d_{32} & d_{33} & d_{34} & d_{35} & d_{36} \end{pmatrix} \cdot \begin{pmatrix} E_x^2 \\ E_y^2 \\ E_z^2 \\ 2E_y E_z \\ 2E_x E_z \\ 2E_x E_y \end{pmatrix} \quad (6.22)$$

However due to crystal symmetry (or to the symmetry of the point group of the system under study) the 6X3 matrix representing the polarization tensor simplifies to a few elements. Taking L as the active nonlinear layer and integrating eq. 6.18 the electric field and the intensity of the generated harmonic are obtained:

$$E_{0,2\omega}(L) = i \frac{\omega}{n_{2\omega} c} |E_{0,\omega}| \int_0^{\frac{L}{\cos \theta_{2\omega}}} d_{eff}(z'') e^{-i\Delta k'' z''} dz'' \quad (6.23)$$

$$I_{2\omega}(L) = \frac{2\omega^2}{n_{2\omega} n_\omega^2 c^3 \varepsilon_0} I_\omega \left| \int_0^{\frac{L}{\cos \theta_{2\omega}}} d_{eff}(z'') e^{-i\Delta k'' z''} dz'' \right|^2 \quad (6.24)$$

In order to apply practically eq. 6.24 further corrections for real cases are needed. In fact eq. 6.24 gives the intensity of the second harmonic inside the material, whereas experimentally the only detectable powers are outside the material. Thus correction factor for reflection between air-sample and sample-air interfaces have to be included.

The following considerations rely the case of polarization of the incident electric field lying in the incidence plane (the plane containing both the normal to the surface and incident light beam), called *p-pol*. Reflection losses are calculated by the well known Fresnel's equations for transmitted light:

$$\begin{aligned}
 T^\omega(\theta) &= 1 - \left(\frac{n_\omega \cos \theta - \cos \theta_\omega}{\cos \theta_\omega + n_\omega \cos \theta} \right)^2 && \text{Air-sample interface} \\
 T^{2\omega}(\theta) &= 1 - \left(\frac{\cos \theta_{2\omega} - n_{2\omega} \cos \theta}{n_{2\omega} \cos \theta + \cos \theta_{2\omega}} \right)^2 && \text{Sample-air interface} \\
 T(\theta) &= (T^\omega(\theta))^2 \cdot T^{2\omega}(\theta) && \text{Total Fresnell loss coefficient}
 \end{aligned} \tag{6.25}$$

Moreover the last correction is the beam factor correction, that is a measure of the beam power per unit area inside and outside the material due to refractions. We can derive the beam correction factor $a(\theta)$ from geometrical considerations:

$$\begin{aligned}
 S_\omega &= S' \cos \theta_\omega = S \frac{\cos \theta}{\cos \theta_\omega} && \text{air-sample correction factor} \\
 S_{2\omega} &= S' \cos \theta_{2\omega} = S \frac{\cos \theta_{2\omega}}{\cos \theta} && \text{sample-air correction factor} \\
 a(\theta) &= \left(\frac{\cos \theta}{\cos \theta_\omega} \right)^2 \frac{\cos \theta_{2\omega}}{\cos \theta} && \text{beam correction factor}
 \end{aligned} \tag{6.26}$$

Introducing the correction parameters in eq. 6.24 and solving the integral the expression describing the output of the MF pattern (second harmonic power as a function of incidence angle) is finally obtained:

$$P_{2\omega}(\theta) = \frac{1}{S} \frac{2\omega^2}{\varepsilon_0 c^3 n_{2\omega} n_\omega^2} a(\theta) T(\theta) \frac{L^2}{(\cos \theta_{2\omega})^2} d_{eff}^2 \text{sinc}^2 \left(\frac{\Delta k'' L}{2 \cos \theta_{2\omega}} \right) \tag{6.27}$$

Chapter 7

Results and discussion

7.1 Poling and Maker Fringe measurements

7.1.1 Poling

Poling treatments were carried out with the configuration described in 6.2.1. Steel screws, 10 mm in diameter, were used as blocking electrodes. Since this work was exploratory the thermal poling strategies were not uniform in poling treatment. Table 7.1 summarizes the magnitude and duration of applied voltage on the samples under study.

sample	Voltage (V) / Duration
KNS 202555	200/5'→400/5'→600/5'
	→800/5'→ 1000/5'→1200/5'
	→1400/5'→1200/5'→oven off (0.5 d)
KNS 232750	200/2h→400/30'→600/30'→800/30'
	→1000/15'→1200/15'→1400/15'
	→1600/15'→1800/20'oven→ off (0.5 days)
KNS 252550	200/5'→400/5'→600/15'
	→800/45'→1000/1h→oven off (0.5 d)
KNS 303040	200/2h→400/2h→600/1h→oven off (0.5 days)

Table 7.1: Poling treatments of the sample under study. Table resumes the voltage steps and their duration in minutes. After the last voltage step oven were turned off with the d.d.p. still applied.

Current-time and temperature of the poling processes are summarized in fig. 7.1, the observed currents are of the order of $0.5 \mu\text{A}$, that corresponds to current density of several hundreds of $\mu\text{A}/\text{cm}^2$.

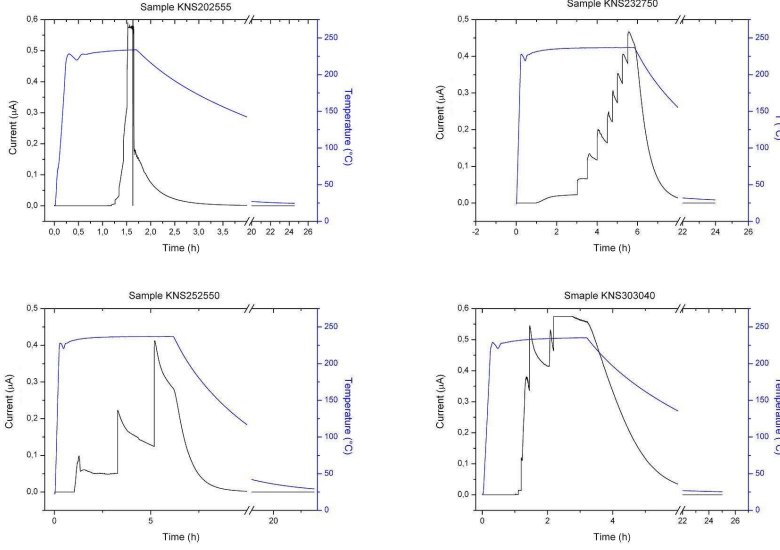


Figure 7.1: Current (black, left axis) and temperature (blue, right axis) variations during poling thermal treatment. Spikes correspond to voltage steps, see Tab. 7.1.

The spikes, followed by an exponential decrease, in current-time plot occur in concomitance to voltage steps, moreover, from such a plot it is possible to estimate the total mobilized charge:

$$Q = \int_{t_{in}}^{t_{fin}} I dt \quad (7.1)$$

As an example for KNS 232750, the calculated value for mobilized charge results to be 1.4 C cm^{-2} , corresponding to the charge of K^+ ions in $10 \mu\text{m}$ thick layer.

7.1.2 Maker Fringe

Optical bench improvement In section 6.2.2 we have derived the expression underlying the non linear characterization measured with the Maker fringe technique. Eq. 6.27

gives the second harmonic power measured as a function of the angle of the incident pumping beam and the normal at the surface of the sample. Below we give a brief description of our experimental set up. A scheme of the optical bench is depicted in fig. 7.2.

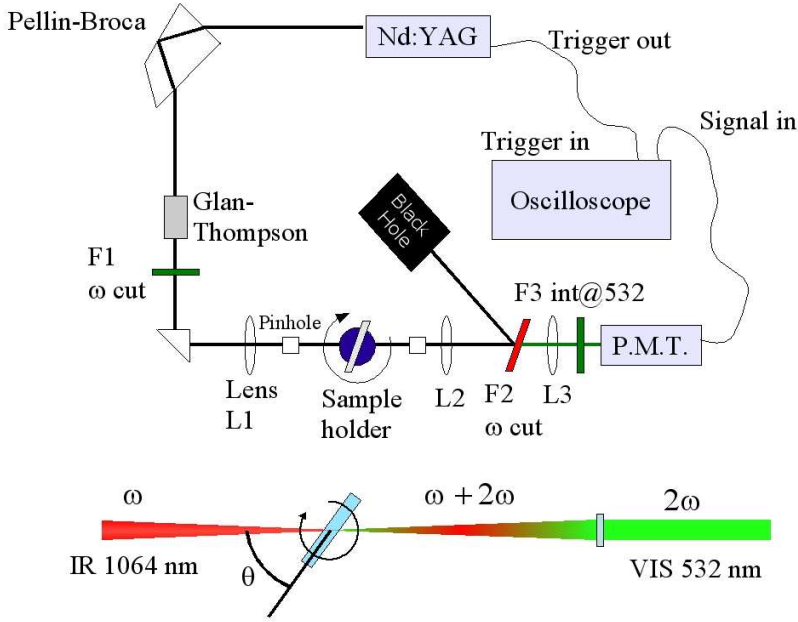


Figure 7.2: Sketch of the optical bench.

The pump beam is the 1064 nm spectral line of a Q-switched $\text{Nd}^{3+}:\text{YAG}$ laser; repetition rate of 10 Hz, pulse duration of ~ 10 ns, pulse energy of ~ 70 mJ, spot 0.7 cm in diameter. Since the light coming from the laser cavity may contain additional wavelengths beyond the 1064 nm line a first Pellin-Broca prism spatially separates spurious light. Then light is linearly polarized by mean of Glan-Thompson polarizer and an additional filter (F1) cuts the light in the green region of visible. A lens system focuses light onto the sample (L1 and L2 are confocal, usually $f_{L1} = 160$ mm and $f_{L2} = 80$ mm) and collimates the output on the active region of a photomultiplier tube P.M.T.. Before entering the P.M.T. infrared light is deviated in a black hole with a harmonic separator,

and finally an interference filter centered at 532 nm transmits the second harmonic to be analyzed. In our first experimental set up the sample was mounted on a goniometric sample holder and measurements were taken every 2 or 4° from -90° to 90°. Fig. 7.3 (left panel) shows a measure carried on the quartz reference, fringes are clearly visible, but the pattern is still asymmetric, particularly for $-20 \leq \theta \leq 20$, that is the one used for calibration.

