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Optical Nonlinearities in Glasses

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Abstract

The field of photonics has been the target of constant innovations based on a deep knowledge of the nonlinear optical (NLO) properties of materials and especially on information/data technologies. This chapter compiles some of the main physical aspects needed to understand NLO responses, especially in glasses. Any deviation from the linear correlation between a material's polarization response and the electric component of an applied electromagnetic field is an example of nonlinear optic behavior. Heavy metal oxide and chalcogenide glasses offer the largest nonlinear response. For example, high refractive index and high dispersion glasses fall in the type of non-resonant devices, while the resonant ones comprise metal nanoparticle doped glasses. Metal nanoparticles' doped glasses can be prepared by the sol-gel method. The optical absorption spectrum of Ag-doped silica glass shows the presence of an absorption band of surface Plasmon Resonance due to Ag nanoparticles at 420 nm and Z-scan has been used to study the NLO properties. This chapter contains a brief discussion of the basic principles of nonlinear optics, the review of the nonlinear optical of glass in general, and two separate sections concerning the nonlinear optical effects in the glasses doped with quantum dots and metals, respectively.

Keywords: glass, photonics, nonlinear optical (NLO), Kerr effect (third-order nonlinearity)

1. Introduction

Photonics, a field that aims at the study of generation, manipulation, and detection of light, has become essential in modern life. Photonic devices as all-optical switches and modulators play a key role in worldwide data optical communications or optical computing. Since the invention of lasers in the 1960s, there has been a huge increase in the use of devices that use photons (light) instead of electrons. In 1985, a research group of the Southampton University showed the potential of silica glass fibers doped with Er^{3+} ions for applications in long optical transmission systems, at the wavelength region of 1.55 μm , without the need of electronic repeaters [1]. The invention of the erbium-doped fiber amplifier (EDFA) was a key factor in enabling the transmission of long-distance data through silica fiber. The 1.55 μm optical waveband falls in the low-loss transmission window of silica fiber and the amplification band of EDFA's. Sadly, they are still restricted to amplification in the C and L bands. Therefore, optical fibers using linear near-infrared light transmission are only a small fraction of what can be exploited by extending the operating region to the mid- and far-infrared. In fact, silica optical fibers have a

non-negligible attenuation of the emitted signal, so if the range of transparency were extended to longer wavelengths, it would have less attenuation. Hence, transparent glasses in the mid and far-infrared wavelength range are well suited to long-distance communication systems due to the Rayleigh dispersion attenuation coefficient varying with λ^{-4} . Nowadays, almost all data flow, including internet, phone calls, etc., goes through fiber optic transmission lines [2] and the field of communications continues to expand to higher data rates and shorter delays to allow more capacity. The demands of the modern world are looking for high-speed communication and therefore it is expected that an overload of data traffic may occur in the telecommunications window that currently operates in the C and L bands. Therefore, an expansion to a wider bandwidth is required which would facilitate data transmission and new amplification materials are needed beyond EDFA's to provide amplification over the optical fiber. This requires overcoming the limitation of peak water absorption around 1.4 μm . All wave fiber was the first to be designed for optical transmission across the entire telecommunications window from 1.3 μm to 1.67 μm (**Figure 1**) [3]. On the other hand, rare-earth (RE) have low solubility in silica glass which limits the interaction length of active devices based on RE doped silica [4]. Besides, silica has high phonon energy which implies that the RE ions transitions will decay non-radiatively; also exhibit a low nonlinear refractive index and so, nonlinear devices based on silica will require high intensities to operate. Finally, silica has a high transmission loss at wavelengths above 2 μm [3].

The necessary increase in the bandwidth excludes the use of EDFA's, leaving fiber Raman amplifiers as the main devices used for that proposes [5]. In fact, amplifiers based on stimulated Raman scattering and four-wave mixing offer additional advantages over EDFAs [6], operate without the need for doping, and can be used at any spectral region [7]. Moreover, the wavelength of the pump laser can be chosen to give a maximum gain at any wavelength range (S, C, or L-band), and the gain bandwidth is higher than that offered by EDFA's (> 100 nm versus 35 nm), which can be enlarged by an appropriate choice of the material [6]. On the other hand, fiber Raman lasers are excellent options for high-power fiber lasers, mainly because of their high output power and broad gain bandwidth, especially in the near-infrared region.

Although silica is widely used in the near-infrared, it limits the wavelength operating range. To overcome these limitations new glasses for optical device

Figure 1. Loss of standard and all wave silica fibers showing the region of minimum attenuation and the six conventional bands of optical telecommunications [3].

applications and photonics have been investigated. These include heavy metal oxide, fluoride, and chalcogenide glasses.

Glasses containing chalcogenides are the basis for the manufacture of devices operating in the mid-infrared region. In addition, glasses based on heavy metal oxides, such as Sb, Bi, Pb, W, Ga, Ge, Te, allow applications such as optical switches, due to their characteristics of low linear and nonlinear loss, large Kerr nonlinearity, and ultra-fast response. Fluoride-based glasses are used as optical amplifiers in telecommunication as well as in the manufacture of lasers.

Photonics is also used in medical applications, such as lasers used for LASIK surgery, and biomedical diagnostics exploit optical components for bioimaging. Integrated photonics also enables the advance of computing, information technology, sensing, and communications. The integration on a simply planar substrate of several photonic devices (optical sources, beam splitters, couplers, waveguides, detectors, etc.), as proposed by Miller in 1964 [8], enables the control of light on a significantly reduced scale where components are expected to exhibit a very reduced size and achieving a multiplicity of functions, including splitting, combining, switching, amplifying, and modulating signals. Many of these functions are nonlinear. For example, fiber nonlinearities are the basis of several devices such as amplifiers and switching. These nonlinear effects can be divided into two types. The first type is owing to the Kerr-effect (or intensity dependence of the refractive index of the material), which in turn can display phase modulation and wave mixing, depending upon the type of input signal. The second type is related to the inelastic-scattering phenomenon, which can induce stimulating effects such as stimulated Brillouin-Scattering and stimulated Raman-Scattering [9].

