Chapter 13

Progress on oxide glasses. Applications in photonics

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Abstract

The improvement of the high performance oxide glasses and the evolution of the basic structural and dynamic studies, that received a strong impulse since the 1950's, have provided the access to applications in the recently developed field of electro-optical devices, called photonics. The first part of this chapter presents a brief review of some basic topics, as the local structure, radiation-induced defects, the application of several experimental techniques, doping with transition metal and rare earth ions, and the development of theoretical models, computer simulation and topological concepts. The second part is devoted to a review of optical functions of photonic oxide glasses and their potential applications. The first important property is the transparency of the glasses, whose minimum value reaches 0.15 dB/km ($\alpha = 3.5 \times 10^{-7}$ cm^{-1}) near the theoretical limit. Some special applications of oxide glasses in photonics are covered, as the photonic band gap optical fiber, magneto-optical systems, photochemical hole-burning materials and holographic techniques. Finally, there are given some recent general informs about the economic and technological scenario about the role of quantum dots photonic glasses.

Introduction

Glass as an optical material has fascinated the humankind throughout the history [1,2], but its full potential use has only recently been recognized in the information age, when glass was rediscovered as an ideal optical medium for the transmission of light [3]. In the course of centuries the glass manufacture has been rather an art than a science, developed mainly on the practical knowledge gathered by means of diligent work and sagacity of glassmakers. The discovery of several procedures lead to the obtaining of specific color and transparency effects, temperature resisting glasses and industrial production of windows, lenses, bottles, glass ceramics, and so forth.

The nature of the amorphous state is characterized by negative assertions such as the absence of periodicity and long range order, no unique ground state, the Bloch theorem does not apply, broad spectral lines, and the concepts are generally not well defined, with many fundamental questions remaining not yet well resolved. Therefore, the progress of glass science has lagged for decades the crystalline solid-state physics. A definite impulse of the glass science has occurred in the 1950's, when there was raised the interest about the fundamental questions related with microscopic structural and dynamical properties of glasses.

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The optical silica glass is perhaps the most remarkable material implied in the photonic revolution of our present day. The silica optical fiber makes it possible to transmit very dense information in the form of bundles of short optical light pulses over thousands of kilometers. Such a magnificent performance we owe to the recent dramatic improvement that took place in materials processing, and chemical vapor deposition (CVD) purification methods of the silica glass. Optical fibers in use today operate at their theoretical minimum value of 0.15 dB/km in optical loss (absorption coefficient $\alpha \approx 3.5 \times 10^{-7}$ cm^{-1}). Even though the silica glass technology has presently achieved an entirely mature condition, a constant effort is going on for improving the fiber manufacturability and the cost reduction. It is widely believed that novel processes like sol-gel can perform a large quantitative production at a substantially reduced cost, which is an important issue in a competitive market.

Although silica finds a widest use as the most transparent optical glass, there are many other glasses with different physical and chemical properties that provide better matches in specific applications [4]. Transparency is one of the most important properties of an optical glass, and it is determined by the characteristic electronic and vibrational properties of the material, which couples and absorbs the light. The window of transparency of an oxide or insulating glass is defined by an UV absorption edge at short wavelengths and a multiphonon absorption edge at longer IR wavelengths. For silica this window extends from 0.3 to 2 μm. Within this window, the main contribution to light attenuation comes from intrinsic density fluctuations of the glass which behave like the Rayleigh scattering, and is roughly proportional to λ^{-4}, i.e. the attenuation decreases with increasing wavelength. Thus, in order to seek the best condition for the transmission of light, it is desirable to operate at longer wavelengths close to the IR edge and choose a glass having an IR edge shifted towards a longer wavelength. Transition metal (TM) impurities and some structural defect states in this window are also major sources of light attenuation. Also IR glasses become useful materials in the production of efficient wave-guides and light amplifiers, such as the rare earth (RE) doped active glasses, where the excited state lifetimes depend strongly on the energy of the host lattice vibrations. Typically, if the energy difference between the two electronic states is less than few times of the phonon energy, the de-excitation takes place by releasing this energy to the phonons and the fluorescence will be strongly quenched. The phonon energies are small in IR glasses, whose valence band edges lie beyond 6 μm, where the light scattering effects are negligible, so that they are very efficient laser glasses.

There are thousands of different glass compositions being developed over the years, and a very large number of glass applications in photonics. In the following sections we are going to examine the evolution of the knowledge about the local structure of oxide glasses, as well some universal properties common to any amorphous material, and some contributions to the progress of the optical functions of the oxide glasses achieved throughout the five last decades are reviewed.

Local structure

Since the historical paper of Zachariasen [5], when the concept of continuous random network (CRN) was proposed in order to describe the amorphous structural chain of covalently bonded atoms of the glass structure, there was always present the trend towards a solution to the puzzle of the identification and distribution of local symmetric groupings of atoms throughout the whole glass matrix. The small coordination number of the glass network former atom X implies that a local structural unit (SU) of triangular or pyramidal XY_3 or tetrahedral XY_4 atomic arrangements is created, were Y is a bridging oxygen (BO) for the case of oxide glasses. As the forces between the atoms are essentially the same as for the corresponding crystalline materials, these structural units in the glass must also be the same, except for the lack of periodicity of a long-range order.

Thereafter, Warren and collaborators [6-11] carried out a series of X-ray diffraction (XRD) on the addition of network modifier cations cause structural rearrangements such that the CRN is interrupted in several chain positions finished with non-bridging oxygen (NBO), resulting thus a modified continuous random network (MCRN). These rearrangements occur differently in the silicate, borate and phosphate glasses, determining thus their physical and chemical properties.

Systematic early studies of oxide glasses modified by alkaline and alkaline earth metals compared with crystals of corresponding stoichiometry led to the concept of glass local super-structural units (SSU). The contribution of Krogh-Moe [12-19] has given a new impulse to the structural understanding of borate oxide glasses that readily became the better understood. The following progress was well resumed by the milestones contained in the excellent review of Griscom on borate glass structure [20]. Many contributions using different experimental techniques and methods have contributed with complementary information on the structure of glasses. A.C. Wright et al. [21-23] have reviewed the contribution of XRD, neutron diffraction and extended X-ray absorption fine structure (EXAFS) measurements. A comprehensive review on optical absorption (OA) and reflectance data on oxide glasses were given by G.H. Sigel [24]. The nuclear magnetic resonance (NMR) for ^{11}B to study structure and bonding in glasses was introduced by Silver and Bray [25]. The following work, conducted by Bray and co-workers, could give a definite answer to the question of "borate anomaly" and more recently the pure nuclear quadrupole resonance (NQR) studies of the ^{11}B and ^{10}B responses could allow clear identification of the structural groupings in glasses [26-28].

A considerable progress on the knowledge on the local structure and bonding in oxide glasses was achieved by the systematic studies of electron paramagnetic resonance (EPR) of defect states rendered paramagnetic on ionizing X- or γ-irradiation or by the inclusion of paramagnetic impurities.

The intrinsic radiation-induced electron and hole centers in oxides are produced as well in crystals as in glasses and each one leaves a characteristic EPR spectrum. The first reports on E' centers in crystalline materials were issued independently by Weeks [29] and Stevels and Kats [30] and the following EPR studies in glasses are well known. A wealth of excellent review articles covering the silicon E' centers in silica glasses and their modeling are available [31-34]. Also the oxygen hole-center (OHC) in silicate glasses have received a careful

attention as, for example, the "wet" OHC and "dry" OHC [35,36] and O_2^- or peroxy radicals [37], as reviewed by Griscom [20].