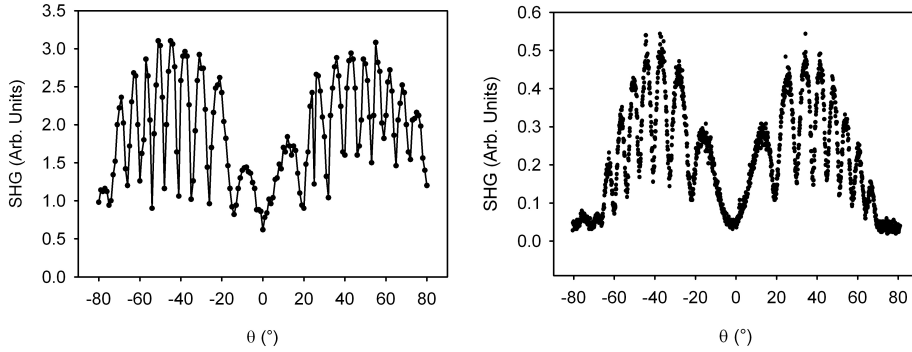


Figure 7.3: Maker Fringe Pattern of a quartz slab (thickness 1.23 mm) before (left panel) and after (right panel) optical bench improvement.

In order to significantly improve the Maker fringe measurement the manual goniometric stage had been replaced with a motorized one. The remote control of the stepper was coupled with the signal coming from the oscilloscope using the software LabView. Fig. 7.3 (right panel) shows the quartz signal after the optical bench improvement. The pattern is symmetric which respect $\theta = 0$ and the high angle resolution (tenth of degree) clearly resolves the fringes. The fitting equation of Maker fringe pattern is the following:

$$P_{2\omega}(\theta) = \textcolor{blue}{K} \left[\frac{a(\theta)T(\theta)}{n_{2\omega}n_{\omega}^2} \frac{L^2}{(\cos \theta_{2\omega})^2} \textcolor{red}{d_{eff}}^2 \textcolor{red}{sinc}^2 \left(\frac{\Delta k'' L}{2 \cos \theta_{2\omega}} \right) \right] \quad (7.2)$$

where the terms in eq. 7.2 have been divided in three classes:

blue: scaling factor peculiar of the specific experimental set-up: spot size, focus, P.M.T. voltage, pump power...

black: refers to optical properties specific of the material under study. These parameters depends mainly on refractive indices at ω and 2ω .

red: non linear optical parameters to be measured (except for reference material)

Measurement of second order nonlinear parameters consists in the calibration of the optical bench with quartz, then the pattern is fitted in order to evaluate K . Then the quartz crystal is replaced by the glass under study, and eq. 7.2 (with the right scaling factor K) is used to find the non linear thickness L and d_{eff} from which the second order susceptibility $\chi^{(2)}$ is derived.

Maker Fringe measurement Following the procedure described in 7.1.2, we have determined the non linear coefficient and thickness of poled glasses except for KNS 252550, for which the signal was too low. Fig. 7.4 resumes the Maker fringe patterns of samples, all measurements are collected in the same experimental condition.

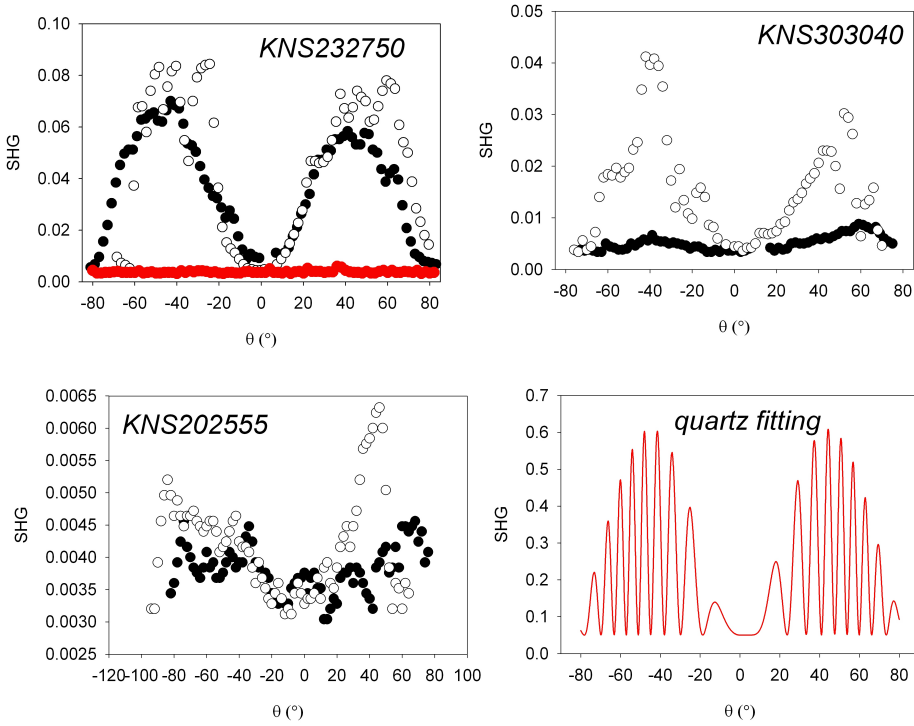


Figure 7.4: Maker fringe patterns and quartz signal fitting of poled glasses, units are the same for the four plots. Red circles in KNS232750 represent the SH signal in a zone outside the poled region.

Thus, the second harmonic intensity in the four graphs are plotted in the same units and can be compared. For each sample, measurement with the anode (filled circles) and the cathode (empty circles) as front surface in the Maker fringe configuration are compared. Furthermore, a representative control measurement with laser beam focused outside the electrode region is shown in red in the case of KNS232750. Indeed, in all samples, SH signal turns out undetectable outside the electrode regions. Some general conclusion can be inferred:

- SHG in potassium niobium silicate glasses arises as an effect of thermal poling treatment

- SH intensity is only one order of magnitude lower than 1 mm quartz sample
- The pattern with only two modulation peak in 180° suggests that the non linear thickness is probably less than $10 \mu\text{m}$
- Asymmetry of SHG with respect to the two surfaces suggests a nonlinear layer localized at one surface, transmission and/or surface scattering determining the different efficiency

Further experiments (described in 7.2) have been carried out in order to better understand thickness, morphology and localization of the active layer. Table 7.2 resumes the results of non linear optical parameters.

sample	$L(\mu\text{m})$	d_{eff} (pm/V)	
		Anode	Cathode
KNS 232750	9.1	1.73	1.95
KNS 252550	not detectable		
KNS 303040	8.8	0.31	1.21
KNS 202555	7.8	0.14	0.26

Table 7.2: Non linear thickness and effective nonlinear optical coefficient of poled glasses. Anode and cathode refer to the front face.

7.2 Mechanism of S.H.G.

7.2.1 Structural modifications

Structural modification caused by poling are evidenced by μ -Raman spectroscopy. Fig. 7.5 shows Raman spectra at the surface of the four materials, outside (black) and inside the the electrode region (Green=cathode, red=anode).

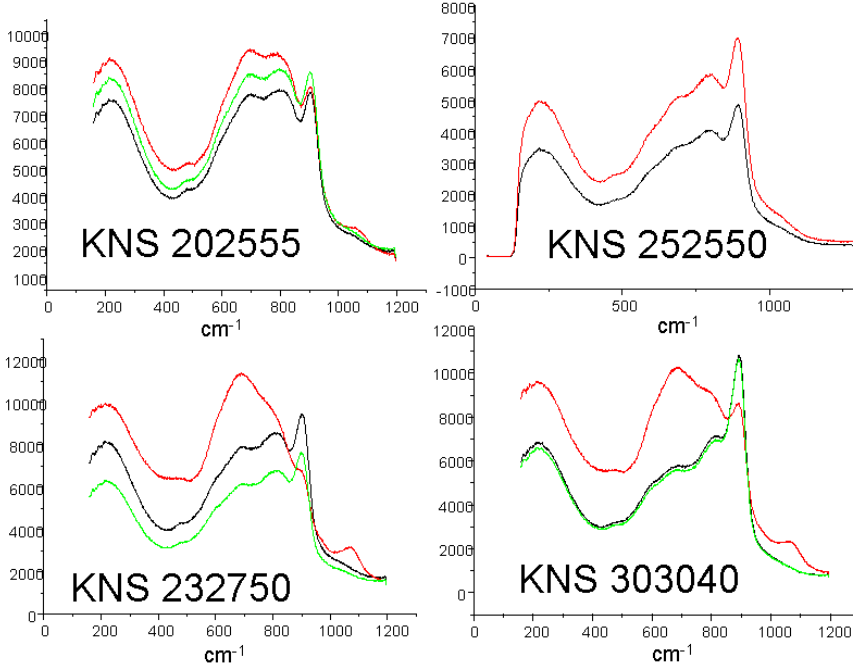


Figure 7.5: Raman spectra of poled glasses, spectra were taken: outside the poled region (black), at the cathodic (green) and anodic (red) surface.

Outside the electrodes regions, the spectra show differences from sample to sample ascribable to the different composition. Furthermore, differences are also noted KNS 232750 and KNS303040 (samples with highest d_{eff} , cfr. tab. 7.2), within the single sample, between regions inside and outside the zone faced to the anode during poling. No relevant difference is instead observed in the cathode region. So, these results indicate that poling treatment modifies the material inducing a structural modification in the region below the anode. The Raman spectra of unpoled regions exhibits three important broad bands:

650-720 cm^{-1} : NbO_6 without non bridging oxygen

770-850 cm^{-1} : NbO_6 octahedra sharing a corner with at least one other NbO_6 octahedron

870-910 cm^{-1} : vibrational modes of highly distorted NbO_6 octahedra having at least one bond pointing toward an alkali ion: $\text{Nb-O} \cdots \text{K}^+$. This is also the feature with the highest relative amplitude

On the other hand, for the Raman spectra collected on the anodic region the most important feature is located at 690 cm^{-1} and a new band at 1065 cm^{-1} appear. This latter band lies outside the niobium related frequencies and it is ascribable to SiO_4 tetrahedra. Moreover, the confocal optics of the μ -Raman spectrometer was exploited to perform the analysis of the structural modifications along the thickness of the sample KNS 232750. Fig. 7.5 shows spectra taken at different depth from the anode surface at steps of $1 \text{ }\mu\text{m}$.