NLO is an important issue of advanced photonics and enables technical development in many fields including optical signal processing and quantum optics. It refers to the study of phenomena that occur due to modifications in the optical properties of a material in the presence of light. However, only laser light has sufficient intensity to promote these changes. Indeed, nonlinear optical phenomena (e.g. multiphoton absorption, harmonic generation, self-focusing, self-phase modulation, optical bistability, stimulated Brillouin scattering, and stimulated Raman scattering) require high electromagnetic field intensities to manifest.

2. Basic principles of NLO

In the linear optical domain, photons interact with the glass structure leading to various optical effects, such as dispersion, refraction, reflection, absorption, diffraction, and scattering. For example, the linear refractive index of a material, n , describes how light propagates through it, and the index defines how much light is bent, or refracted when it across the material. However, these properties may become nonlinear if the intensity is high enough to modify the glass optical properties, resulting in the creation of new beam lights of different wavelengths.

A nonlinear optical behavior is a deviation from the linear interaction between a material's polarization response and the electric component of an applied electromagnetic field [10]. This phenomenon involves various optical exchanges such as frequency doubling, conversion, data transformation, etc. Because the magnetic component of light can be ignored in a glass (photons and magnetic fields usually do not interact), the electric component (E) becomes the main field that interacts with the medium. The polarization (P) induced by this interaction produces nonlinear responses that can be explained due to the distortion/deflection of the electronic structure of any atom or molecule (deformation of the electron cloud) due to the

application of the electric field, thus producing a resulting dipole moment (vector that separates the positive and negative charges).

Once an external E field is applied to the material the positive charges tend to move in the opposite direction of the electrons. This interaction causes a charge separation that gives rise to microscopic dipole moments within the material. Under the influence of an electric field, these dipoles oscillate at the same frequency (ω) of the incident light. The sum of all the microscopic dipoles of the medium oscillating with time gives rise to material polarization. At low light intensities, Hook's law is valid and the deformation of the electrons cloud is proportional to the applied field strength of the incident light: the light waves and excited electrons oscillate sinusoidally. The induced polarization is also oscillatory and is directly proportional to the incident electric field, as described by:

$$P = \epsilon_0 \chi^{(1)} E \quad (1)$$

where ϵ_0 is the vacuum permittivity and $\chi^{(1)}$ (or χ) is the linear susceptibility, which, in this case, depends on the frequency, and thus is directly linked to the linear refractive index, but does not depend on the amplitude of the electric field, which implies that the frequency of light does not change as it passes through matter. However, at high intensities, the electrons are extremely deflected from their orbit, and their movements become distorted giving rise to important deviation from harmonic oscillation. As a result, the amplitude of dipoles oscillation increases, and they emit light not only at the wavelength that excites them but in other frequencies (new color!!!) (**Figure 2**) [11]. At large intensities, P is a nonlinear function of E whereas, at low intensities, the interaction is a linear function. So, for materials with nonlinear characteristics, in which the polarization given by the Eq. (1) is no longer valid, P must be written in a more general form, as a power series of E:

$$P = \epsilon_0 \left(\chi^{(1)} E^1 + \chi^{(2)} E^2 + \chi^{(3)} E^3 + \dots \right) \quad (2)$$

where the values of $\chi^{(2)}$ and $\chi^{(3)}$, are, respectively, the second-order and third-order susceptibilities which appear due to the nonlinear response of charged particles and are determined by the symmetry properties of the medium. Consequently, nonlinear refractive index (n_2), second ($\chi^{(2)}$), and third-order ($\chi^{(3)}$) nonlinear

Figure 2.

(a) Linear optics, a light wave acts on the material constituents, which vibrates and then emits its own light wave that interferes with the original light wave, (b) nonlinear optics. Adapted from [11].

susceptibilities can be measured. In isotropic, nondispersive, and homogeneous mediums, the material susceptibilities can be considered constants. However, in anisotropic media where properties are directionally dependent, the susceptibilities of the material are tensor quantities and therefore, depend on the microscopic structure (electronic e nuclear) of the material [12].

Considering the relations $n^2 = 1 + \chi^{(1)}$, $c = \frac{1}{\sqrt{\epsilon_0 \mu_0}}$, and $n = \frac{c}{c_0}$, where n represents the linear refractive index, c is the speed of light in vacuum, c_0 the speed of light in the material, and μ_0 the vacuum permeability; Maxwell's equations can be used to obtain the wave equations in a nonlinear material:

$$\nabla^2 E - (1 + \chi) \epsilon_0 \mu_0 \partial_t^2 E = \frac{1}{\epsilon_0 c^2} \partial_t^2 P \quad (3)$$

where the term $\partial_t^2 P$, represents a measure of the acceleration of the charges that constitute the material, which plays a fundamental role in the theory of nonlinear optics. This term acts as a source in the generation of new radiation field components, producing oscillating electric fields within a linear medium of refractive index n .

Assuming an external electric field of the type $E(t) = E \exp(-i\omega t) + c.c$, where $c.c$ denotes "complex conjugate", the term related to second order polarization is given by:

$$P^{(2)} = \epsilon_0 \chi^{(2)} E^2 = 2\epsilon_0 \chi^{(2)} |E|^2 + \epsilon_0 \chi^{(2)} E^2 \exp(-2i\omega t) + c.c \quad (4)$$

being responsible for the generation of a field with twice the frequency of the incident radiation (2ω), taking the designation of the second harmonic generation process. However, in centrosymmetric materials, or isotropic materials like glass, which have macroscopic inversion symmetry, the polarization must reverse when the optical electric field is reversed, which implies that $\chi^{(2)}$ must be zero, i.e., all second-order components of the susceptibility tensor are null and GSH does not manifest unless the glass has been poled. It is possible to induce GSH in glasses to break its centrosymmetry, using heat treatments or high energy excitation in the UV [13]. But, without the use of this strategy to eliminate glass's isotropy, only a $\chi^{(3)}$ is $\neq 0$ and may lead to NLO character in glass [10] and the dominant term in (2) is then the third order:

$$P^{(3)} = \epsilon_0 \chi^{(3)} E^3 \quad (5)$$

which will give rise to frequency tripled light, called third-harmonic generation (THG). According to (5) this nonlinear polarization contains a component of frequency ω and an additional one at 3ω :

$$P^{(3)} = \underbrace{3\epsilon_0 \chi^{(3)} |E|^2 E}_{P(\omega)} + \underbrace{\epsilon_0 \chi^{(3)} E^3}_{P(3\omega)} \quad (6)$$