The overview on the early EPR studies on electron and hole centers in irradiated borate glasses can also be summarized as follows. Lee and Bray [38] carried out the first EPR study of the boron hole center and later on, a detailed model was proposed by D.L. Griscom et al. [39] on the basis on a molecular-orbital scheme and using computer simulation of the experimental spectra. There still remained some controversies that were properly discussed and reviewed by Friebele and Griscom [40], when the common designation of boron-oxygen hole center (BOHC) was adopted both for the "four-line" and "five-line-plus-a-shoulder" EPR spectra. The boron electron center (BEC) was first studied by Griscom [41] and interpreted as analogous with the E' center [36] such as proposed by Feigl et al. [42].

Similar intrinsic irradiation-induced centers were found also for the phosphate glasses. The original EPR data reported by Karapetian and Yudin [43] were shown by Schreurs and Tucker [44] to be of trapped-hole nature and the term phosphorus-oxygen hole center (POHC) is now well accepted [40]. The phosphorus E' center (PEC) was demonstrated by Weeks and Bray [45] to exist as ^{31}P hyperfine doublets of large splitting corresponding to different distinct centers. Further examples of intrinsic electron and hole centers for germanium and aluminum, alkali-associated trapped electron centers and the EPR and OA of many other defect centers can be found in the interesting review of Friebele and Griscom [40]. The EPR of arsenic electron center in arsenic oxide glass, reported by Pontuschka and Taylor [46], is another example of the characterization of an intrinsic center by computer simulation technique. For another interesting report on OA and EPR of silicate, borate and phosphate glasses, the reader is referred to the review of A. Bishay [47].

More recent ideas originally developed in the study of amorphous semiconductors have proven to be applicable in the modeling of defect centers in oxide glasses. The concept of valence alternation pair (VAP) was first proposed and described by Kastner, Adler and Fritzsche [48] was used in further of two closely related E' center models developed respectively by Greaves [49,50] and Lucovsky [51-53]]. A thorough discussion on these and other related models is found in the review of J. Robertson [54] covering atomic defects of amorphous semiconductors and silica.

Shkrob et al. [55,56] have performed systematic studies on radiation-induced point defects in oxide glasses using some alternative advanced magnetic resonance techniques in order to solve some obscure points left about paramagnetic defects in wide-gap oxide glasses. In order to seek for solutions to many questions that remained unanswered so far, they applied pulsed EPR to show that electrons and holes in irradiated B_2O_3 and alkali borate glasses are trapped on VAP defects (holes in under-coordinated and electrons in over-coordinated oxygen). The techniques of electron nuclear double resonance (ENDOR) and electron spin echo envelop modulation (ESEEM) were used to describe the behavior of some specific types of OHC's, E' centers, peroxy radicals and a L-center, a luminescence center discovered by Brekhoviskikh and Tyul'kin [57]. The reader, wishing a careful background covering the recent evolution of a multiplicity of models for the radiation-induced and bonding boron and silicon oxide glasses, is referred to both

papers of Shkrob et al. [55,56] as an excellent review on the most recent achievements.

Another important structural contribution comes from the vibrational and Raman spectroscopy. Galeener [58] pointed out the distinction between the bond types, distances and angles involved in the short range order of a SU and the intermediate range order of a SSU. Two additional ranges, namely the long range order and global range order were also defined for an amorphous solid. He discussed six approximations to the Zachariasen-Warren model [5-11], choosing for the Sen and Thorpe [59] central forces-only model to discuss vibrational spectra of tetrahedral glasses, that was later generalized by Thorpe and Galeener [60,61]. An extensive comparison of the model with infrared, Raman and inelastic neutron scattering data was made by Galeener, Leadbetter and Stringfellow [62].

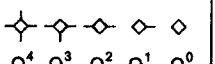
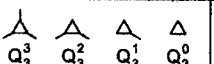
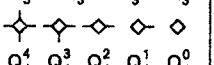
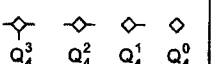
The thermodynamic studies using methods of calorimetric, electro moving forces (EMF) and mass spectrometry have provided another powerful means for the modeling of properties of glasses and melts. Shultz [63] has reviewed the results of the experimental data. Shakhmatkin, Vedishcheva, Schultz and Wright [64] and others have reported a basis for modeling the physical and transport properties extracted from the concentration dependence of the free energy of mixing, partial entropies and chemical potentials of alkali oxides in alkaline oxide melts. Their results were found to be in good agreement with quantitative and qualitative description of the refractive index, molar refractivity, molar volume and electrical conductivity of a wide variety of systems.

The enormous development of computer science and technology of the last years has provided the means to a continuous checking and improvement of a wide range of structural models. A detailed description of the main improvements in the field is beyond the scope of the present chapter. The interested reader can chose to examine, as examples, the following few remarks on applications to the structural modeling and simulations of oxide glasses, as well as the comments about the adequacy of the comparisons with experiment. Takada, Catlow and Price [65,66] presented a survey on previous molecular dynamics (MD) simulation studies and a method of application of coordination-dependent potentials in crystalline and vitreous B_2O_3. Examples of some current structural models using MD, Reverse Monte Carlo (RMC) and ab initio calculations for general glass systems are given by A.C. Wright [21], Allan and Teter [67] and Park and Cormack [68]. The incorporation of alkali metal oxide into a CRN of vitreous B_2O_3 and SiO_2 was simulated by Kondakova, Dembovsky and Zyubin [69], showing that the transformations processes are affected by some hypervalent configurations leading to the switching of bonds instead of their breaking.

The basic local glass SU and SSU of silicate, borate and phosphate glass systems is given in Table 1.

In addition to the local SSU of the MCRN of a given glass, there is evidence of ring structures (RS) as a result or closed polygonal sequences of SU bonded by the vertices. There is no direct experimental technique to measure the dimensions and distribution of such RS. Perhaps the potential of the kinetic studies of neutral atomic hydrogen and silver stabilized in glass [70] is a possible approach.

Table 1. The basic local glass structural units (SU) and super-structural units (SSU) of silicate, borate and phosphate glass systems.

Glass System	Structural Units (SU)	Super-Structural Units (SSU)	
Silicate	 Q_4^4 Q_4^3 Q_4^2 Q_4^1 Q_4^0	Quartz	Cristobalite
		Tridimite	Metasilicate
Borate	 Q_3^3 Q_3^2 Q_3^1 Q_3^0  Q_4^4 Q_4^3 Q_4^2 Q_4^1 Q_4^0	Boroxol	Pentaborate
		Triborate	Diborate
		Metaborate	Orthoborate
Phosphate	 Q_4^3 Q_4^2 Q_4^1 Q_4^0	Metaphosphate	Pyrophosphate
		P_2O_7 dimer units	Ultraphosphate

The common picture of a general glass network may be reduced to a set of glass SU of XY_3 or XY_4 bonded through the vertices forming non-periodic chains which can be cross-linked or not, can be planar or three-dimensional, depending of the numbers of BO's and NBO's distributed throughout the particular positions of the overall glass network. Beside this structure, outside of the SU's there are electrically charged glass modifier cations attracted to the positions where the charge compensation is necessary to maintain the neutrality of the glass internal volume. The impurities can be introduced in the glass either by substitution of the glass forming atoms in the center of the SU's or placed in the sites at the interstices between the chains made up by SU's, ordinarily occupied by the glass modifier cations, which are in general coordinated by 5, 6, 7 (or more) oxygen atoms belonging to the SU's of the glass forming chain. In short, we can state that impurities having sufficiently small ionic radii can occupy the "substitutional" positions of the glass forming ions inside the SU's, or the "interstitial" positions placed outside. The impurities of greater ionic radii appear always in the interstitial sites (outside the SU's). It is important to notice that there is a basic difference between a stoichiometric glass and a corresponding crystal in the volume available for the interstitial sites. The volume of the interstitial sites of a crystalline structure is limited by the rigid lattice positions determined by its periodic structure, whereas in the glass this constraint does not exist. For this reason the doping limitation of a crystalline structure is by far overcome by the glass matrix. This is one of the most important advantages of the glass as application for the production of high power lasers.