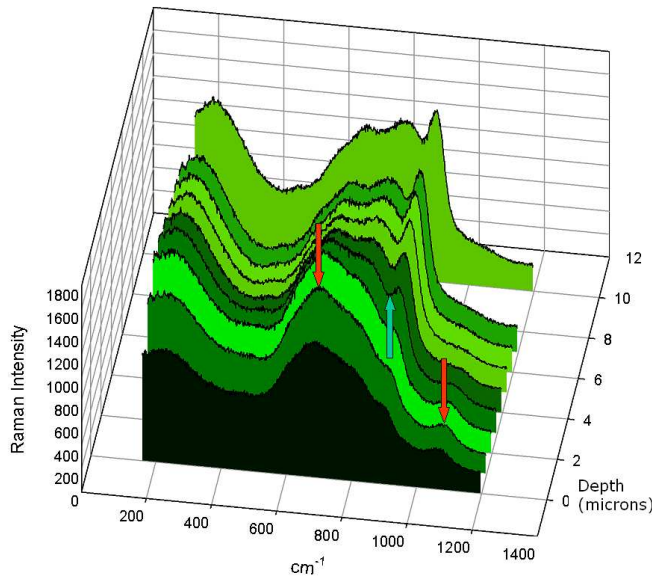


Figure 7.6: Confocal Raman mapping of KNS 232750, spectra were taken at different depths from anodic surface.

After a few μm the spectra resemble that of the unperturbed material, and no further modification is observed. Going from the anodic surface toward the interior of the sample, the spectrum gradually changes, showing an increase of the component at 896 cm^{-1} and a decrease of the bands at 690 cm^{-1} and 1065 cm^{-1} .

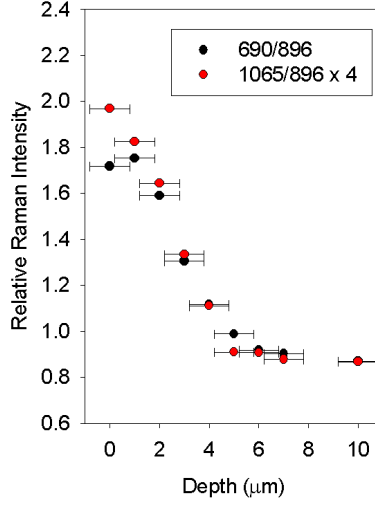


Figure 7.7: Spatial evolution of Raman signals at 690 and 1065 cm^{-1} normalized respect to the mode at 896 cm^{-1} .

In order to have an estimation of the depth of the structural modified layer in fig. 7.7 we have plot the relative amplitude of the components at 690 cm^{-1} and 1065 cm^{-1} normalized respect to the peak at 896 cm^{-1} vs. the depth. This analysis show a gradual profile of about 7 μm thick.

7.2.2 Optical interference of modified layer

A further confirmation of the formation in the poled area of a layer with different optical properties with respect to unpoled area is highlighted from optical absorption spectroscopy. Fig. 7.8 shows optical transmission in the 200-1000 nm range before and after the poling processes for samples showing SHG.

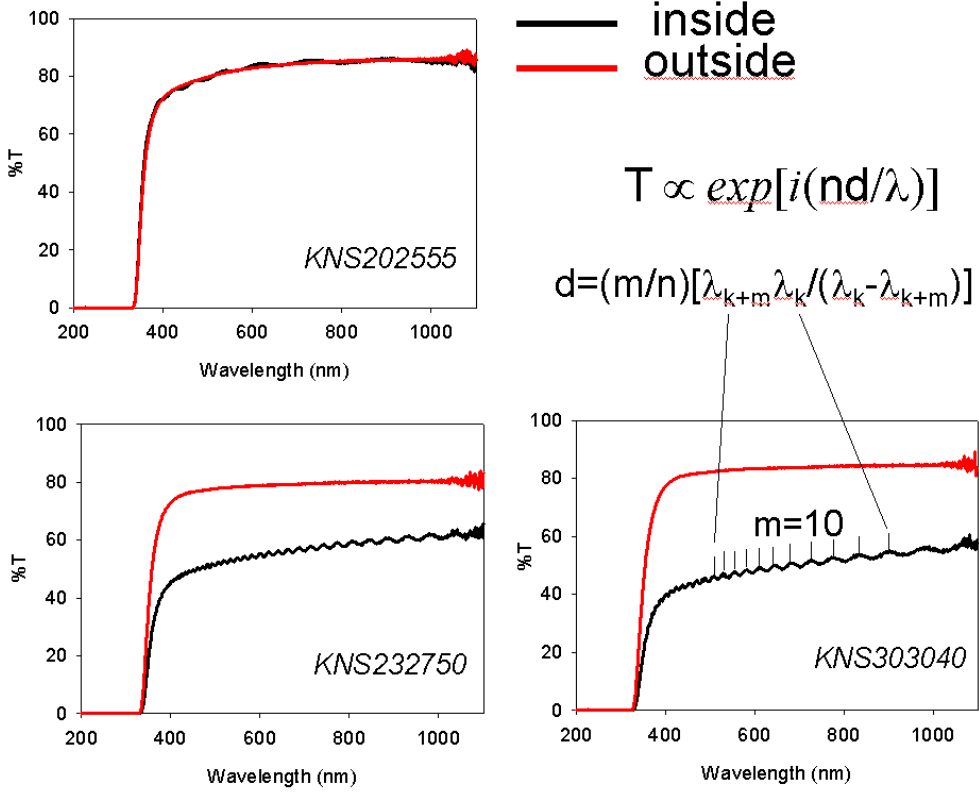


Figure 7.8: Optical transmission of poled glasses, inside and outside the poled region showing thin film interference.

Although the transmittance is, in general, lowered by the moderate opalescence of the treated region, there is a significant modulation that can be ascribed to thin film interference. Probably due to a slight change in the refractive index after structural modification. By modeling the periodic pattern with a Fabry-Perot like interference one can deduce the thickness d of the layer from the spacing between ripples by the equation:

$$T \propto \exp \left[i \left(\frac{2\pi}{\lambda} \right) 2dn \right] \quad (7.3)$$

Thus according to eq. 7.3 the thickness d is about 5-6 μm for sample KNS 232750, of

the same order of magnitude as that of thickness L measured either by mean of Maker Fringe technique and from Raman spectra analysis.

7.2.3 Localization of the active layer

To clarify where the active layer is located, we measured second harmonic signal as function of pump beam power after mechanical removal of $\sim 20 \mu\text{m}$ of material from either the anode and cathode surface.

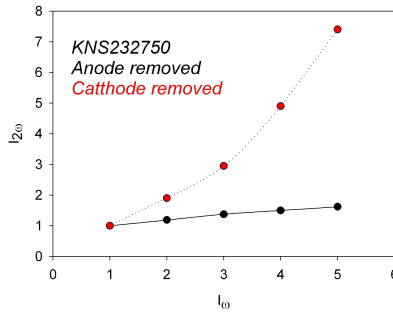


Figure 7.9: SH signal as a function of pump power after mechanical removal of anodic (black) and cathodic (red) surface.

Evidence of the localization of the active layer is given in fig. 7.9, showing that the intensity at 532 nm, the non linear origin of which is confirmed by the quadratic dependence on the incident power, is indeed much more depleted after removal of the anode surface (filled circle) than after removal of the cathode region (empty circles), thus clarifying that the non-linear portion is located under the anode, that is the same structurally modified.

7.2.4 Proposed model

Some relevant facts may be remarked from the reported results:

- the optical nonlinearity is related to structural modifications inside the amorphous material taking place within the non-linear thickness

- the structural modifications follow a charge transport process with a total displaced charge consistent with the number of alkali ions contained in a depletion layer of the same order of the non-linear layer
- the material keeps a glass structure after the poling treatment
- the observed nonlinearity is stable over several months after the poling process

These features bring us to pay particular attention to the mechanism of charge transport during poling, as well as to the structural modifications of the material, in order to clarify the possible origin of the poling-induced nonlinearity in the investigated glass. Since stainless steel electrodes strongly reduce the possibility of ionic injection, the poling process in our case is merely capacitive and all the current or the most part of it produces charge accumulation. The current, sustained by pre-existent charge carries, indeed decays exponentially in the time. Main charge carriers during the poling process in the investigated glass are mobile K^+ ions that go away from the anode surface toward the interior of the glass producing a K^+ depletion layer under the anode surface. This depletion layer, similarly to other poled glasses, is responsible for the second order optical nonlinearity (SON) induced by the thermal poling. In the literature, the thickness of this layer depends on glass composition as well as on poling condition, and can reach several μm (3-7)[51]. In our case, from three independent experimental methods (Maker fringes, optical interference fringes, and confocal Raman mapping) the data indicate that the poling-induced nonlinearity is consequent to a structurally modified layer $7 \pm 1 \mu m$ thick. Both the Raman spectrum (showing the enhancement of the degree of network cross-linking and the decrease of alkali-terminated non-bridging groups) and the value of the integrated poling current (which is congruent with the charge of all the mobile K^+ ions contained in a volume equal to the estimated modified layer) bring to propose that the poling process creates a K^+ depleted layer with a consequent modification of the glass structure.