The term $P(3\omega)$ shows that the THG of light is produced while the term $P(\omega)$ denotes an incremental change of the susceptibility ($\Delta\chi$) at the frequency ω , given by:

$$\epsilon_0 \Delta\chi = \frac{P(\omega)}{E} = 3\chi^{(3)} |E|^2 = \frac{6}{n\epsilon_0 c} \chi^{(3)} I \quad (7)$$

Where I is the intensity of the incident light that become significantly the value of $\chi^{(3)}$. The $\chi^{(3)}$, which gives the dependence of refraction on the intensity of the

propagated optical beam, is responsible for the lowest order nonlinear effects in the glass as self-phase modulation and other parametric effects.

Since $n^2 = 1 + \chi$, $\Delta\chi$ is equivalent to an incremental change in the refractive index, Δn is an increase (or decrease) of the total refractive index due to nonlinear effects:

$$\Delta n = \left(\frac{\partial \chi}{\partial n} \right)^{-1} \Delta \chi = \frac{\Delta \chi}{2n} = \frac{3}{n^2 \epsilon_0^2 c} \chi^{(3)} I = n_2 I \quad (8)$$

where n_2 is the nonlinear refractive. This change of the linear refractive index, n , is proportional to the light intensity, and therefore it becomes a linear function of I :

$$n(I) = n + n_2 I \quad (9)$$

$$n_2 = \frac{3}{n^2 \epsilon_0^2 c} \chi^{(3)} \quad (10)$$

The intensity-dependent refractive index is generally given as:

$$n(I) = n + n_1 E + n_2 E^2 \quad (11)$$

where n_1 is the Pockel's coefficient (insignificant for isotropic materials as glasses) and n_2 is known as the Kerr coefficient (from the optical Kerr effect) [10]. However, the classical wave theory says that the intensity of the electric field of the light is equal to the square of its amplitude, and thus one can also write $n(I)$ in the form of Eq. (9). The optical Kerr effect is very sensitive to the operating wavelength and polarization dependence and so the prevalent non-linearity occurs at a frequency well below the glass band gap and this effect is called non-resonant [10].

Typical values of the Kerr coefficient (in cm^2/W) are 10^{-16} to 10^{-14} in transparent crystals and glasses. Silica glass (e.g. silica fibers), has an n_2 index of $2.7 \times 10^{-16} \text{ cm}^2/\text{W}$ at the wavelength of 1500 nm, whereas most of the chalcogenide glasses exhibit higher values, about several orders of magnitude larger than silica [14]. Since the values of the nonlinear refractive index in glasses are very small, resulting in a slight change of $\Delta n = n_2 I$, the effect is measurable only for very intense light beams (lasers) of the order of 1 GW cm^{-2} . From **Figure 3**, it can be noted that n and n_2 are usually directly correlated, such that high index (n) glasses, like chalcogenides, have also high n_2 [16] and exhibit ultrahigh n_2 greater than silica, as plotted in **Figure 3**.

For all-optical signal processing and switching devices, glasses with large n (hence a large n_2) are very attractive. **Figure 4** shows the relationship between the linear refractive index (n), and the third-order nonlinear optical susceptibility $\chi^{(3)}$ of various types of glass. High index (n) glasses, like chalcogenide ones, have also high n_2 , which seem to have the largest non-resonant third-order optical nonlinearities related so far. As previously mentioned, $\chi^{(3)}$ arises from light-induced changes in the refraction index that result in the Kerr effect or in parametric interactions (mixing of optical beams). In a glass fiber, the third-order susceptibility is related to n_2 by Eq. (10) and the magnitude of the corresponding nonlinear effect is given by:

$$\gamma = \frac{2\pi}{\lambda A_{\text{eff}}} n_2 \quad (12)$$

where λ is the free-space wavelength and A_{eff} is the efficient core area [6]. Since 1999, single-mode silica fibers with γ of $20 \text{ W}^{-1} \text{ km}^{-1}$ were fabricated [18] with a

Figure 3.
Nonlinear refractive index, n_2 , versus refractive index, n , for various glasses, and silica glasses. Adapted from [15].

Figure 4.
Relationship between linear refractive index and third-order optical susceptibility. Adapted from [17].

core that was only $10.7 \mu\text{m}^2$, but typical A_{eff} values in silica fibers can reach $50 \mu\text{m}^2$ for $1.5 \mu\text{m}$ wavelengths. The self-phase modulation is a phenomenon arising from the dependence between the refractive index of a nonlinear medium and the strength of the electric field, which induces a phase shift of the propagating light, $\phi_{\text{NL}}(z)$:

$$\phi_{\text{NL}}(z) = \gamma P_0 z = \frac{z}{L_{\text{NL}}} \tag{13}$$

where P_0 is the input power and L_{NL} is the non-linear length that corresponds to the propagation distance at which the phase modulation becomes relevant, being defined by:

$$L_{\text{NL}} = (\gamma P_0)^{-1} \tag{14}$$

If the input power is only 1 mW at $\lambda = 1.55 \mu\text{m}$, and the $A_{\text{eff}} = 50 \mu\text{m}^2$, the L_{NL} is $\sim 500 \text{ m}$ [6]. As the refractive index in silica is weakly dependent on power, nonlinearities are introduced into the signal propagation and significantly increase in optical networks over relevant distances.