However, one must be aware that the increase of available volume in the glass network capable to admit a greater deal of doping material does not imply the opening of voids in the structure in ordinary glass, as already pointed out in the early work of Warren [7,10] on small angle X-ray scattering (SAXS). Obviously the ring structures of the MCRN were not "broken" by the inclusion of glass modifier cations or impurities, but the weakened structure of the MCRN has

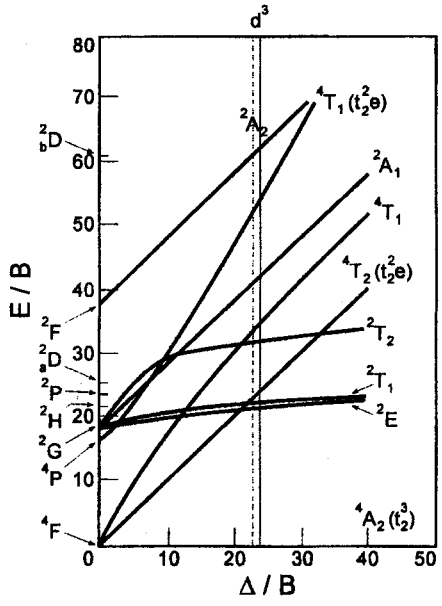


Fig. 2. Position of the local octahedral Cr^{3+} sites of the glass samples (1) (solid line) and (2) (dashed line) in the Tanabe-Sugano diagram [71,72].

Four elementary structural transformations in 3D were defined by D. Weaire and N. Rivier [78] in order to probe the non-generative homogeneity necessary for a topological disorder of a general amorphous state (see Fig. 3): a) T_1 or neighbor-switching; b) T_2 or cell disappearance; c) mitosis or cell division and d) face disappearance (3D). However, the covalent networks (CRN) only have T_1 transformations that imply there a local valence or bond exchange. This neighbor-switching process restricts topological stability to 3-(in 2D) and 4-coordinated vertices (in 3D). This particular model has assumed the nodes occupied by an atom of fixed valence (4 for Si) and the straight lines by bonds of fixed distances and angles. In order to advance further in this field, we can ask about what would happen with oxide glasses CRN or MCRN lattices if the nodes are substituted by SU's and their coordination numbers distributed from 0 to 4, equal to the BO's existing in their corners? (The T_1 is different from the valence alternation pairs, which are non-local transformations, to be discussed further in the text).

Another universal characteristic of the amorphous systems, which have no counterpart in crystals, associated with anomalies observed at low temperatures such as the linearity of specific heat with temperature, observed by Hornung et al. [79] and Zeller and Pohl [80] for vitreous silica and a-$Zr_{0.7}Pd_{0.3}$ below 1 K and the thermal conductivity ($T \leq 10$ K) behavior, shown by Hunklinger [81] to be proportional to T^2, presenting values lower than those of the corresponding crystalline material. This behavior was attributed to localized elementary excitations consisted of tunneling modes between double-well potential minima in the so-called two-level systems (TLS), proposed by Anderson, Halperin and Varma [82] and Philips [83]. A comprehensive review with additional on ultrasonic and dielectric data, obtained from measurements of vitreous silica and other dielectric

merged naturally from the melt (or from the reactions occurring on deposition). From this point of view one is expected that the increase in concentration of the glass network modifier cation will not introduce additional distortion to the local symmetry on the SU's, in contrast with the addition of an impurity of greater ionic radius, when a small amount is sufficient to produce observable immediate effects. As an example, a shift in the ligand field intensity Δ in the Tanabe-Sugano (TS) diagram [71] produced by the addition of 0.6 mol% of Sb_2O_3 in the glass of composition $20Al_2O_3 \bullet 50B_2O_3 \bullet 30BaO$ doped with 0.3 mol% of Cr_2O_3 [72]. The OA effect of doping with a small amount of antimony ion of ionic radius of 0.9 Å is shown in Fig. 1, where the Cr^{3+} $^4T_2$ OA band has shifted by approximately 250 nm toward the longer wavelengths. It is equivalent to a shift of Δ in the TS diagram as indicated in Fig. 2. It was observed also that the parameter Δ is rather insensitive to substantial increase of glass network modifier ion Ba^{2+} in the chemical composition of this system of glasses. These results lead to the suggestion that it is possible to introduce small changes in the optical properties of a glass doped with TM of RE ion by adding a controlled amount of a suitable ion of sufficiently large ionic radius.

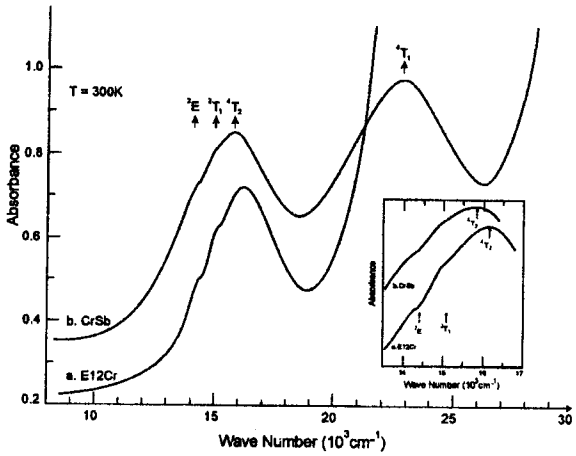


Fig. 1. Optical absorption spectra of $20Al_2O_3 \bullet 50B_2O_3 \bullet 30$ BaO (mol%) glasses (1) doped with 0.3 Cr_2O_3 (wt%) and (2) doped with 0.3 Cr_2O_3 + 0.6 Sb_2O_3 (wt%). The inset shows a closer view of the range from 14000 to 165000 cm^{-1} [72].

The structure of glass from a topological viewpoint evolved with the interesting contribution of Rivier, Weaire, Thorpe [73-78] and others. The methodology consisted to identify and relate the physical properties that are both universal and specific to disordered condensed matter. The CRN of a covalent glass was defined as a graph where the vertices and edges are atoms and bonds, respectively, where the non-planar face, rings and cells do not have a direct physical interpretation. As the atoms have fixed valence, so that the regular graph has fixed vertex coordination z (z = 4 for Si) and dangling bonds are permitted. Rivier [73] has distinguished the main structural features of the amorphous state: i) non-collinearity of local reference frames; ii) overall, but non-generative homogeneity and iii) odd lines (that we are not going to discuss here).

and metallic glasses, was presented by Shickfus [84]. Another important characteristic of the TLS is the coherence that permits analogy with the familiar experiments of electron spin and nuclear magnetic resonance, as reported by Joffrin [85], leading to the observation of the phonon-echo. A coherent survey on the basic ideas and perspective, containing description of experiments of heat capacity, thermal expansion and thermal conductivity, more specific acoustic and optical measurements, is given in a book devoted to the subject [86].