Before discussing the source of SON from such a layer, we have to justify such a drastic depletion process looking for a sustainable transport mechanism. In fact, in a glass with a number of charge carriers of the order of 10^{22} cm^{-3} , alkali depletion cannot occur on such a scale without a charge compensation, as reported by Mariappan and Roling[68]. They found in poled glass a Na^+ depletion layer about $1.5 \text{ } \mu\text{m}$ thick and demonstrated that it should be less than 10 nm thick without charge compensation. The need of charge compensation was raised by other authors too ([68],[69],[46]) that hypothesized the existence of free mobile O^{2-} in the glass followed by oxygen evolution at the anode, although in a glass oxygen migration is somewhat unlikely. Others charge compensation mechanisms were proposed, as injection of protons, but all the literature data claim that none of them can account for a μm wide depletion layer, at least when the number of charge carriers is of the order of 10^{22} cm^{-3} . A possible explanation may be drawn from the structural role of alkali ions in glasses. Cations in a glass are distributed in the interstices of the network and they either modify such network by breaking its connectivity producing non-bridging oxygen atoms (NBO) or they compensate the negative charge of some structural units as $[\text{AlO}_{4/2}]^-$, $[\text{NbO}_{6/2}]^-$ or $[\text{BO}_{4/2}]^-$. As a result, moving from modifying or compensating positions, mobile alkali cations can migrate along percolating paths running randomly through the network, jumping between almost equivalent positions, with an Arrhenius temperature dependence of the conductivity. Cation migration leaves an excess of negative charge that drives structural changes of the anionic network of the glass[68],[69]. Such structural modification could become irreversible if a charge compensation occurs, and structural changes are indeed testified by the Raman spectra in Fig. 7.5 Similar effects were seen also by Carlson et al.[46] by IR reflection spectra in alkali-lead silicate glass. They found that the depleted anodic surface area was more polymerized than the unpoled surface and, heating the glass for 1 h at $600 \text{ }^\circ\text{C}$, they observed surface crystallization except for the poled area. This latter fact indeed evidences the higher cross-linking of the poled area and indicates that poling-induced structural changes are lasting to the heating.

The decrease of electric current during the poling is only partially to be attributed to the build-up of charges, since it is mainly related to the increase of electric resistance of the depleted layer that can also overtake several orders of magnitude [68],[69]. This increase of resistance can be related both to the decrease of charge carrier concentration (alkali ions) and to the increase of glass network cross-linking.

The above considerations, giving some insight into the relations between the role of alkali ions on the network and the structural changes consequent to alkali removing from the depletion layer, may be further elaborated starting from the work of Greaves and Ngai [70]-[71], which suggested that the alkali hopping in silicate glasses is associated with a change in the neighboring NBOs and BOs configuration. Specifically, two close oxygen atoms can change their role without changing their position. The mechanism of NBO-BO bond switching was proposed to occur in melts and in glasses at temperature below T_g and more recently in the modeling of ion migration in glasses [72]-[73]. Following this approach, NBOs can randomly move in an oxide glass by means of NBO-BO switching processes caused by thermal fluctuations, enabling alkali ions to move to new positions where charge compensation is given by nearby NBO, without any real transport of oxygen atoms in the single NBO-BO switching event [74]-[75]. Nevertheless, the whole process, because of the disappearance of NBO in the depletion layer and the consequent increase of cross-linking, is indeed equivalent to an oxygen migration compensating the potassium charge. According to this picture, the system during thermal poling cannot be considered as a simple electrolytic cell and the glass cannot be treated as a simple electrolytic solution. In particular, the electric current produces transformations in the glass that are more than a simple building up of space charge. When alkali cations move away from the anode to the inner of the glass, the anionic network of oxygen atoms in the alkali depleted layer transforms itself becoming more polymerized owing to the lower content of NBOs. The decrease of contributions of non-bridging Nb-O bonds in the Raman spectrum in Fig. 7.5 confirms this model, which also explains the change of electric response. As the

poling process proceeds, the alkali concentration in the layer near the anode gradually decreases and the cross-linking increases leading to a higher electrical resistance [69]. As a consequence, almost all the applied voltage drops in the alkali depleted layer and only in this layer structural changes are produced. In fact Ziemath et al. [76], comparing reflectance infrared spectra of anodic, cathodic and unpoled surfaces, found pronounced changes at the anodic surface only. The increase of polymerization degree of the glass anionic network is sometimes the starting point for further and more drastic structural transformations as phase separation. An and Fleming [77], also reported that phase separation stabilizes the SON of poled glass retarding its loss upon annealing. In our potassium niobosilicate glass, from the inner of the glass toward the anodic surface, the intensity of the bands at 690 and 1065 cm^{-1} increases, indicating that less distorted NbO_6 octahedra are formed together with SiO_4 . The increase of NbO_6 octahedra without NBOs indicates that the glass becomes progressively more polymerized. Therefore, the migration of K^+ ions induces a structural change in the depleted layer with a decrease of NBOs, related to a mechanism of NBO-BO bond switching that enable K^+ ions to move along the electric field. Such a mechanism allows to spread the charge piled up by the poling process on a thicker layer. Based on this analysis, the observed second order optical nonlinearity is likely to depend upon more than one process, because the built-in electric field generated by the depletion of K^+ ions is accompanied by extremely important structural processes that may have a crucial role in determining both the relatively large non-linear susceptibility with respect to poled silica and also the time stability of its value. In fact, on one hand, the structural re-adjustment in the depleted layer closes the backwards path to K^+ ions for a diffusion-induced alkali redistribution into the sample; on the other hand, the reconstructed network possesses a largely more reticulated niobium sub-network, suitable to give an own contribution to the second-order nonlinearity of the system.

Chapter 8

Conclusion

Our investigation of poling effects in potassium niobium silicate glasses has shown a relevant second order optical nonlinearity that we have demonstrated to be related to structural modifications accompanying the poling process. The structural changes, investigated with several different analysis, result from a charge transport mechanism that causes network reconstruction in an alkali depleted layer with thickness as comparable with that of the non-linear layer. Structural and electrical data depict a different poling mechanism with respect to that proposed up to now for silica-based materials, also explaining the observed stability of the induced nonlinearity over several months after the poling. The stable and relatively high nonlinearity, together with the perspective of optimizing the poling conditions so as to minimize transmittance lowering, make this system promising for further studies on the feasibility of waveguides and integrated devices.

Part III

Tapered silica optical microfibres for gas sensors

Chapter 9

Introduction

In the last years tapered silica fibres[95]-[98] have attracted much interest in photonic research, because of peculiar properties emerging in waveguide with lateral dimensions of the same order of the guided modes. In particular, in these structures the large evanescent field enables some interesting properties: such as microfluidic sensors and high Q resonators fabricated by coiling the tapered fibre, non-linear effects and supercontinuum generation. In this project, carried out at the University of Southampton (UK) in the group of Dr. Gilberto Brambilla, we explore the feasibility of an innovative optical absorption device, based on cavity ring down spectroscopy. In this case we are interested in a sensor for in-line application: a fluidic channel wrapped with tapered fibre in which the analyte can flow. The large power fraction outside the fibre interacts with the flowing medium and any change in the environment optical properties (refractive index or absorption coefficient) lead to a modification of the recorded light intensity propagating in the fibre. The idea is to exploit ring down time of a silica tapered microcoil resonator as an indicator of the absorption coefficient of a gas (or a liquid) flowing in the channel.

Chapter 10

Materials and methods

10.1 Modes in a cylindrical waveguide

An optical fibre consists in a core-cladding structure in which light travel along its length. The refractive index of the core n_1 is higher than that of the surrounding cladding n_0 , thus the light beam, for angles lower than a critical angle, is confined inside the core by total internal reflection. The simplest case of optical fiber is the step-index fiber where the refractive index of both core and cladding are constant along the radius of the fiber. In tapered fibres air acts as cladding material and the mode is confined inside the fibre itself. Light launched into one end of the fibre is guided along the core, i.e. it propagates mainly in the fibre region, although the intensity distribution may extend beyond the waveguide. Aim of this section is to provide a general theoretical background for the simulation of the mode profile (shape and energy) along a tapered fiber as a function of the main experimental parameter: refractive index of the medium surrounding the fiber, operational wavelength and fiber radius. The results of the modeling will be discussed in ??[100].

Once more, as in 6.2.2.1, the starting point are Maxwell's equation (Eqs. 6.2 and 6.3),

assuming $\rho = 0$, $\vec{J} = 0$, $\vec{M} = 0$, $c = \frac{1}{\sqrt{\epsilon_0 \mu_0}}$, and $n = \sqrt{\epsilon_r \mu_r}$:

$$\begin{aligned}\nabla \times \vec{E} &= -\mu \frac{\partial \vec{H}}{\partial t} \\ \nabla \times \vec{H} &= \epsilon \frac{\partial \vec{E}}{\partial t}\end{aligned}\tag{10.1}$$

If we consider an electromagnetic wave having angular frequency ω and propagating in the z direction, the electric and magnetic fields can be expressed as:

$$\begin{aligned}\vec{e} &= \vec{E}(\vec{r}) \exp[i(\omega t - \beta z)] \\ \vec{h} &= \vec{H}(\vec{r}) \exp[i(\omega t - \beta z)]\end{aligned}\tag{10.2}$$

where $\beta = k \cdot n = \frac{2\pi}{\lambda}$ is the propagation constant and $\vec{r}$ is the direction in the plane transverse to the propagation axis. Substituting eq. 10.2 in 6.2 and 6.3, the following set of equations are obtained in cylindrical coordinates:

$$\begin{aligned}\frac{1}{r} \frac{\partial E_z}{\partial \theta} + i\beta E_\theta &= -i\omega\mu_0 H_r \\ -i\beta E_r - \frac{\partial E_z}{\partial \theta} &= -i\omega\mu_0 H_\theta \\ \frac{1}{r} \frac{\partial}{\partial r}(rE_\theta) - \frac{1}{r} \frac{\partial E_r}{\partial \theta} &= -i\omega\mu_0 H_z \\ \frac{1}{r} \frac{\partial H_z}{\partial \theta} + i\beta H_\theta &= i\omega\epsilon_0 n^2 E_r \\ -i\beta H_r - \frac{\partial H_z}{\partial r} &= i\omega\epsilon_0 n^2 E_\theta \\ \frac{1}{r} \frac{\partial}{\partial r}(rH_\theta) - \frac{1}{r} \frac{\partial H_r}{\partial \theta} &= i\omega\epsilon_0 n^2 E_z\end{aligned}\tag{10.3}$$

$$\tag{10.4}$$

However, this set of partial differential equation do not determine univocally the electromagnetic field. We must know the boundary condition in order to choose the correct wave function from the infinite solution of the Maxwell's equation. Thus, for a discontinuity in the refractive index from medium 1 (fibre) to medium 2 (surrounding medium) the

tangential components of electric and magnetic field should satisfy:

$$\begin{aligned} E_t^{(1)} &= E_t^{(2)} \\ H_t^{(1)} &= H_t^{(2)} \end{aligned} \quad (10.5)$$

where the superscript indicate the medium and the subscript the tangential component to the boundary. Moreover, the electric and magnetic fields must vanish at infinity. Substituting eqs. 10.2 into 10.4 we obtain two set of equations as:

$$\begin{aligned} \frac{\partial^2 E_z}{\partial r^2} + \frac{1}{r} \frac{\partial E_z}{\partial r} + \frac{1}{r^2} \frac{\partial^2 E_z}{\partial \theta^2} + [k^2 n(r, \theta)^2 - \beta^2] E_z &= 0 \\ \frac{\partial^2 H_z}{\partial r^2} + \frac{1}{r} \frac{\partial H_z}{\partial r} + \frac{1}{r^2} \frac{\partial^2 H_z}{\partial \theta^2} + [k^2 n(r, \theta)^2 - \beta^2] H_z &= 0 \end{aligned} \quad (10.6)$$