The various nonlinearities can be expressed in terms of the real and imaginary parts of each of the nonlinear susceptibilities $\chi^{(1)}, \chi^{(2)}, \chi^{(3)}, \dots$ that appear in (2). The real part is associated with the refractive index and the imaginary part with a time or phase delay in the reply of the material, giving rise to loss or gain. **Table 1** exhibits the principal third-order NLO effects usually showed by dielectric materials like most glasses. For example, the nuclear contribution to stimulated Raman scattering (resulting in loss or gain) can be expressed in terms of the imaginary part of a $\chi^{(3)}$ susceptibility, while the four-wave mixing, which is only of electronic nature and almost an instantaneous effect, result in frequency conversion and in related to the real part of the $\chi^{(3)}$ susceptibility [6]. The imaginary part of $\chi^{(3)}$ provides a change in the absorption coefficient, α , as a function of light intensity:

$$\alpha(I) = \alpha_0 + \beta I \tag{15}$$

where α is the linear absorption, and β is the non-linear absorption coefficient. As a result, occurs a prevalence of non-linearities at frequencies above the electronic absorption edge is known as resonant. The third-order non-linearity may be analyzed in phase conjugate mirrors, like in Mach-Zehnder interferometer pulse selectors or in Fabry-Perot interferometers filled with a nonlinear medium.

The $\chi^{(3)}$ susceptibility is often measured by degenerate four-wave mixing, by the maker fringe method (THG method), or by the Z-scan method. The latter is by far the most used and meticulous method involving the analysis of third-order nonlinear optical properties arising from pulsed laser or CW irradiation at a given wavelength [20].

3. Nonlinear optical properties of glass

Glass is defined as a solid material of amorphous (non-crystalline) structure while crystals possess long-range order, the amorphous materials only possess

Order	Tensor	Effect	Description
3	$\chi^{(3)}(-\omega;\omega,-0,0)$	Kerr's effect	Under the action of two electric fields, there is a change of the refractive index in the NLO medium.
3	$\chi^{(3)}(-\omega;\omega,-\omega,\omega)$	Nonlinear refractive index also called Kerr's effect, self-phase modulation.	The refractive index of the medium changes with intensity according to the formula: $n = n_0 + n_2 I$. Self-focusing and self-defocusing of a laser beam are special cases.
3	$\chi^{(3)}(-3\omega,\omega,\omega,\omega)$	Third harmonic generation.	There is an emission of light with triple frequency under the illumination of the medium.
3	$\chi^{(3)}(-\omega_4;\omega_1,\omega_2,\omega_3)$	Multiwave mixing.	When illuminated with three light sources with different frequencies a generation of light occurs whose frequency equals the sum of the three excitation frequencies.

Table 1.
Third-order NLO effects are usually shown by dielectric materials. Adapted from [19].

short-range order. Therefore, glasses are typically brittle and optically transparent because they lack internal structure. The silica-based glass was undoubtedly the most studied given its multiple applications. Glasses that do not include silica as a main constituent exhibit other properties that make them useful for various applications, for example in optical fibers that work in different frequency domains than SiO₂ fibers. These include fluoride glasses, tellurite glasses, aluminosilicates, phosphate glasses, borate glasses, and chalcogenide glasses. Common glasses are transparent materials in the spectral range of the visible and near-infrared region, although opaque in the far IR and UV region. The visible transparency threshold ends, for high wavelengths (λ), with UV absorption, due to electronic transitions between valence band levels and unfilled conduction band levels. For applications in photonics, there are two main categories of special glasses: chalcogenide glasses (CGs) and heavy metal oxide glasses. Chalcogenide glasses are based on the chalcogen elements S, Se, and Te. These glasses are formed by the addition of other elements such as Ge, As, Sb, Ga, etc. Heavy metal oxide and chalcogenide glasses offer the largest nonlinear response.

Most of the glasses are prepared by the melt of precursors. In solid form, glass is a non-crystalline (or amorphous) material. The deposition from a liquid solution (sol-gel method) is an alternative approach to obtain glass, especially in films form. Some compositions may otherwise be rather difficult to prepare by melt and that's why in practice this method is limited to a relatively small number of compositions. Therefore, the sol-gel processes allow the synthesis of glasses of extended composition ranges, allowing the fabrication of multiple oxide composition, but also non-oxide glasses, with a high degree of homogeneity, because reagents are mixed at the molecular level at temperatures lower than those required for conventional melting. However, the OH content of the sol-gel glasses is high and OH absorptions usually limit transmission at 1.4 μm .

Optical glasses are optically homogeneous glass that are applied in several optical functionalities. The first optical quality (flint) glasses were created at the end of the 19 century by Otto Schott, who also invented Ba crown glass, allowing the production of adjusted lenses for chromatic aberration [21]. X-ray diffraction (XRD) allows distinguishing a glass from a crystalline material. The pattern of SiO₂ glass contains only a few, very broad peaks, which cannot be correlated by the Bragg law with planar distances (as in the case of crystals). SiO₂ consists of a matrix of SiO₄ tetrahedra (**Figure 5**) [22].

The presence of a glass modifier together with the glass formers (SiO₂ or P₂O₅) breaks up the oxide network M–O–M (M = Si, P) and drives the transformation of the bridging oxygens (BO) into nonbridging oxygens (NBOs). The structural unit of SiO₂ has Si–O atomic bonds whose electronic transitions occur in the UV range. For high λ , the transparency threshold ends due to the vibrations of the ions in the network (in resonance with the incident radiation). The amorphous character of the glass explains the absence of grain boundaries in its structure and, therefore, the absence of internal dispersion and reflection phenomena, which are always present in crystalline materials. Glasses are dielectric materials and therefore exhibit a large energy gap between the valence band and the conduction band in accordance with the band theory of solids. Their optical transmission is limited by electronic transitions (Urbach tail) for low wavelength, and multiphonon absorption at high wavelength, in the IR spectrum. The multiphonon absorption process is related to the fundamental vibration frequencies of the glass.

The transmittance spectrum varies from glass to glass, but the main differences are observed outside the transparency range (**Figure 6**). The glass has an optical transparent window which strongly depends on the compositions. Glasses made for use in the visible region have high transmittance across the entire wavelength range

Figure 5. A schematic representation of the structure of vitreous silica. The tetrahedral SiO_4 units in silica are represented by triangular units [22].