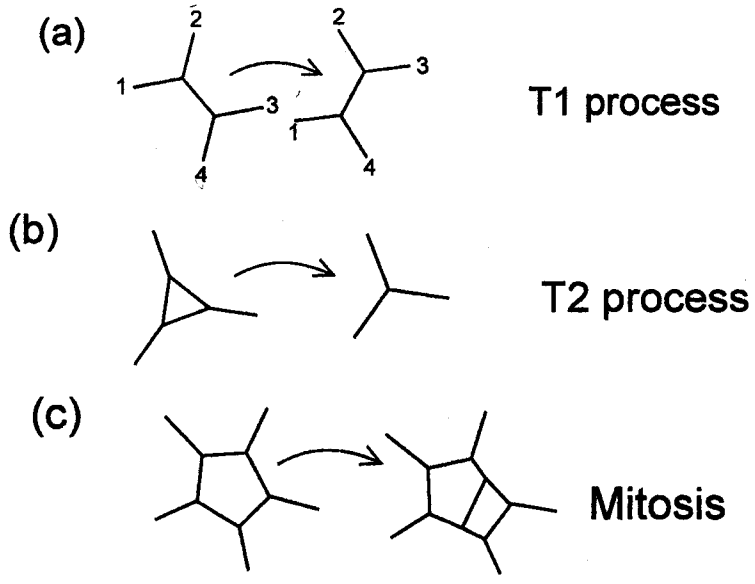


Fig. 3. (a) T_1 or neighbor switching; (b) T_2 or cell disappearance and (c) mitosis or cell division [75].

New methods of oxide glass formation

Recent advances in science and technology have created great demands for new high perfomance oxide glasses. In order to satisfy such demands, many attempts have been made to develop new preparation methods. Since new methods such as deposition of vapors, precipitation from liquid solutions or heat treatment of gels produce oxide glasses without melting raw materials, they may not be called the glass forming methods in the old sense. In this sense, new methods can be categorized into the following three major groups:

1. Unconventional melting methods
2. Deposition methods
3. Solution methods

For high silica the deposition method is the most used in the world, but for special oxide glasses a very high number of new methods is available, related with the preparation of optical fibers.

For the fabrication of special oxide glass optical fiber, two basic techniques have been used to produce core/clad optical fiber from silicates, phosphate, germinates and telluride oxide glasses, namely, the redraw of performs into fibers and the direct draw of fibers from a crucible. Many variations of these two basic techniques have been developed, including preparation of performs using CVD, rod-in-tube, ion exchange, leaching, sol-gel processing, and up-draw from a melt.

The various techniques used to fabricate special oxide glass performs can be divided into two major classes, namely the bulk cast performs and the tubular performs. The former represent performs which possess the desired core/clad geometry and are draw directly into optical fibers. The second class represents performs which are formed into tube shapes and subsequently need to be collapsed prior to or during fiber drawing.

A well-known method called clad-over-core process, the clad melt is poured around a core rod placed inside a metal mold. While the resulting perform possessed a uniform clad-to-core diameter ratio, there were numerous bubbles trapped at the core/clad interface and reheating at the core/clad interface led to crystallization. Fibers fabricated from these performs had high transmission losses.

Another variation is known as built-in-casting process. The cladding melt is poured into a metal mold held at the glass transition temperature. After waiting a few seconds, the mold is inverted and the melt from the central region of the mold flows out, leaving behind a tubular-shaped void in the center. Next, the core melt is poured in to fill up the void and the perform subsequently annealed. While this is a simple technique, interfacial and core bubbles still remain a problem.

The modified-built-in-casting process reduced the taper associated with the built-in-casting method described above. In this process, a precise amount of the cladding melt is poured into a special designed mold. Prior to the central part of the cladding melt solidification, the core melt is cast onto the cladding melt. The mold assembly was then shifted over to a section where the bottom of the plate was missing. Next, the cladding melt from the central section is drained from the mold, and, as it does so, the core melt is drawn into the glass along the mold axis.

The suction-casting process is a somewhat more refined version of the modified-built-in-casting technique that has been used to fabricate single-mode fiber. In this process, the cladding melt is poured into a specially designed cylindrical mold having a reservoir at the bottom and is preheated close to the glass transition temperature. Next, the core melt is cast onto the cladding melt before it solidifies. On cooling, volume constriction of the melts occurs, which results in the formation of a tubular cladding tube. This procedure results in a suction effect on the core glass melt down to the bottom, thereby filling up the cladding tube. The single-mode geometry was obtained by inserting the perform inside an outer cladding tube of similar composition to the inner cladding tube and subsequently drawing this configuration into a single-mode fiber.

In the rotational casting process, the cladding glass is first melted in a platinum crucible and then poured into a gold-plated mold preheated at about the glass transition temperature. This is subsequently spun at several thousand rpm to form a highly concentric cladding tube whose diameter is precisely controlled by

the amount of cladding glass. Next, the tube is set vertically and the core glass melt is either cast in the tube or the tube is dipped into the core melt. The cast perform is then annealed to prevent cracking.

The extrusion process is advantageous for use with oxide glasses that exhibit a strong tendency to crystallize and vaporize because performs can be formed at a higher viscosity (10^8 – 10^9 Poises). Core and cladding glass disks formed by melting casting are both polished without water. The polished glass disks are placed inside a cylinder and heated to the deformation temperature in a dry atmosphere after which they are extruded under a pressure of 50 bars using a punch.

The rod-in-tube process requires a high-quality oxide glass rod that is usually fabricated by melting, casting, and subsequently polishing. This is inserted into a cladding tube that was obtained by the rotational casting method. During fiber drawing, the interface is evacuated so that the cladding tube collapses around the core rod. While bubbles in the core can be avoided with this method, the fibers typically exhibit high scattering due to interfacial defects.

The deposition method can be divided into the non-reactive and reactive types. The former one involves only physical processes and the later involves chemical reactions to form a vitreous phase.

The chemical vapor deposition is the most effective method to produce a bulk glass among various deposition methods, although it requires a post sintering process to make a dense transparent bulk sample. This method has been explored extensively as a method to fabricate high-purity optical fibers and it is now well established. In principle, vaporizable-decomposable organic-metallic or halide compounds are oxidized in flame or in glow discharge plasma to produce ultra-fine glass particles that are deposited on the solid surface, forming high-purity glass soot. The soot is then sintered to make a solid inclusion-free glass body. In the case of optical fibers, a variety of ways have been attempted and developed to deposit the glass particles and make soot. Among them, three major processes are as follows: the Outside Vapor Phase Oxidation (IVPO) is to deposit them on a removable rod target. The Inside Vapor Phase Oxidation (IVPO) or the Modified Chemical Vapor Deposition (MCVD) is to deposit them on the inside walls of a glass tube. A new process of Vapor Axial Deposition (VAD) is the simultaneous deposition of core and cladding glass soot. The graded index type glass rod is made in one step by using a mixture of $SiCl_4$ and $GeCl_4$ and controlling the deposition temperature.

In the case of the sol-gel process, there are two major routes. One is the chemical polymerization route and other the colloidal route. To initiate the chemical reaction, an appropriate chemical is added to the solution of an organic-metallic compounds or metallic salts to obtain a sol, which transform into a gel at low temperatures. By heat-treating it at a relatively low temperature, glass is obtained.