Since, we assume axially symmetric optical fibres, the refractive index is not dependent on θ . Thus, the transverse electromagnetic fields are related to E_z and H_z as follows:

$$\begin{aligned} E_r &= -\frac{i}{[k^2 n(r)^2 - \beta^2]} \left(\beta \frac{\partial E_z}{\partial r} + \frac{\omega \mu_0}{r} \frac{\partial H_z}{\partial \theta} \right) \\ E_\theta &= -\frac{i}{[k^2 n(r)^2 - \beta^2]} \left(\frac{\beta}{r} \frac{\partial E_z}{\partial \theta} - \omega \mu_0 \frac{\partial H_z}{\partial r} \right) \\ H_r &= -\frac{i}{[k^2 n(r)^2 - \beta^2]} \left(\beta \frac{\partial H_z}{\partial r} + \frac{\omega \varepsilon_0 n(r)^2}{r} \frac{\partial E_z}{\partial \theta} \right) \\ H_\theta &= -\frac{i}{[k^2 n(r)^2 - \beta^2]} \left(\frac{\beta}{r} \frac{\partial H_z}{\partial \theta} + \omega \varepsilon_0 n(r)^2 \frac{\partial E_z}{\partial r} \right) \end{aligned} \quad (10.7)$$

The modes in a waveguide consist of TE modes ($E_z = 0$), TM modes ($H_z = 0$) and hybrid modes ($E_z \neq 0, H_z \neq 0$). We have assumed linearly polarized (LP) modes as solution of Maxwell's equation. However, even if the complete solution is beyond the scope of this thesis, we will introduce some important parameters for optical fibre. In particular we will define the normalized transverse wave numbers u and w and the normalized frequency v

for a cylindrical fibre of radius a .

$$\begin{aligned}
 u(a, \lambda, \beta) &= a\sqrt{k^2 n_1^2 - \beta^2} \\
 w(a, \lambda, \beta) &= a\sqrt{\beta^2 - k^2 n_0^2} \\
 u^2 + w^2 &= v^2 \\
 v^2 &= k^2(n_1^2 - n_0^2)a^2
 \end{aligned} \tag{10.8}$$

10.1.1 Propagation constant

In order to simulate the propagation of an electromagnetic wave inside and outside an optical fibre a precise knowledge of the propagation constant β is necessary. From eq. 10.8 we know that the value of β has some constrain, in particular we have:

$$n_0 k \leq \beta \leq n_1 k \tag{10.9}$$

Thus, its value has been calculated by solving the above equation using the $u - w$ relation (Eq. 10.8)¹.

$$\begin{aligned}
 \left[\frac{J'_1(u)}{uJ_1(u)} + \frac{K'_1(w)}{wK(w)} \right] + \left[\frac{J'_1(u)}{uJ_1(u)} + \left(\frac{n_0}{n_1} \right)^2 \frac{K'_1(w)}{wK(w)} \right] \\
 = \left(\frac{1}{u^2} + \frac{1}{w^2} \right) \left[\frac{1}{u^2} + \left(\frac{n_0}{n_1} \right)^2 \frac{1}{w^2} \right]
 \end{aligned} \tag{10.10}$$

It is worth noting that the solution of eq. 10.10 gives the exact value of the propagation constant. In fact, for tapered fibre, unlike step-index fibre, the approximation $n_1/n_0 \sim 1$ is no longer valid. Hence the weak guiding approximation should not be applied in tapered

¹The wave functions in cylindrical waveguides are usually Bessel function of order n ($n \in \mathbb{Z}$). A Bessel function is a solution $y(x)$ of the general Bessel's differential equation: $x^2 \frac{d^2 y}{dx^2} + x \frac{dy}{dx} \pm (x^2 + n^2)y = 0$.

J_n represents Bessel function of n -order ($x^2 \frac{d^2 y}{dx^2} + x \frac{dy}{dx} + (x^2 + n^2)y = 0$, $y(x) = J_n(x)$).

K_n represents modified Bessel function of n -order ($x^2 \frac{d^2 y}{dx^2} + x \frac{dy}{dx} - (x^2 + n^2)y = 0$, $y(x) = K_n(x)$).

fibres.

10.1.2 Electromagnetic fields - Explicit forms

Fields inside the fibre ($0 \leq r \leq a$):

$$\begin{aligned}
 E_r &= -i\beta \frac{a}{u} \left[\frac{(1-s)}{2} J_0 \left(\frac{u}{a} r \right) - \frac{(1+s)}{2} J_2 \left(\frac{u}{a} r \right) \right] \\
 E_\theta &= i\beta \frac{a}{u} \left[\frac{(1-s)}{2} J_0 \left(\frac{u}{a} r \right) + \frac{(1+s)}{2} J_2 \left(\frac{u}{a} r \right) \right] \\
 E_z &= J_1 \left(\frac{u}{a} r \right) \\
 H_r &= -i\omega \varepsilon_0 n_1^2 \frac{a}{u} \left[\frac{(1-s)}{2} J_0 \left(\frac{u}{a} r \right) + \frac{(1+s_1)}{2} J_2 \left(\frac{u}{a} r \right) \right] \\
 H_\theta &= -i\omega \varepsilon_0 n_1^2 \frac{a}{u} \left[\frac{(1-s)}{2} J_0 \left(\frac{u}{a} r \right) - \frac{(1+s_1)}{2} J_2 \left(\frac{u}{a} r \right) \right] \\
 H_z &= -\frac{\beta}{\omega \mu_0} s J_1 \left(\frac{u}{a} r \right)
 \end{aligned} \tag{10.11}$$

Fields outside the fibre ($r \geq a$):

$$\begin{aligned}
 E_r &= -i\beta \frac{a J_1(u)}{w K_1(w)} \left[\frac{(1-s)}{2} K_0 \left(\frac{w}{a} r \right) + \frac{(1+s)}{2} K_2 \left(\frac{w}{a} r \right) \right] \\
 E_\theta &= i\beta \frac{a J_1(u)}{w K_1(w)} \left[\frac{(1-s)}{2} K_0 \left(\frac{w}{a} r \right) - \frac{(1+s)}{2} K_2 \left(\frac{w}{a} r \right) \right] \\
 E_z &= \frac{J_1(u)}{K_1(w)} K_1 \left(\frac{w}{a} r \right) \\
 H_r &= -i\omega \varepsilon_0 n_0^2 \frac{a J_1(u)}{w K_1(w)} \left[\frac{(1-s_0)}{2} K_0 \left(\frac{w}{a} r \right) - \frac{(1+s_0)}{2} K_2 \left(\frac{w}{a} r \right) \right] \\
 H_\theta &= -i\omega \varepsilon_0 n_0^2 \frac{a J_1(u)}{w K_1(w)} \left[\frac{(1-s_0)}{2} K_0 \left(\frac{w}{a} r \right) + \frac{(1+s_0)}{2} K_2 \left(\frac{w}{a} r \right) \right] \\
 H_z &= -\frac{\beta}{\omega \mu_0} s \frac{J_1(u)}{K_1(w)} K_1 \left(\frac{w}{a} r \right)
 \end{aligned} \tag{10.12}$$

where

$$\begin{aligned}
 s &= \frac{\frac{1}{u^2} + \frac{1}{w^2}}{\left[\frac{J'_1(u)}{uJ_1(u)} + \frac{K'_1(w)}{wK_1(w)} \right]} \\
 s_1 &= \frac{\beta^2}{k^2 n_1^2} s \\
 s_0 &= \frac{\beta^2}{k^2 n_0^2} s
 \end{aligned} \tag{10.13}$$

10.1.3 Propagating power

The power carried by an optical mode is defined as the surface integral of the Poynting vector $\vec{S} = \vec{e} \times \vec{h}$ along the z -axis:

$$P = \int_0^{2\pi} \int_0^\infty S_z dr d\theta = \frac{1}{2} \int_0^{2\pi} \int_0^\infty (E_r H_\theta^* - E_\theta H_r^*) r dr d\theta \tag{10.14}$$

The explicit forms of integral 10.14 for the power carried inside and outside the optical fibre are the following.

Power inside the fibre ($0 \leq r \leq a$):

$$\begin{aligned}
 P_{in} &= \frac{1}{2} \int_0^{2\pi} \int_0^a (E_r^{in} H_\theta^{*in} - E_\theta^{in} H_r^{in*}) r dr d\theta = \\
 &\frac{\pi}{4} \omega \varepsilon_0 n_1^2 \beta \frac{a^2}{u^2} \left[(1-s)(1-s_1) \int_0^a J_0^2 \left(\frac{u}{a} r \right) r dr \right. \\
 &\quad \left. + (1+s)(1+s_1) \int_0^a J_2^2 \left(\frac{u}{a} r \right) r dr \right]
 \end{aligned} \tag{10.15}$$

Power outside the fibre ($r \geq a$):

$$\begin{aligned}
 P_{out} &= \frac{1}{2} \int_0^{2\pi} \int_a^\infty (E_r^{out} H_\theta^{out*} - E_\theta^{out} H_r^{out*}) r dr d\theta = \\
 &\frac{\pi}{4} \omega \varepsilon_0 n_0^2 \beta \frac{a^2 J_1^2(u)}{w^2 K_1^2(w)} \left[(1-s)(1-s_0) \int_a^\infty K_0^2 \left(\frac{w}{a} r \right) r dr \right.
 \end{aligned}$$

$$+(1+s)(1+s_0) \int_a^\infty J_2^2\left(\frac{w}{a}r\right) r dr \Big] \quad (10.16)$$