Figure 6. Typical transmittance spectra of silica, fluorides, sulfide, selenide, and telluride glasses [23].

of $\sim 400\text{ nm}$ – 800 nm . However, the structure of silicate glasses limits its transmission in the infrared region to above $3\text{ }\mu\text{m}$. They have strongly bound electrons but non-bridging oxygens, with their weakly bound electrons, reduce transmission. Chalcogenide glasses, heavy metal fluoride glasses, and heavy metal oxide glasses extend this transmission to higher wavelengths. The telluride glasses have larger atoms and weaker bonds than oxide glasses and so its vibrational resonance occurs at a lower frequency, shifting the fundamental absorption cut-off to longer wavelengths (**Figure 6**).

The interest in chalcogenide glasses backs from 1950s when was reported high infrared transparency of the As_2S glass, up to $12\text{ }\mu\text{m}$ [24]. The structure of chalcogenide glasses such as Ge-Sb-Se consists of covalently bonded atoms, like amorphous SiO_2 , with lacking periodicity. They include sulfide, selenide, and telluride-based glasses. As dielectric materials, their optical transparent window is dependent on electronic absorption at low wavelengths and multiphonon absorption at high

wavelengths. They have a band gap (E_g) that is dependent on the composition and decreases according to Sulfides < Selenides < Tellurides. A specificity of tellurides that differentiates it from the sulfides and selenides in its crystalline structure and physical properties is the large atomic number of Te. The energy gap may be taken from the glass absorption spectrum $\alpha(\hbar\omega)$ by extrapolating the linearized Tauc equation:

$$\alpha\hbar\omega \propto (\hbar\omega - E_g)^{1/2} \quad (16)$$

The absorption coefficient, α , varies exponentially with the photon energy, $\hbar\omega$ in the Urbach tail.

It is interesting to note that n and n_2 are usually directly correlated, such that low index (n) glasses, like certain fluorides and phosphates, have also low n_2 . On the other hand, a relationship between the material band gap and the n_2 was also established. For example, the n_2 value obtained for pure As_2S_3 was about $2.9 \times 10^{-18} \text{ m}^2/\text{W}$ while for fused SiO_2 was about $2.8 \times 10^{-19} \text{ m}^2/\text{W}$ [25], which is comparatively about 10 times lower. So, materials with lower band gap seem to exhibit an increase in the nonlinear optical behavior; SiO_2 has a gap of about 9 eV while that of As_2S_3 is 2.3 eV [19].

The increase of the nonlinear absorption coefficient (β), third-order nonlinear optical susceptibility ($\chi^{(3)}$), and nonlinear refractive index (n_2) and decreasing the optical band gap (E_g) can be attributed to the formation of BO bonds and ions of higher polarizability in the glass matrix. It has been recognized the effect of the glass composition on the dependency of $\chi^{(3)}$. In most multicomponent oxide glasses, there are both BO and NBO oxygens in the glass network (e.g. for a silicate glass, $\text{Si-O}^+\text{Na}^-$). The NBO bonds possess larger n_2 than the BO of the more covalent Si-O-Si bonds [26]. It was also established that third-order nonlinear optical susceptibility of the glasses increases with increasing optical basicity and tendency for metallization of the glasses. This fact is associated with the polarizability of the anions ($\text{F}^- < \text{O}^{2-} < \text{S}^{2-} < \text{Se}^{2-}$) and the small optical band gap [19], which is related to the increasing metallicity of the oxides [27]. The theory of metallization of the condensed matter says that in the Lorentz–Lorenz equation, the refractive index becomes infinite when metallization of covalent solid materials occurs [27]. SiO_2 , B_2O_3 , and GeO_2 based glasses exhibit low refractive index and have low polarizability, large metallization tendency, and small $\chi^{(3)}$. Tellurite and TiO_2 based glasses, as well as B_2O_3 glasses containing a large amount of Sb_2O_3 and Bi_2O_3 with high refractive index, show large polarizability, small metallization tendency, and large $\chi^{(3)}$ (Figure 7). Consequently, under the point of view of polarizability, high-refractive-index glasses with an increased tendency for metallization are promising materials for application as components of nonlinear optical devices.

Glass materials are excellent non-linear optical materials, being isotropic and transparent in a wide spectral range, combining low cost of fabrication with high optical quality, manufacturable not only as bulk shapes, or fibers, but also as thin films (e.g. nonlinear planar waveguides). Furthermore, when compared to polymers, glass is more stable and has the advantage over crystals since its atomic composition is easily tailored: a nonlinear optical glass can be obtained with any refractive index in a wide range [28]. Its properties can be adjusted through doping and compositional changes to fit the specified requests of each application. Its disordered structure allows light propagation inside that medium like no other material. They also exhibit good compatibility with silica-based systems and waveguide production in which high optical intensities and long interaction lengths can be achieved [28], giving rise to nonlinear structures in integrated optical devices [29].

Figure 7.
Line-up of the Kerr effect among various glass compositions [19].

For the fabrication of all-optical systems in information technology and integrated photonics, the chosen materials should exhibit high nonlinearities. Rather, low nonlinearities are essential for fibers in optical communications to avoid phenomena of self-focusing, self-phase modulation, Raman and Brillouin scatterings. NLO was considered the threshold to the total of information that can be transmitted in a single optical fiber. As laser power levels increase, NLO limits data rates, transmission lengths, and the number of wavelengths that can be transmitted simultaneously. Optical nonlinearities give rise to many “secondary” effects in optical fibers. These effects can be damaging in optical communications, but they find other applications, especially for the integration of all-optical functionalities in optical networks. The optical nonlinearities can give rise to gain or amplification, the conversion between wavelengths, the generation of new wavelengths or frequencies, the control of the temporal and spectral shape of pulses, and switching [6]. Thus, they can be distinguished in two types: that from scattering (stimulated Brillouin and stimulated Raman) and that from optically induced changes in the refractive index, resulting either in phase modulation or in the mixing of several waves and the generation of new frequencies (modulation instability and parametric processes, such as four-wave mixing). So, the nonlinear refractive index, also referred optical Kerr nonlinearity (n_2), offers a means to achieve switching and amplifying functions in photonic devices and produces nonlinear effects, namely self-phase modulation, and four-wave mixing. Self-phase modulation implies changes in the phase and rising frequency of a pulse, which can cause spectral broadening. Four-wave mixing is a kind of nonlinear frequency conversion generated by the Kerr nonlinearity which enables, for example, high-speed communications, frequency conversion, sensing, and quantum photonics. The effect of ultrafast response time (10^{-15} s) provides broad bandwidths, that can pull actual GHz electronic computing forward to PHz (10^{15}) rates using all-optical signal processing [30]. In addition, spectral broadening, produced by changes in phase from the nonlinear refractive index, can enable the production of short-pulsed sources [30]. Four-wave mixing, on the other hand, can be used to generate optical frequency combs [30], which can measure precise frequencies of light and span spectral ranges useful for spectroscopic investigations.