Optical functions of photonic glasses

Potential photonic applications of oxide glasses

The invention of lasers in 1960's and the production of low-loss optical fibers in 1970's brought about the dawn of the optical information age. Since then, wide varieties of optically functional of photonic materials have been developed. Among the most currently designed optical functions of photonic material groups, high transmittance, homogeneity, isolation and deflection, amplification, light generation, ultra-high speed optical switching, optical memory and optical display are examples of promising applications of advanced materials.

The glasses have proven to be excellent and flexible sources of infinitely varied compositions eligible to fulfill some special characteristics in order to perform efficiently previously selected specific functions. Notwithstanding their transparency, great multiplicity of compositions, easy processing of various sizes and shapes, it is possible to incorporate increased amounts of functional ions and colloidal particles, to induce gradual changes in the structure and properties under the application of external stimuli, and a wealth of different fabrication techniques are available. New optical functional properties require the development of new materials and the glasses provide a wide set of characteristics correlated with novel photonic applications.

The future of photonic glasses can be stated on the assumption that the development can be achieved on the following principles: (1) further improvement of the performance of the existing glasses; (2) discovery of novel characteristics in glasses; (3) use of appropriate shapes, sizes and compositions in the development of fibers, coating films and large glass pieces.

Activity in this field range from improving the properties and developing better manufacturing methods of silica and to develop compounds of heavy metal oxide glasses with improved IR properties. The oxide glasses exhibit best chemical and mechanical durability, they are good and stable glass formers and are environmentally kind and are more economically manufactured.

Important applications have been the use of tellurium oxide glass as a host material for broadband (80 nm) Er-doped amplifiers [87]. Broadband optical amplifiers offer a better utilization of the optical transparency window available in silica fiber networks. Additionally, using other rare-earth dopants like Tm and Pr (and also in tellurite glasses), one can build amplifiers for 1470 and 1300 nm bands, dramatically increasing the channel capacity of the optical fibers. The strong hyper-polarizability increasing the channel of tellurium oxide also makes it a good switching material. Tellurite glass can be poled to yield strong Pockels non-linearity [88] and also exhibits a strong Kerr non-linearity [89] typically 30 times greater than that of the silica. Future photonic switches potentially are going to use these properties.

Glasses based on phosphorus oxide also exhibit good transparency. These glasses have good rare-earth solubility and excellent mechanical properties, translating into short device lengths [90]. Some of the 1.5 μm devices are applied in cladding pumped lasers, preamplifiers, amplifiers and planar devices. Background losses are well below 1 dB/m, and are acceptable for these applications.

The magnitude of the band gap of an insulating glass can be defined in close analogy with the formalism adopted in the study of amorphous semiconductors. The differences are rather quantitative, but the basic features of the optical window are essentially the same. The optical absorption is determined by the density of states and in amorphous systems the band edges penetrate into the gap (see Fig. 4) [97].

Several books and review articles are available containing excellent information on the origin and an ingenious interpretation and description of the evolution of the related concepts and models is given by Mott and Davis [98] We are going merely to notice the main parts A, B, C of the absorption edge, as defined by J. Tauc [97], where A is the parabolic part ($\alpha > 10^4$ cm^{-1}), B the exponential part (10^1 cm$^{-1} \leq \alpha < 10^4$ cm^{-1}), and C is the weak absorption tail ($\alpha \leq 10^1$ cm^{-1}). Typical silica optical fiber attenuation in function of wavelength is shown in Fig. 5.

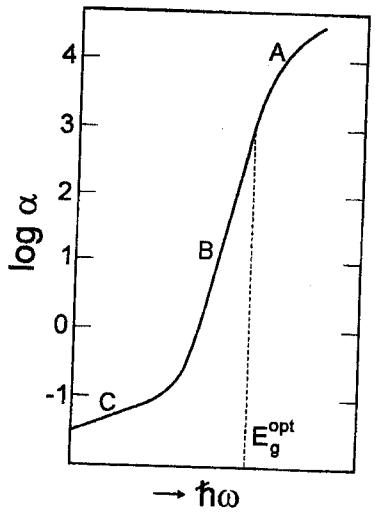


Fig. 4. Density of states of the band edge versus photon energy [97].

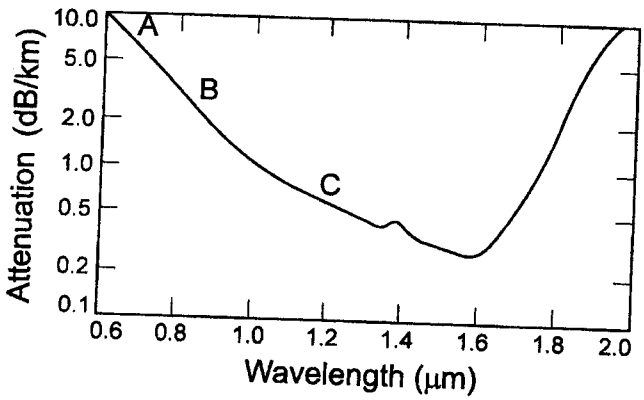


Fig. 5. Attenuation of a typical silica optical fiber versus wavelength.

Another system of heavy metal oxide glasses of great interest is comprised by the bismuth-oxide based glasses for broad-band (>80 nm) Er-doped glass amplifiers and for non-linear applications [91]. Again the interest is directed to the Dense Wavelenght Demultiplexing Multiplexing (DWDM) amplifiers that can operate in Er and other bands. An all-optical switch faster than 200 femtosecond has also been demonstrated as feasible in these fibers [92].

The transparent ceramic glasses comprise a class of optical materials that allow combining the desired properties of different materials. Nanometric grains of one material are dispersed in a transparent glass host. One example is the Pr-doped 1.3 μm amplifier being developed in (Pb-Cd)F_2-silicate ceramic glass system [93]. Pr is trapped in a fluoride environment and therefore the radiative decays become very efficient, and the silicate oxide matrix gives the mechanical and chemical durability to the system.

Similarly ferroelectric-ceramic glasses can be developed. Ferroelectric materials like Strontium-Barium-Niobate (SBN) or Barium Titanate (BTO) have orders of magnitude of better figures of merit compared to the Lithium-Niobate (LNO) material [94]. A substitution of these ferroelectric materials, in principle, would lower the operational voltages and increase the switching speed. The transparency requirement can be met by a small grain size and matching refractive indices. The SBN and BTO have refractive indices near to 2, matching to the telluride glass. Such systems have been demonstrated to be compatible with SBN, BTO and LNO ceramic glasses.

Transparency

More than half a century ago, Morey [95] has reported a quite complete picture on the status of the knowledge dealt with the properties of glass at the time. A large deal of experimental data was collected in regard to the action of glass on light. It was stated the need of the development of different glasses designed for special optical applications, so that the window of transparency could be placed either in the visible, infrared, UV or X-rays. A glass transparent in a given region of the electromagnetic spectrum is opaque in the other. The optical measurements were limited on the macroscopic properties of glasses such as the index of refraction, absorption and dispersion. For practical purposes the existing theoretical formulas were considered as useful empirical equations. The best optical glasses were found over 99% of transmittance throughout the visible spectrum ($\alpha = 5 \times 10^{-2}$ cm^{-1} assuming a thickness of 2mm), while a common window glass has a transparency of about 90% ($\alpha \approx 5 \times 10^{-1}$ cm^{-1}).