10.2 Optical resonance in microcoils

One of the main advantage in using optical microfibre is the possibility to easily fabricate optical resonators. The operation principle is to make a microcoil with a pitch of the same order of both the wavelength of the propagating wave and the diameter of the fibre; in such conditions self-coupling between adjacent turns is achieved and resonances may occur. Microcoil resonators are complementary to the two established methods used to obtain optical resonator: the classic Fabry-Perot interferometer (standing waves) and the optical ring resonator (traveling waves). In Fabry-Perot etalons the resonance is due to the multiple reflection that light experiences at two mirrors at the end of the cavity. In ring resonators resonance take place between the traveling wave in the closed loop and in the adjacent waveguide. In microcoil resonators there are not turning points and the closed loop is absent, however the wave traveling along the coil can, in part, recirculate in the loop providing the resonance condition. The following analysis will take in account three important parameters: L the loop length, $\gamma = 1 - \Gamma^2$ is the fractional power loss (Γ is the amplitude loss per pass), and K the power coupling coefficient. The scattering matrix $\bar{\bar{S}}$ describes the linear relationship between the incoming amplitude $\vec{E}_1$ and the outgoing wave amplitude $\vec{E}_2$: $\vec{E}_2 = \bar{\bar{S}}\vec{E}_1$. In the case of single loop the scattering matrix has the following form:

$$S_{21} = \frac{E_2}{E_1} = \Gamma \frac{\Gamma \exp[-(\alpha + i\beta)L] + iK}{1 - i\Gamma\sqrt{K} \exp[-(\alpha + i\beta)L]} \quad (10.17)$$

where $\exp[-(\alpha + i\beta)L]$ is the transmission coefficient of the feedback loop. Introducing $\sigma = \sqrt{1-\gamma} \exp[-\alpha L]$ the overall amplitude loss per turn, and $\theta = \beta L$ the round trip

phase shift we obtain from eq. 10.17 the relative intensity transfer:

$$|S_{21}|^2 = \Gamma^2 \frac{K + \sigma^2 - 2\sigma\sqrt{K}\sin(\theta)}{1 + \sigma^2 K - 2\sigma\sqrt{K}\sin(\theta)} \quad (10.18)$$

This last equation is periodically modulated with a free spectral range $FSR = c/n_{eff}L$ where n_{eff} is the effective refractive index of the fibre ($\beta = n_{eff}k$). At resonance wavelength λ_0 the amplitude of the scattering matrix $|S_{21}|^2$ reaches the minimum value:

$$|S_{21}|_{\lambda_0}^2 = \Gamma \frac{(\sqrt{K} - \sigma)^2}{(1 - \sigma\sqrt{K})^2} \quad (10.19)$$

Thus, if the coupling coefficient reaches the critical value $K_r = 1 - \sigma^2$ the interference is totally destructive and the resonator acts as a notch filter and there is no transmission. Beyond these considerations, it is helpful to relate some experimental output (summarized in Fig. 10.1) to the theory described above.

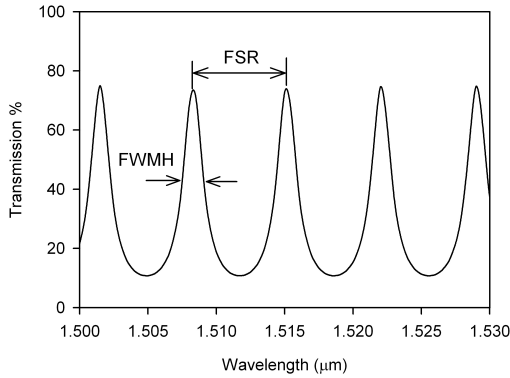


Figure 10.1: Representative transmission spectra of an optical resonator ($L=1\text{mm}$, $n = 1.5$)

In particular we are interested in an analytical definition of:

Free Spectral Range (FSR) is the frequency difference between maxima (or minima),

and it is the inverse of round trip time:

$$FSR = \frac{c}{n_{eff}L} = \frac{k \cdot c}{\beta \cdot L} \quad (10.20)$$

Full Width at Half Maximum ($FWHM$) of an interferometer can be derived from eq. 10.19, in fact it is defined as the frequency in which a detuning equal to $|S_{21}|^2 = (1/2)(1 + |S_{21}|_{min}^2)$:

$$FWHM = \frac{FSR}{\pi} \frac{1 - \sigma\sqrt{K}}{(\sigma\sqrt{K})^{1/2}} \times \quad (10.21)$$

$$\sqrt{\frac{a^2(\sqrt{K} - \sigma)^2 - (1 - \sigma\sqrt{K})^2}{a^2(\sqrt{1 - K} - \sigma)^2 - (2a^2 - 1)(1 - \sigma\sqrt{K})^2}} \quad (10.22)$$

Finesse ($\mathcal{F}$) It is defined as the FSR divided by the full width at half maximum ($FWHM$) of resonance in the interferometer. It is independent of the length of the loop, and it is determined from the losses and coupling efficiency of the system:

$$\mathcal{F} \equiv \frac{FSR}{FWHM} = \frac{\pi}{\arccos\left[\frac{2K\sigma}{(1+K^2\sigma^2)}\right]} \quad (10.23)$$

Q -Factor(Q) the quality factor Q of an oscillating system is a measure of the intensity of the damping of its oscillation. Thus, Q can be represented as the ratio of the energy stored respect to the energy dissipated per cycle can be view as: $Q = \omega \times \frac{\text{Energy Stored}}{\text{Power Loss}}$. However the simplest representation for a resonance with maximum at frequency ν_0 :

$$Q = \frac{\nu_0}{FWHM} \quad (10.24)$$

10.3 Optical cavity ring-down spectroscopy

As already mentioned, the central idea of the project is the exploitation of the peculiar microcoil resonance properties for sensors based upon optical absorption. Moreover, these optical absorptions are not direct, but estimate from the decay time of light pulses launched in the microfibres. Thus, before describing the physics of such a phenomenon in microcoils, we will shortly discuss the basis of this technique. Optical ring-down spectroscopy refers to a spectroscopic method that enables the measurement of the optical extinction coefficient of gases. In its classical configuration, the medium to be analyzed is placed between two highly reflecting mirrors (typically $R > 99.9\%$) and a laser beam enters the cavity. Then the laser is turned off and the optical absorption coefficient is estimated by the exponentially decaying light intensity leaking from the cavity. During the decay, light is reflected back and forth several times (depending on the cavity finesse) and the effective optical path length can reach few kilometers, enabling measurements of either strong absorptions of species present in trace amounts or weak absorptions of abundant species.

The intensity of light within the cavity is determined as an exponential function of time:

$$I(t) = I_0 \exp(-t/\tau) \quad (10.25)$$

the decay constant τ is the ring-down time. Its value depends on the speed of light in the medium, the optical losses due to mirrors and spurious effects (γ), the cavity length (l), the reflectance (R) and the absorption coefficient of the absorbing medium (α):

$$\tau = \frac{t_r}{2[(1 - R) + \gamma + \alpha l]} \quad (10.26)$$

where $t_r = nl/c$ is the round trip time of a laser pulse in the cavity. Thus a measure of the decay time for an empty cavity permits the evaluation of $t_r/2[(1 - R) + \gamma]$, while

the presence of absorbing species lead to an increase of denominator in eq. 10.26 and a consequent decrease in the ring-down time. The difference between empty and filled cavity gives the absorption coefficient of the species under study. It is worth noting that usually this kind of technique is applied in meter sized cavities with very high finesse ($R \sim 99.99\%$), so a rough estimation of ring down time (without losses and absorbing species in the cavity) is about $20 \mu s$, value largely measurable with the current technologies.

Chapter 11

Result and discussion

11.1 Simulation

In this section we will examine the main parameter estimated from the equations given in 10.1. The program used for simulation is Mathematica 7 (Wolfram Research), first we will analyze results for propagation constant β . The parameter β has been evaluated as a function of wavelength, fibre diameter and for two different surrounding medium: air and Teflon. The β value is the starting point for all the simulations, in fact from its value is it possible to find the shape of the propagating electromagnetic field (inside and outside the optical fibre) and the power carried by the mode. Moreover we simulate the expected ring-down time for optical fibre microcoils.

11.1.1 Propagation constant

The propagation constant β has been evaluated by means of eq. 10.10 under the constraint that $n_0k \leq \beta \leq n_1k$, fig. 11.1 shows the value of propagation constant as a function of fibre diameter embedded in Teflon and air. No dispersion has taken in account for air (assuming $n = 1$) and Teflon ($n = 1.3$), while for silica fibre a Sellmeier equation was

adopted (λ expressed in μm):

$$n(\lambda)^2 = \frac{0.6961663 \lambda^2}{\lambda^2 - (0.0684043)^2} + \frac{0.4079426 \lambda^2}{\lambda^2 - (0.1162414)^2} + \frac{0.8974794 \lambda^2}{\lambda^2 - (9.896161)^2} \quad (11.1)$$

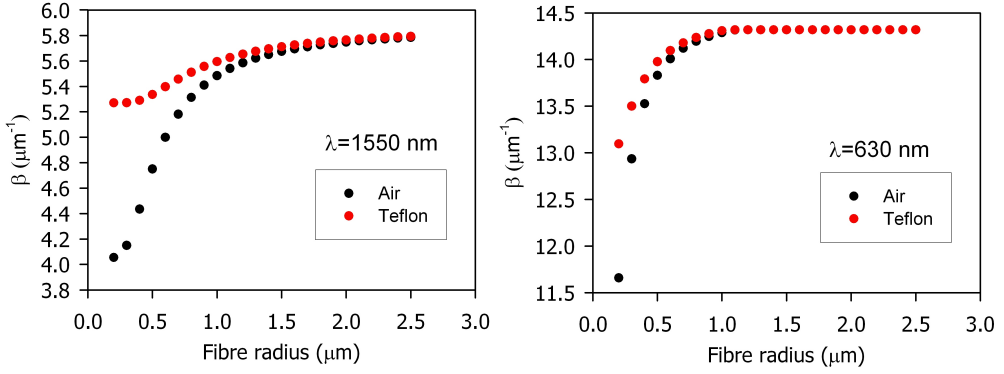


Figure 11.1: β values as a function of fibre diameter embedded in teflon (red) and in contact with air (black), for $\lambda=1.55 \mu m$ (left panel) and $\lambda=0.63 \mu m$ (right panel)

11.1.2 Propagating power

The propagation constants calculated in 11.1.1 allows to simulate the electromagnetic field propagating in the fibre; fig. 11.2 shows the intensity profile of a beam in a fibre with radius $0.5 \mu m$ (A) and $1.5 \mu m$ (B).