Although these applications are of great practical interest, the Kerr effect (n_2) is often small for common optical glasses ($\sim 10^{-20}$ to 10^{-19} m²/W) [30], leading to high thresholds for nonlinear effects and requiring special sources of high-power excitation.

Transparent optical glasses exhibiting nonlinearities, e. g. large nonlinear refractive index and nonlinear absorption coefficient are good candidates for fiber telecommunication and for nonlinear optical devices such as optical switches, self-focusing, and white-light continuum generation. Glasses that exhibit significant nonlinearity are good candidates as Raman gains media to provide enhanced Raman gain over an extended wavelength range. Chalcogenide (As–Se) glasses and fibers are examples of good candidates as well tellurite fibers because of the high refractive index of TeO_2 (2.3–2.4) [6] compared to the SiO_2 (1.46). An As_2S_3 fiber exhibit a Raman coefficient is 300 times greater than that of silica fiber [6]. However, chalcogenide fibers have lesser chemical stability. In spite of that, chalcogenide glass has wide transparency transmission from 0.5 to 25 μm [31], enhancing their potential applications on the mid-IR. As shown in **Figure 8**, the long-wavelength cut-off edges of chalcogenide glasses depend on the mass of anionic elements and are extended between 12 and 20 μm . Their nonlinearity (Kerr effect) is 200–1000 times larger than that of the silica glass at a wavelength of 1.55 μm [32].

The nonlinear optical properties of glasses have been considered of great interest for photonic devices to be used in several technological applications with a broad spectrum of phenomena, such as optical frequency conversion, optical solitons, phase conjugation, and Raman dispersion. Most of the previous investigations were devoted to crystalline materials such as Quartz, LiNbO_3 , KTiOPO_4 , and $\alpha\text{-BaB}_2\text{O}_4$ [19]. Nevertheless, recently the development of special glass compositions exhibiting NLO properties have extended the research into practical applications of glass transparent materials for a wide range of effects, such as fast intensity-dependent index, third-harmonic generation (THG), stimulated emission (or stimulated Raman scattering), second harmonic generation (SHG) and the multiphoton absorption [29]. Nonlinear phenomena in glasses, such as nonlinear refractive index, multiphoton absorption, and Raman and Brillouin scattering, depend on the glass itself, its nature (composition and structure), which is responsible for the nonlinearity. On the other hand, in glasses doped with RE ions or semiconductor nanoparticles, in which the glass assumes the role of host, the nonlinearity is produced by interactions between dopant ions, domains, and different phases (such as in glass-ceramics).

The first nonlinear effect in history is often associated with the beginning of the NLO [33], had occurred in 1875, when J. Kerr observed changes in the refractive index of a liquid (CS_2) in the presence of an electric field. The Kerr effect or quadratic electro-optic effect is directly related to the third-order nonlinearity, $\chi^{(3)}$. Pockels, 20 years later, observed another phenomena, the linear electro-optic effect [34], through the modification of the index of refraction of light in a

Figure 8.
 Typical infrared (IR) transmission spectra of S-, Se-, and Te-based chalcogenide (ChG) glass [32].

non-centrosymmetric crystal (Quartz) placed by an electric field. For a long time thereafter, these phenomena were little studied and found of non-practical applications. However, the decisive prerequisite for work out such effects demands high laser pump intensities and suitable phase-matching conditions. Significant effects of NLO (e.g., frequency conversion by taking advantage of second and third harmonic generation) only began to be observed experimentally in the early 60s, after laser invention, due to the fact that such NLO effects require high electromagnetic field intensities to manifest, which was only possible using high-power lasers. P. Franken reported the first observation of the SHG in 1961 after focusing a pulsed ruby laser ($\lambda = 694 \text{ nm}$) into a Quartz crystal; the red incident beam generated an emitted blue light ($\lambda = 347 \text{ nm}$) [35]. THG was soon experimentally reported in 1965 [36]. Since the late of the 80s the interest in NLO properties in glass began to increase [19]. As already mentioned, the nonlinear optical response of glasses is closely related to their anionic polarizability [29, 37] which is described as the deformation of electron clouds (dipoles) when the electromagnetic field is applied. The selection of suitable glass structure and composition can contribute to efficiently optical Kerr effect, self-focusing, intensity-dependent refractive index, and other $\chi^{(3)}$ -related effects. In the literature, several reports have shown that the Kerr effect of non-conventional glass compositions is a viable option for self-phase modulation and broadband light generation in the near-infrared [29]. The $\chi^{(3)}$ in resonant mode is an additional possibility. Due to the bandwidth requirements for transmitting information for both long-haul and local area networks, Raman amplification is considered a good option to face out the recent developments in the telecommunications fiber industry and diode laser technology. Compared, for instance, with Er^{3+} -doped silica fiber amplifiers, in which the wavelength is fixed at 1550 nm, Raman gain bandwidths are larger, and the operational range only varies with the pump wavelength and the bandwidth of the Raman active medium (the glass nature) [29]. It is well known that the Kerr effect and Raman gain follow the polarity of the glass medium and are deeply impacted by the structure of some specific glasses, such as TeO_2 glass, which have large electronic polarizability. Additionally the small length of Te–O bond (2.01 Å) [37, 38] is considered responsible for the large third-order nonlinear optical susceptibility of these kinds of glass [38]. Its $\chi^{(3)}$ value was as high as $1.4 \times 10^{-12} \text{ esu}$ about 50 times as large as that of SiO_2 glass [38].