In the 1970's Siegel [24] has summarized concepts of electronic excitation and vibration spectroscopy applied to glass and described measurement methods of optical absorption and reflectance of common oxide glasses, as silicates, borates and phosphates. He has reported, for high-purity silicate glasses, absorption coefficients less than 10^{-5} cm^{-1} (optical losses < 4.3 db/km) minimum values near IR, in the 0.8 – 1.1 μm range. Thus, the oxide glasses are among the most transparent optical materials. Recent development on IR halide glasses [96] has extended further the transparency limit reaching values as low as $\alpha \approx 2.3 \times 10^{-7}$ cm^{-1} (0.01 dB/km), very close to the theoretical limit.

The contributions of impurities as the transition metal ions or OH, obscuring the intrinsic tails of the UV- and IR-edge, respectively, are always present and are very difficult to be removed if it is desired to produce a glass of high transparency. Another limiting condition is determined by the Rayleigh-like scattering of light due to the inhomogeneous fluctuations of density and composition in the glass [99].

There are alternative definitions of the energy gap E_g of amorphous systems: a) the optical energy gap obtained from the extrapolation of the parabolic envelope of density of states (part C), as defined by J. Tauc [97]; b) the electronic E_g, or mobility gap, which is a measure of the energy difference between the mobility edges of valence and conduction band, respectively [100]. The optical gap is the measure of the width of the window for the transmission of light, whereas the mobility gap is the magnitude of the barrier for the photoconduction of the material.

Optical wave-guide fibers and plates

In the last decade we have seen the drastic development of new optical devices in which glass plays an important role. These include optical wave-guide fibers with low levels of attenuation, optical data storage, planar optical wave-guides, nonlinear optical materials including semiconductor-doped glasses as well as glasses containing heavy metal ions, novel fiber optic bundles for imaging and glass lasers including fiber lasers and light amplifiers.

The remarkable expansion in the glass as an optical material is reasonable since glass is transparent and has a valuable characteristic in that any element can be dissolved in it the necessary amount required for a good resistance to a laser beam. Indeed, the potential for optical materials and devices seems outstanding and the coming decades will almost certainly see the emergence of innumerable novel optical materials and systems using glasses. In spite of these advances in glass research, the further innovative ideas are required to make the glass more active.

Active applications need to utilize the photo-induced structure. It was recently found that if this capability is combined with temperature modification and applied electric fields, the glass center of symmetry can be broken, thus liberating glass from its previously conceived limit to only passive roles. For instance, if a high voltage is applied across SiO_2 glass plate at a high temperature and the material is subsequently cooled, the resulting glass is capable of converting infrared laser light up to blue light (second harmonic generation) [101]. Another method to get the visible yellow, green and even blue laser light is to utilize the upconversion phenomenon (two photon absorption). So far, a blue laser diode has not been realized at room temperature (limited to infrared light). However, by doping some rare earth ions into suitable glass fiber, stable upconversion laser light is produced. Through the physical process of how the field changes the electronic structure of glass is not yet perfectly known, the modified glass fiber somehow combines the energy of two photons into one photon. This room temperature short-wavelength blue light will greatly increase the information-storage capabilities in CdS and other materials.

electronic materials. A crystal is a periodic arrangement of atoms or molecules; that is, a crystal lattice results when a small, basic building block of atoms or molecules is repeated in space. A crystal therefore presents a periodic potential to electron propagation through it, and the geometry of the crystal dictates many of the conduction properties of the crystal.

In particular, the lattice might introduce gaps into the energy band structure of the crystal, so that (due to Bragg-like diffraction from the atoms) electrons are forbidden to propagate with certain energies in certain directions. If the lattice potential is strong enough, the gap might extend to all possible directions, resulting in a complete band gap. For example, a semiconductor has a complete band gap between the valence and conduction energy bands.

The optical analogy is the photonic crystal, in which the periodic "potential" is due to a lattice macroscopic dielectric media instead of atoms [119].

Magneto-optical systems

The Faraday rotation of a polarized light crossing a medium is proportional to the strength of the applied field. The constant of proportionality (Verdet constant) was first measured by Borrelli [120] for different types of glasses. It was shown that the Verdet constant increased for higher concentrations of ions that have sp-s^2 transitions and rare-earth paramagnetic ions. Recently C. B. Pedroso et al. [121] have measured the magneto-optical rotation for systems of multicomponent oxide glasses obtaining Verdet constant as high as 0.162 min G^{-1} cm^{-1}. Examples of interesting applications of optical fibers are the fiber current [122,123], magnetic sensors [124,125] and fiber optical isolators [126].

Today, magneto-optical and phase change type optical memory systems have been developed primarily for optical recording systems, but these are based on using one pit as one bit, so the access semiconductor laser beam diffraction limit of 1 μm determines the upper limit of recording density and the maximum value is about 10^8 bit/cm^2.

Photochemical hole-burning materials

It has also recently been found that photochemical hole-burning materials can be made from glasses that are stable at room temperature [127]. In this process narrow bands of color are selectively burned out of reflecting coatings. The number of colors that can be selectively removed and detected about 100 multiplies the storage capacity of the coating. It may be possible to multiply this storage capacity another 100-fold by applying electric voltages to the materials. This type of nonlinear behavior has the possibility of being applied to optical high-speed memory.

As another important application of the hole burning glass, it has found that it is possible to store the picture within a very small (0.5 cm^3) piece of glass by using the multiplexed frequency, where one frequency corresponds to one picture. Each image is contained within the whole glass, and at a low temperature (77K) it is obtained a very clear image. A number of 10,000 such pictures can be stored in just one piece of glass. This is just like a hologram. However, in this case, the

element of time is added to that of space by scanning the wavelength while applying a Fourier transform (wavelength multiplexing), resulting in a movie, rather than just an image, yielding an equivalent of 30 video tapes compressed to just one piece of small glass.

Photochemical Hole-Burning (PHB) optical memory is a frequency multiplexed type of device enabling to write-in and red-out with light of various different frequencies at one pit, so the recording density can be increased 10^3 to 10^9 times compared with conventional optical memories. The host materials causing PHB are organic dyes and rare earth ions with optical absorption bands in the visible, which are doped into organic polymers and inorganic glasses, respectively. At present, PHB optical memories are primarily those in which polymer materials are doped with an organic dye, but they fail to burn holes at room temperature and the use of organic materials raises the problem of denaturing with high output laser beams.

It was found that PHB materials could be made from Sm^{2+} doped inorganic oxide glasses in which holes can be burned at room temperature [127]. Sm^{2+} doped borate glasses were prepared by melting the starting materials of boron oxide, alkali (Li, Na and K), carbonate, aluminum oxide, samarium oxide and subsequent quenching. First, the raw materials are melted at 1100 °C in air during 30 min and remelted at 1400 °C in Ar(98)/H_2 atmosphere during 30 min [127]. The sample is then irradiated with a DCM dye laser at 683 nm. After the irradiation, the excitation spectrum is observed. The hole is detected by comparing the excitation spectra before and after hole-burning. The Sm^{2+} doped borate glasses seem to generate the hole-burning phenomenon at room temperature in terms of the following photo-ionic reaction:

$$Sm^{2+} + (trap) \rightarrow Sm^{3+} + (trap)$$

The electron trap can be tentatively attributed to the BEC.

The generation is most likely due to the lower-electron-donation ability of O^{2+} ions to Sm ions in borate glasses than that in any other oxide glass. The detailed explanation of PHB phenomenon is described elsewhere [128].