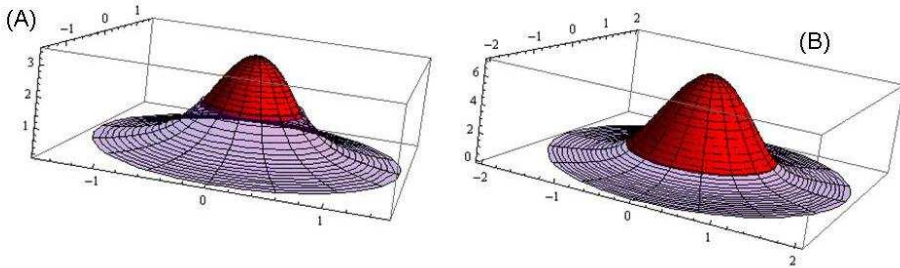


Figure 11.2: Simulation of electromagnetic field intensity. $\lambda=1550$ nm, coating Teflon ($n=1.3$); (A) $0.5 \mu m$ fibre radius and (B) $1.5 \mu m$ fibre radius.

The intensity profile outside the fibre follows an exponential decay: the smaller the fibre and the greater its extension be. Fig. 11.3 shows the propagating power inside a microfibre as a function of fibre diameter, for a propagating wavelength of 1550 nm and 630 nm, for system surrounded by air and Teflon.

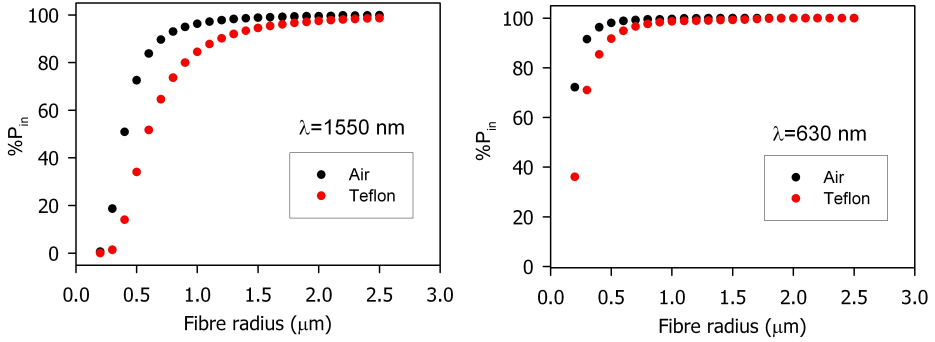


Figure 11.3: Propagating power inside the fiber as a function of fibre diameter embedded in teflon (red) and in contact with air (black), for $\lambda=1.55 \mu\text{m}$ (left panel) and $\lambda=0.63 \mu\text{m}$ (right panel).

In the following we summarize some general conclusion about the propagating power in a tapered microfibre, in particular we have weaker confinement for:

- small fibre diameter
- closeness between refractive indices of silica fibre and surrounding medium
- large wavelengths

11.2 Microcoils

In order to fabricate the device some preliminary experiments have been performed on microcoils. In particular several microfibres have been fabricated starting from commercial telecom silica fibres (external diameter $125 \mu\text{m}$). The fibre is fixed on two translation

stages with submicron precision, the central part of the fibre is heated with a microfurnace close to glass transition temperature. A software controls the translation stages and the fibre is pulled since the length of the tapered zone and its diameter reach the desired value. The typical length of the tapered fibre was 6-8 mm with final diameters ranging from 1.5 to 3 μm . Then the optical fibre microwire is wrapped on a rod with low refractive index, usually a PMMA rod (1 mm in diameter) coated with Teflon, and finally the optical response of these microcoils were studied. Fig. 11.4 shows the response of a coil made with a 2 μm fibre with different number of turns.

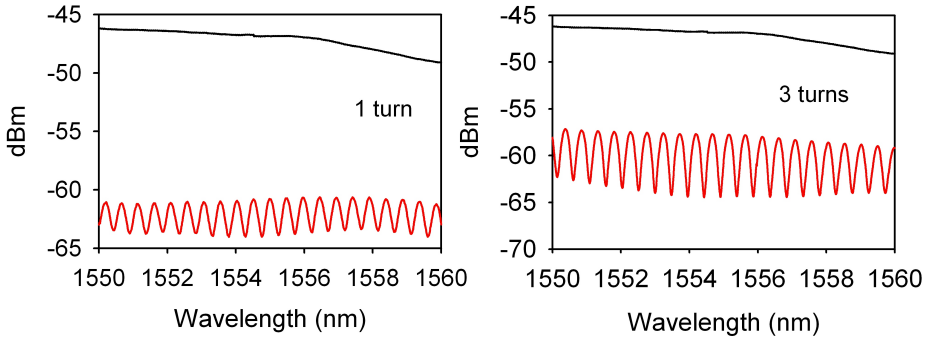


Figure 11.4: Optical response of microcoil resonators.

We used a 1550 nm laser as light source and an optical spectrum analyzer as detector. Even if the losses are quite high, it is clear the resonance condition given by the interference of the evanescent field of different turns coupling to each other. The observed free spectral range (Eq. 10.20) of ~ 0.46 nm (that corresponds to $\sim 5.8 \cdot 10^{10}$ Hz), is consistent with an effective refractive index of $n_{eff} \sim 1.58$.

11.2.1 Device fabrication

The two ends of a PMMA rod (1 mm in diameter, 2 mm length) are inserted in two Teflon pipelines (internal diameter 1 mm, external diameter 1.2 mm). A tapered optical fiber (with a diameter $1 < r < 3$ μm) is then wrapped on the PMMA rod (Fig. 1 A) and the

structure is coated with Teflon (Fig. 1 B). After thermal treatment (20 min at 80 °C) the PMMA rod is removed by dipping the device in acetone for 1 day (Fig. 1 C).

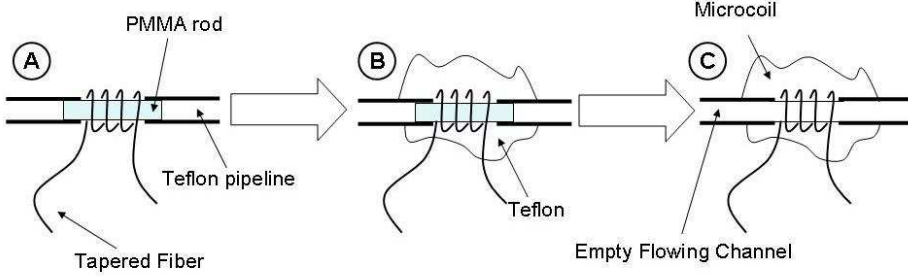


Figure 11.5: Schematic of device fabrication procedure.

In order to insure mechanical stability the device is fixed on a glass slide with a UV-curing polymer as low-loss glue. The ends of the fluidic channel are connected by a heat-shrink tubing to teflon pipeline with a diameter of 1.5 mm, then the device is completed with two valves and the liquid (or gas) to be analyzed is inserted with a syringe.

11.2.2 Absorption measurements

The device has been tested with aqueous solutions of an organic dye (Brilliant Blue FCF $\lambda_{max}=630$ nm) at different concentration and using a supercontinuum generator as light source.

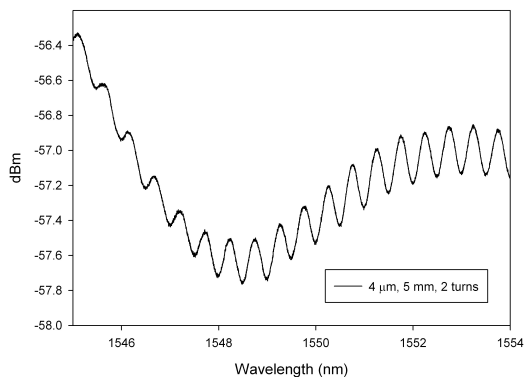


Figure 11.6: Optical response of microcoil with empty channel.

Fig. 11.7 reports the signal recorded with an Optical Spectrum Analyzer after baseline correction with the fluidic channel filled with pure water.

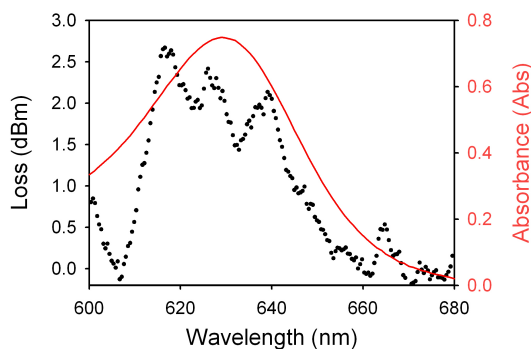


Figure 11.7: Signal loss at fiber end ($C=0.5 C_0$, dots) and optical absorption measured with a spectrophotometer ($C=0.02 C_0$, solid line) after baseline correction with pure water.

The spectrum shows three absorption maxima centered at about 615, 628 and 640 nm, it is worth noting that the measure is hardly affected by the noise fluctuation of the light source. However the spectrum shape is in good agreement with the peak registered with a spectrophotometer (full line in Fig. 11.7). Before analyzing the behaviour of such

device with dyes at different concentration, let us considerate the expected absorption for a coil in contact with an absorbing species.