The field of nonlinear optics of glasses has been mainly focused on two main groups: resonant and non-resonant [28]. Non-resonant interactions occur when the light excitation falls in the transparent wavelengths range of the glass longer than its electronic absorption edge. As no electronic transitions take place, the process can be seen as lossless and so an ultrafast glass response due to third-order electronic polarization is assured. Examples are, in general, high refractive index and high dispersion glasses like heavy flint optical glasses, or heavy metal oxide glasses, or chalcogenide glasses.

The resonant ones include semiconductor (quantum dots), or metallic nanoparticles doped glasses [10, 28] and the interaction occurs when the optical field's frequencies are near the electronic absorption edge so that its high resonant nonlinearity can be exploited. However, the isotropic structure glass and its amorphous state have inversion symmetry and do not exhibit second-order nonlinearity, $\chi^{(2)}$, or Pockels effect which is necessary for applications such as electro-optic switching and modulation or wavelength conversion in photonic technology. Indeed, glass is a good example of optically isotropic material (as well cubic crystals) that does not exhibit (in principle) any behavior that arises from that condition (e.g. optical birefringence). However, this is not always the case because second-order nonlinearity can be achieved in glass upon appropriate modification. For

example, the application of both heat and electric fields (thermal poling) gives rise to SHG. Since $\chi^{(2)}$ is not physically possible in a centrosymmetric material, the creation of an axial symmetry under thermal poling has been demonstrated to be effective to introduce second-order nonlinearity properties [29]. Another route to create an optical SHG is by the introduction of optical non-linear nanocrystals within a glass matrix. Although thermal poling is an efficient way to induce SHG in silicate glasses, $\chi^{(2)}$ also appeared after glass heat treatments to precipitate crystallites of non-centrosymmetric compounds [39]. This strategy gives rise to transparent crystallized glasses (glass-ceramics). Nevertheless, more research is necessary to clarify some aspects, for instance, whether the thermal poling approach is effectively the best choice for raising SHG.

In the glass transparency region, which is found between the ionic (vibrational) and the electronic excitation interactions and where no permanent electric dipoles are present, the light frequency is too high for the ionic polarizability to follow the E field oscillations and too low to resonate with the electronic excitations [10]. Still, multiphoton processes may occur. For example, the probability of two-photon absorption is proportional to the square of the E field intensity [10].

4. Quantum dots doped glasses

Intensity-dependent nonlinear optical effects, such as the optical Kerr one, are very significant for all-optical data processing. Glasses with large nonlinear refractive index and nonlinear absorption coefficient are suitable materials for fiber telecommunication and nonlinear optical devices such as ultrafast optical switches and several photonic applications. Since silica and silicate glasses exhibit a small third-order nonlinear susceptibility $\chi^{(3)}$, the strategy of combining different materials to obtain composite systems, such as glass doped with semiconductor nanocrystals (quantum dots), allowed to obtain optimized nonlinear optical properties because semiconductors exhibit larger susceptibility. Glasses doped with semiconductor nanocrystals (quantum dots, QDs) such as CdS, CdSe, CdTe, PbS, CuCl, etc., are suitable materials for resonant NLO devices with response times on the ps domain. They can be prepared through the dispersion of a nanocrystalline phase in a glass matrix. This approach, through the reduction of bulk size to nanometric scale or quasi-zero-dimensional quantum dots, allow to change the electronic properties of glasses accordingly with enhanced nonlinearity compared with the corresponding bulk semiconductors [40]. Whenever the absorption of a photon of enough energy ($h\nu$ is greater than the band gap, E_g) excites an electron from the valence band to the conduction band in semiconducting materials, a free electron-hole pair may be formed. The hole and electron are attracted by Coulombic forces to keep them in a stable orbit as a bound electron-hole pair, called exciton [10]. Due to electrons and holes being confined in a small volume of radius, the radius of the exciton (distance between the electron and hole in an exciton), will change the available energy levels and the interaction with the photons. As the size of nanoparticles becomes progressively smaller, the quantum size effects of excitons confined in all three dimensions give rise to a series of discrete energy levels [10], and therefore the energy associated with them will depend on the relationship between the crystal size (R) and the exciton Bohr radius. Quantum confinement effects are quite significant in the range of $a \ll R \sim a_B$, where a is the lattice constant of the semiconductors, i.e. when R is similar to Bohr radius of exciton in bulk crystal (a_B). In QDs doped glasses these effects give rise to the so-called blue shift of the linear optical absorption edge. The shift regarding to the bulk E_g varies with R as $\sim 1/R^2$. Smaller R gives rise to larger blue-shift.

The size of semiconductor particles can be calculated by [41]:

$$\Delta E_g = \frac{h^2}{8R^2} \left[\frac{1}{m_e^*} + \frac{1}{m_h^*} \right] - 1.8e^2 / 4\pi\epsilon_0\epsilon_\alpha R - 0.124e^4 / \hbar(4\pi\epsilon_0\epsilon_\alpha)^2 \left[\frac{1}{m_e^*} + \frac{1}{m_h^*} \right]^{-1} \quad (17)$$

where ΔE_g is the shift of the band gap energy (due to the confinement), R is the particle size (radius), m_e^* and m_h^* are respectively the reduced effective masses of the electron (e) and hole (h). It is interesting to note that the second term, related to the kinetic energy of the electron and hole [41] exhibits a $1/R^2$ dependence while the third term, the Coulomb interaction between the electron and hole, has a $1/R$ dependence. Although the kinetic energy of the exciton for nanoparticles of $R \sim a_B$ seems to be predominant, the Coulomb interaction must also be considered [42].

Figure 9 shown that the shift of the exciton resonances to higher energy (blue shift) is a consequence of the increasing quantum confinement as R decreases [43].