Holographic techniques

An important application of the PHB glass besides CD's is real-time recording of a moving image using a holographic technique. It was found that it is possible to store much information within a very small piece of glass using the multiplexed frequency, where one frequency corresponds to one picture. Each image is contained within the whole glass and this is just like a hologram. However, in this case, the element of time is added to that a space by scanning the wavelength while applying a Fourier transform (wavelength multiplexing), resulting in a movie, rather than just an image.

with the square of users numbers, which is more intense than the exponential growth factor. The latter tends to be a market barrier for late entrants.

Technological scenario

Technology boundaries in this field are evolving in two major directions. The first one relates to the possibility of transmitting high rates through wavelength division multiplexing (WDM) systems (multiple channels with different wavelengths), with the transmission rate of each channel at below 40 G bit/s; the second one, in high rate systems, with horizons above 100 G bit/s, is based on special optical fibers and/or solitonic systems. Such systems have posed challenges both in terms of manufacturing technology for optical fibers as well as new optical materials. Among these, we can emphasize the challenges involved in new materials for developing photonic switches. The idea is to replace electronic devices for optical ones in order to increase the transmission rate by magnitude values in relation to those existing today. The entire electronic field is based on electrons, which have charge and mass and are under the strong influence of carrying medium charge. On the other hand, the photons are much faster and travel at light speed. As they have neither mass ($m=0$) nor charge ($q=0$), they suffer little influence of the transmitting medium. However, it is precisely due to the photon weak interaction with the medium that makes control by external agents difficult. Therefore, the development of optical or electro-optical devices (called photonics) to replace electro-electronic devices is one of the major challenges today. Replacing electronics for photonics only makes sense if the information transmission rate outweighs the systems in place. In order to have a magnitude value, let's consider a communication system operating with 100 G bit/s per channel. This means that two optical pulses carrying information are distant in time by only 10 picoseconds, leading to the conclusion that an optical device should be able to operate in as short time as 1 to 3 picoseconds.

The enormous increase in data traffic, largely due to the growth in internet, has spurred rapid growth in broadband communication technologies. Fiber optics, which offers the largest bandwidth of any communication system, is the medium of choice for carrying the multitude of data now being sent through networks. While fiber can theoretically carry over 50 Terabits per second, current optical communication system is limited to 10 Gigabits per second due to the limitations of the switching nodes.

Switching nodes consist of systems dedicated to switching the optical signal-functions between lines as well as providing other signal-processing functions, such as amplification and signal regeneration. Switching nodes include components such as optical switches, add/drop multiplexers, channel converters, routers, and so on.

Actually "optical switches" used in switching nodes are typically not entirely optical of relatively slow operation and have limited bandwidth. The well-known optomechanical switches use moving (e.g., rotating or alternating) mirrors, prisms, holographic gratings or other devices to deflect light beams. The mechanical action may involve motors and piezoelectric elements may be used for fast mechanical action.

fiber lasers, and low noise EDFA's with broad bandwidth that will enable the transmission capacity of WDM system to be increased [112].

Recently, the requirement to overcome loss over long distance optical communication system in a transparent way, has led to the development of special optical amplifiers. Practical devices were developed only after progress in erbium doped fiber amplifiers took place in the mid-80's. EDFA cover the bandwidth around the minimum loss of optical fibers (1530 nm). In order to exploit as much as possible of the available bandwidth that can be transmitted over optical fiber in the low loss region from 1440 to 1630 nm, new optical amplifiers, besides EDFAs are required to cover the whole spectral region. Raman amplifiers, optical parametric amplifiers, semiconductor optical amplifiers and other rare earth doped fiber amplifiers are possible choices [103]. Regarding rare earth doped fiber amplifier amplifiers, erbium doped fiber amplifier cover well the C + L (1530-1630 nm) band, whereas thulium doped fiber amplifiers TDFAs cover the S band (1420-1530 nm). The other types of amplifiers mentioned above can operate in any band, depending on amplifiers parameters such as pump wavelength (for Raman) and minimum dispersion wavelength (for optical parametric amplifiers). In this sense, telluride optical fiber glass is the best host for erbium and thulium rare earth amplifiers.

Photonic band gap optical fiber

Photonic band gap optical fibers are typically all silica optical fibers in which air-holes are introduced in the cladding region and extend in the axial direction of the fiber [113-115]. These fibers, which have been know since the earliest days of silica light guide research [113], come in a variety of different shapes, sizes, and distributions of air-holes. Recent interest in such fibers has been generated through potential applications in optical communications; [113,116] optical fiber based sensing; frequency metrology and optical coherence tomography [117]. The earliest work reported by Kaiser et al [113], demonstrated low loss single material fibers, made entirely from silica. A number of years later Russel et al. [116] demonstrated the so-called photonic crystal fiber. These fibers incorporate a periodic array of air-hole in the cladding region and guide light through modified total internal reflection [116,118].

For the fabrication of photonic band gap optical fiber has been highly labor-intensive and time-consuming process. The typical starting point is an array of hollow capillary silica tubes bundled around a pure silica rod replaced the center capillary. A sleeving tube surrounds the entire assembly, forming the perform. In a fiber draw tower, the manufacturer heats the perform to around 2000 °C and carefully pulls the perform, using gravity and pressure, into a fiber typically 125 μm in diameter. This micro-scale fiber maintains the structure of the perform. A protective polymer coating applied to the outside improves handling characteristics.

The research in the field of photonic band gap fiber was stimulated by the prediction of a photonic band-gap analogous to electronic band-gaps in semiconductor [113].

What sort of material can afford us complete control over light propagation? To answer this question, we rely on an analogy with our successful

A major limitation of optomechanical switches is due to their low switching speeds. Typical switching times are in the millisecond range. The low insertion loss and low cross talk are some of the advantages of the optomechanical switches.

Another optical switch uses electro-mechanical materials that alter their refractive indices in the presence of an electric field. They may be used as electrically controlled phase modulators or phase retarders. When placed in the arm of an interferometer, such as a Mach-Zender interferometer, or between crossed polarizers, the electro-optic cell serves as an electrically controlled light modulator or a 1 × 1 (on-off) switch. The most prevalent technology for electro-optic switching is the integrated optics since it is difficult to make large array of switching using bulk crystals. Integrated-optic wave guides are fabricated using electro-optic dielectric substrates, such as Lithium Niobate ("$LiNbO_3$"), with strips of slightly higher refractive index at the locations of the wave guides, created by diffusing titanium into the substrate. The major drawback of Lithium Niobate technology is the high expense of the material and difficulty in creating low loss wave-guides within it.

Another optical device includes acoustic-optic switches, based on the property of Bragg deflection of light by sound. An acoustic wave propagating along a dielectric surface alternatively puts the material in compression and tension. Thus, the acoustic pressure wave periodically alters the refractive index. The change in the refractive index is determined by the power of the acoustic wave, while the period of the refractive index change is a function of the periodically alternating refractive index is deflected. A switching device can be constructed based on the property that the acoustic wave controls the condition whether a light beam is deflected or not into an output wave guide.

So far, the many proposals of optical switching have not materialized for lack of proper material. Regardless of details, all optical devices are based either on the absorption coefficient variation $\Delta\alpha$ and/or index of refraction variation Δn of certain materials. The ideal material to manufacture a photonic device has too large $\Delta\alpha$ and/or Δn and too fast response time. In totally optical devices, the variation cause of $\Delta\alpha$ and Δn is a light pulse and in electro-optics it is an electrical signal, and so on. An example of a totally optical device is the coupled wave-guide device, as shown in Fig 6.