Part of the evanescent field of the guided mode is directly exposed to the absorbing analyte flowing in the channel, thus leading to optical losses. In this model we assume no coupling between adjacent turns and all the optical losses will be ascribed to the evanescent field absorption. Optical absorption follows an inverse exponential power law that depends on: the concentration C and the molar extinction coefficient ε of the analyte, and the optical path length L . However in a tapered fiber not all the light interacts with the absorbing specimen but only the fraction of the evanescent field in contact with the fluidic channel, thus the well-known law of absorption is corrected by an efficiency factor κ that depends both on the molar absorptivity and the radius of the optical fiber. The light intensity, I , measured at the fiber end is related to the incident intensity I_0 by the following equation:

$$I(\lambda) = I_0 \exp[-\kappa(\varepsilon, a, \lambda) \cdot C \cdot L] \quad (11.2)$$

A first approach to estimate the κ value is to consider the attenuation of the electromagnetic field outside the fiber and in contact with a fluid of molar absorption ε . Starting from the propagation constant $\beta(\lambda, a)$ the total electromagnetic power can be expressed as a sum of three contributions: internal, external in contact with the Teflon layer and external in contact with the analyte.

$$\begin{aligned} P_{tot} &= P_{in} + P_{teflon} + P_{sample} = \\ &= \frac{1}{2} \int_0^{2\pi} \int_0^a (E_r H_\theta^* - E_\theta H_r^*) r dr d\theta + \\ &+ \frac{1}{2} \int_0^{2\pi-\varphi} \int_a^\infty (E_r H_\theta^* - E_\theta H_r^*) r dr d\theta + \\ &+ \frac{1}{2} \int_0^\varphi \int_a^\infty (E_r H_\theta^* - E_\theta H_r^*) r dr d\theta \end{aligned} \quad (11.3)$$

The efficiency factor, for a given molar absorptivity, is calculated from the ratio between the response without and with the absorbing analyte:

$$\kappa = 1 - \frac{P_{abs}}{P_{tot}} = 1 - \frac{P_{in} + P_{teflon} + P_{sample} \cdot \exp[-\varepsilon \cdot x]}{P_{tot}} \quad (11.4)$$

Fig. 11.8 shows the κ factor as a function of the fiber radius for a tapered fiber in contact with Teflon and Brilliant Blue FCF dye solution (assuming $x \rightarrow \infty$ and $\varepsilon = \alpha(\lambda_{max}) = 50cm^{-1}$, where $\alpha(\lambda_{max})$ is the absorption coefficient for a dye solution with concentration C_0 and $\lambda=630$ nm).

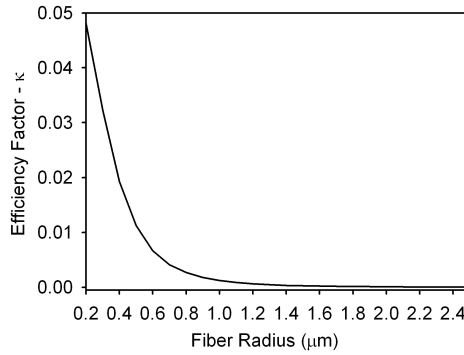


Figure 11.8: Efficiency factor κ as a function of fiber radius.

Thus we carried out absorption measurement as function of nominal concentration of dye solution. Fig. 11.9 shows the averaged optical losses in the range 610-650 nm as a function of the nominal concentration of the analyzed solutions.

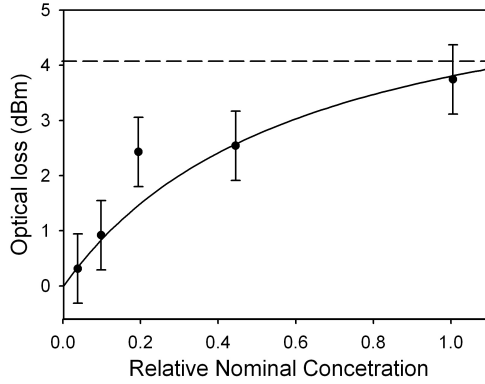


Figure 11.9: Optical loss as a function of nominal concentration: C/C_0 . Dashed line represents the theoretical value for $C = C_0$, solid line is a fitting curve assuming adsorption processes.

Optical losses grow with the nominal concentration, however the expected linear relation (Eq. 11.2) is not observed. Within the experimental error, the measured optical loss for $C = C_0$ is in accordance with the calculated value (dashed line in Fig. 11.9) using Eq. 11.2 and 11.4.

The non-linear behaviour observed in Fig. 11.9 has been interpreted as a consequence of a different physical mechanism relying the absorption process. Eq. 11.2 is valid only for an analyte homogeneously dispersed in a solution (e.g. a dye solution in a cuvette), but in our system the entire process is affected by strong interaction between the nanofibers surface and the surrounding environment. Thus it is possible that the major contribution to the optical absorption comes from the dye molecules directly bound at the silica surface expose to the fluidic channel. On the other hand the tapering process modifies the silica surface properties, with formation of defect sites and hydroxile groups and consequent chemical and physical degradation. Moreover these sites enhance the interaction between analyte and substrate, via physical bonds such as dipole-dipole interaction, hydrogen bond, and Van der Waals forces. In this scenario the effective concentration has to

be corrected taking into account the adsorption processes. In particular a Langmuir adsorption law has been used to fit data in fig. 11.7 (solid line). In surface science the covering of a single layer of adsorbate onto a non-interacting surface is described by the following equation:

$$\Theta = \frac{\alpha \cdot C}{1 + \alpha \cdot C} \quad (11.5)$$

Where Θ is the fraction of the occupied surface sites, C the concentration of the adsorbate, and α is a constant proportional to the binding energy, and represents the “sticky efficiency” of the system.

11.2.3 Preliminary ring-down spectroscopy

The device fabricated with the same procedure described in 11.2.1 has been tested for ring-down spectroscopy.

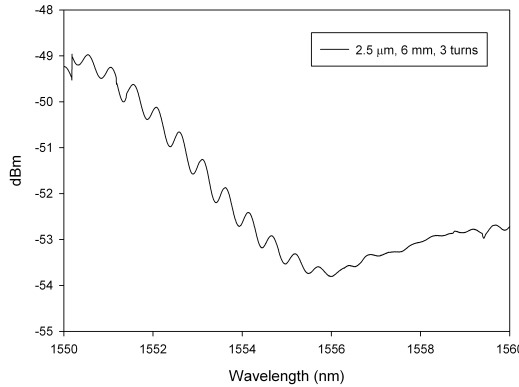


Figure 11.10: Optical response of microcoil with empty channel.

The test has been performed with a pico second mode locking laser ($\lambda = 1.55 \mu m$). Since the signal decay was too fast for life-time measurement carried with traditional technique (such as oscilloscope locked to laser pulses), the pulse duration was measured with a telecom analyzer. Fig. 11.11 shows the gaussian temporal distribution of the beam

before and after microcoiling, as expected the microcoiled fiber shows an effective delay time of the order of 10 ps as expected from Eq. 10.26 (Fig. 11.13).

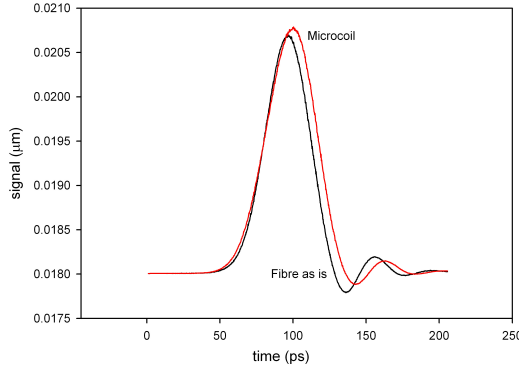


Figure 11.11: Time delay of as is (black line) and coiled microfibre (red line)

However the experimental setup does not permit any accurate measurement because of time limitation. Tests performed with acetylen as gas analyte showed changes in the time profile of the beam, but not stable signal was recorded.

In order to find the ideal conditions for such sensor we simulate ring-down time as a function of recirculating power. The first step is to relate the finesse of a coil resonator to the recirculating power.

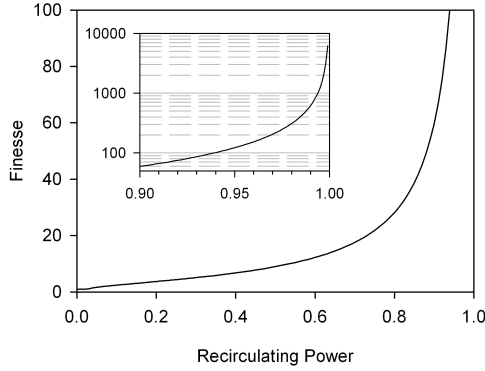


Figure 11.12: Recirculating power as a function of microcoil finesse.

Fig. 11.12 shows the relation between these two parameters, assuming low losses.

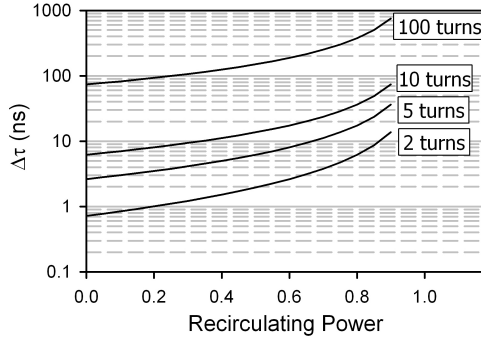


Figure 11.13: Ring down time of empty channel as a function of turn number and recirculating power in the cavity. ($\lambda=1550$ nm, teflon coating)

Then the ring-down time (for an empty channel) was evaluated as a function of recirculating power and number of turns, analysis of this simulation is depicted in fig. 11.13. As expected the ring down time increases with the number of turns and the finesse of the resonator, however ring down time long enough to be measured without excessive experimental complication, may be found in coils with very large number of turn (>100).

Chapter 12

Conclusion

Gas sensors based on tapered optical microfibres have been investigated by both numerical simulation and preliminary experimental tests. In particular, microcoils with internal empty channel have been prepared, the device was mechanical solid and robust. Absorption measurements on fluids flowing in the channel have been performed on both liquid and gas phases. In the first case Brilliant Blue FCF was adopted as analyte, spectra were recorded as a function of nominal solution concentration. The recorded optical response depends on analyte concentration, but the observed behaviour seems to rely on an *adsorption* process rather than a classical Lambert-Beer law. Finally, a first experimental test on ring-down time measurement in microcoil resonator has been performed. The expected delay, of few tenths of nanoseconds, was detected, but we encountered strong time limitation in the experimental setup. Thus, the ring-down spectroscopy has not been employed for absorption measurement. However, the feasibility of such a device was simulated clarifying the suitable conditions for these applications in terms of microcoil finesse and turns number.

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List of Publications

1. P. PERNICE, A. PALEARI, M. FERRARIS, M. FOKINE, E. FANELLI, *LORENZI R.*, G. SPINOLO, A. ARONNE Electric field induced structural modification and second order optical nonlinearity in potassium niobium silicate glass. JOURNAL OF NON-CRYSTALLINE SOLIDS, vol. 355; p. 2578-2582
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