The changes in absorption also lead to refractive index changes, through the Kramers-Kronig transformation:

$$\Delta n(\omega) = \frac{c}{\pi} \int_0^\infty \frac{\Delta\alpha(\omega')}{\omega'^2 - \omega^2} d\omega' \quad (18)$$

where c is the speed of light and ω is the light frequency.

The method allows to correlate the determined change $\Delta\alpha$ in the absorption coefficient to the change Δn in the refractive index [43]. The nonlinear refractive index is then obtained by $n_2 = \Delta n/I$ (Eq. (8)). The value of $\chi^{(3)}$ will be proportional to the reciprocal of the confinement volume and will increase with decreasing R [10]. Is then expected that larger non-linearities are obtained for glasses containing smaller particles and larger volume fractions of QDs [10].

5. Metal-doped glasses

Metal doped glass possesses linear and nonlinear optical properties. Great interest has driven the study of the third-order nonlinear susceptibility of metal particles embedded in dielectric matrices, like glasses [44], which are influenced not only by the type and size of the metal particles but also by the metal-dielectric constant. The most significant effect of the confinement of metal particles in optical properties of nanocomposite glasses is the appearance of the surface plasmon resonance, which

Figure 9. Absorption spectra of CuCl-doped quantum dot glasses: 22 Å (solid); 27 Å (dot); 34 Å (dash) [43].

deeply enhances the glass $\chi^{(3)}$ responses with picosecond temporal responses. For example, the optical absorption spectrum of Ag-doped silica sol-gel glass shows the presence of an absorption band of surface plasmon resonance due to Ag nanoparticles at ~ 420 nm (**Figure 10**).

Figure 10.
 Absorption spectra of Ag-SiO₂ cermet (at a concentration of 8% Ag) and SiO₂ matrix (without Ag).

Plasmons deals with a coherent interaction between the free-electron gas surrounding metal and the incident radiation. The motion of these free electrons can be described by the plasma Drude model, along with a plasma frequency of the bulk metal ω_p . In accordance with the Drude free-electron model, the dielectric constant of metal particles is given by [45]:

$$\epsilon_m = \epsilon'_m - i\epsilon''_m = 1 - \omega_p^2 / [\omega(\omega - i/\tau)] \quad (19)$$

Where τ is the time between collisions among electrons. The real (ϵ') and imaginary (ϵ'') parts of the complex dielectric constant are expressed as [45]:

$$\epsilon'_m = n^2 - k^2 = 1 - \omega_p^2 \tau^2 / [1 + (\omega\tau)^2] \quad (20)$$

$$\epsilon''_m = 2nk = \omega_p^2 \tau / \left\{ \omega [1 + (\omega\tau)^2] \right\} \quad (21)$$

From the above equations is possible to infer the existence of an interaction between the free-electron gas and the incident electromagnetic field, which gives rise to an excitation of the electrons at the metal surface, associated with collective oscillations of electrons in the metal nanoparticles, called surface plasmon. The large value of $\chi^{(3)}$ of metal-doped glasses arises predominantly from the local electric field enhancement near the surface of the metal nanoparticles (Ag, Cu, Ni, or other metal nanoparticles) due to their surface plasma resonance, leading to a variety of optical effects.

When the diameter (d) of metal particles is much lower than the wavelength of light (λ), scattering is negligible. As well, the total collisional impacts of the electrons with the particle surfaces become significant and a new-found relaxation time, τ_{eff} , appeared, given by [45]:

$$1/\tau_{\text{eff}} = 1/\tau_b + 2v_F/d \quad (22)$$

Figure 11. Transmission electron microscopy micrographs of Au-SiO₂ thin films: a) cross section view of a film with Au volume fraction $p = 23\%$, and b) plan view of a film of Au volume fraction $p = 8\%$ [46].

where τ_b is the bulk value and v_F is the electron velocity at the Fermi energy. Spherical metal nanoparticles embedded in a glass matrix with a real dielectric constant ϵ_d exhibit NLO properties. **Figure 11** exhibits homogeneous size distribution of spherical Au nanoparticles in a SiO₂ thin film on a metal substrate [46]. For the conditions.

The equation usually considered to obtain the $\chi^{(3)}$ of metal/glass composites, is given by [45]:

$$\chi^{(3)} = 3pf^4\chi_m^{(3)} \quad (23)$$

Where $\chi_m^{(3)}$ is the bulk metal third-order susceptibility, f is the local electric field near the metal particles and p is the metal volume fraction. The optical response of metal particle/glass composites can be determined by the local field enhancement inside the nanoparticles (dielectric confinement):

$$f = \frac{E}{E_0} = \frac{3\varepsilon_d}{\varepsilon_m + 2\varepsilon_d} \quad (24)$$

f is given by the ratio between the field E inside a metal particle and the applied field E_0 , with ε_d the dielectric constant of the glass matrix and ε_m the one of the metal.

So, if one assumes $\chi_m^{(3)}$ independent of particle size, then $\chi^{(3)}$ will increase as the volume fraction of metal particles and their size increases [45].

6. Conclusions

In the last decades, the development of optics, as the science that deals with light and its applications, has had an enormous growth not only through new or recognized theoretical concepts but also in new optical techniques and new instruments. Several factors contributed to this, namely: 1) the emergence of new light sources, such as lasers, which allowed the advent of new applications associated with light manipulation, such as those based on the nonlinear optical properties of materials; and 2) the development of new glasses or the modification/optimization of others through the addition of dopants (e.g., metallic nanoparticles or QDs), also allowed the creation of new photonic devices (light sources, all-optical switches, modulators, etc.) and new technologies associated with them. These developments also gave rise to the so-called integrated optics, which allowed a reduction in the size of optical systems, while maintaining their high nonlinear optical performance. Many of these technologies are used in the field of communications and other sectors of activity, such as health and information. In terms of materials, NLO glasses have grown as indicated by the numerous scientific publications on the subject. Glasses have great versatility and offer great flexibility to modify their nonlinear responses by manipulating their composition, refractive index, gap, etc. Because of their structural inversion symmetry, glasses do not possess second-order optical nonlinearity. Yet, it is possible to induce this optical response in the glass by thermal electric poling.

Conflict of interest

The author declares no conflict of interest.

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