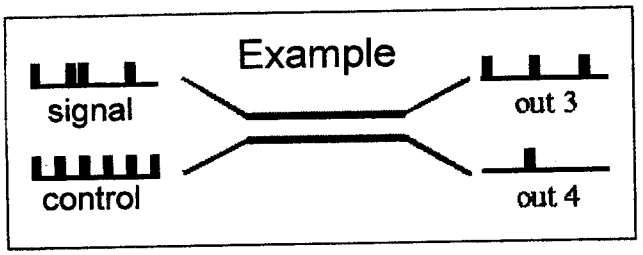


Fig. 6. Example of a totally optical device.

In this device a light pulse can control whether the signal exits through door 3 or 4. The device is built with a certain length so that the incoming signal by door 1 exits through door 4 in the absence of a controlling pulse, but exits through door 3 in the presence of a controlling pulse. A situation where two wave-guides

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are coupled is similar to a two coupled pendulums system, with two normal modes, symmetrical and asymmetrical, with different group velocities, as shown in Fig.7.

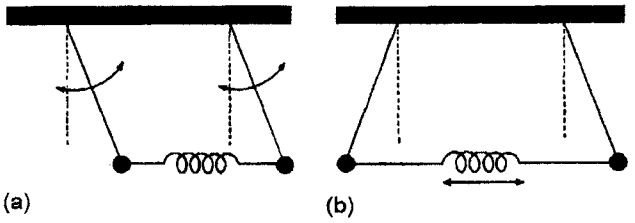

Fig. 7. (a) Symmetric Mode: the spring is neither compressed nor expanded. (b) Asymmetrical Mode: the spring is expanded and compressed.

The initial presence of the signal pulse in channel 1 can be decomposed like the superposition of the two normal modes shown in Fig. 8a. As each mode propagates at different group velocity, the phase between the two modes changes as the pulse propagates, eventually reaching the π value. At this point, the two modes should be subtracted rather than added. This is the superposition shown in Fig. 8b where the light is totally contained in channel 2. The wave-guide channels in this device have exactly this size, so that an incoming signal by door 1 exits normally through door 3. However, the total light coupling of channel 1 and channel 2 is only total if the two wave-guides are identical and the distance where it occurs depends on the indexes of refraction, both inside and outside the channel, as well as on the channel dimensions and the gap between them. When the controlling pulse changes the index of channel refraction, this coupling no longer occurs and the light is kept in channel 1.

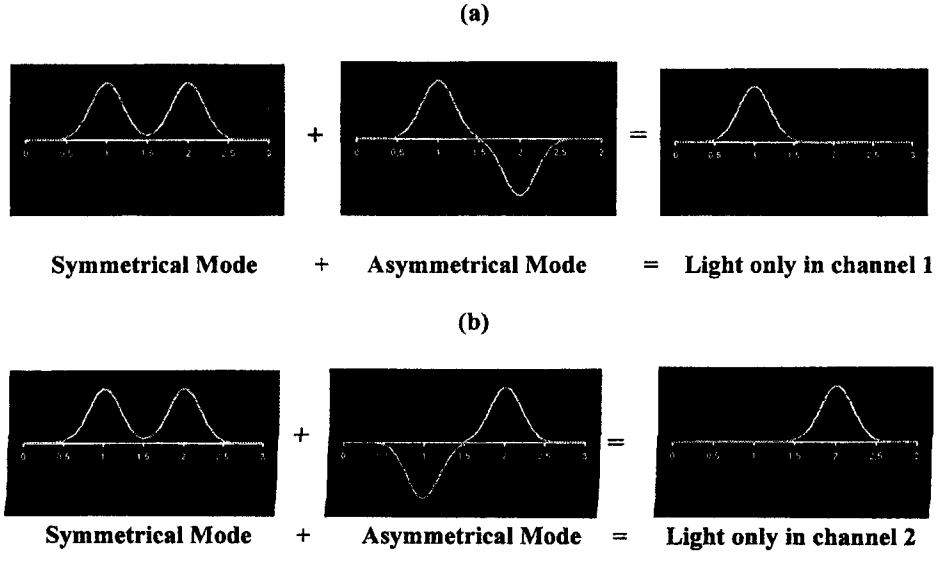

Fig. 8. Superposition of symmetrical and asymmetrical modes results in light in (a) channel 1 only (b) in channel 2 only.

These are not the only examples of optical switches proposed so far. There are quite a number of them using other strategies based on interference, diffraction transient grids and total absorption/transparency of the signal and even temporal delay of two pulses. What they all have in common is their dependence on a variation of the absorption coefficient or on the refraction index of the material medium, as stated above. These characteristics impose certain restrictions on the properties required from a material in order to make it suitable for the photonic switch physical medium.

(1) It should present high $\Delta\alpha$ and/or Δn values.
(2) It should be non-linear with ultra fast response time, from units to tens of picoseconds.
(3) It should operate in the wavelength used in optical communications, from 1 to 2 μm.
(4) The material must allow the production of optical fibers or planar wave-guides.

In general, there is a commitment between non-linear optical values and material response time. In resonance the absorption intensities and refraction indexes are high but the response time is long, as there was a real transition of the electron from one state to another and the return, or recombination (semiconductors), to the initial state is slow, in the range of mili to nano-seconds. On the other hand, away from the resonance, the response time is too short, but $\Delta\alpha$ and Δn are extremely small.

In the context addressed above, the doped glass with semiconductor quantum dots becomes an excellent option because: (1) they are included in the resonant materials presenting therefore high values for $\Delta\alpha$ and Δn and (2) the response time is short. Quantum dots are formed from semiconductors in a glass matrix, smaller than the Bohr radius of the exciton (one for electron-hole) in the bulk semiconductor, usually in a scale from 10 to 100 Å. With dimensions of this magnitude, they present quantum confinement effects in 3 dimensions. In such materials, the confinement both of electrons and holes reduces the recombination time, as they cannot move away from each other.

Theoretical studies of non-linear effects associated to effects of quantum confinement [129] show that glasses with QD's with great Bohr radius potentially qualify best for high nonlinearities [130-133], since, due to the confinement effect, each optical transition will contribute for $\Delta\alpha$ and Δn with a factor strongly dependent on the Bohr radius of the bulk semiconductor and the QD radius of the format.

$$\Delta\alpha \equiv \Delta n \propto \left(\frac{R_{Bohr}}{R_{QD}}\right)^3$$

This is why these glasses show huge resonant nonlinearities. Despite the resonant, the recovery time occurs in a scale of femto/pico-seconds. Such a fast recovery for a real transition is only possible because the quantum confinement keeps the electrons and holes together, substantially increasing the recombination

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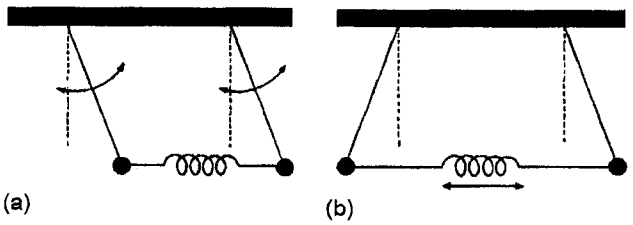

Fig. 7. (a) Symmetric Mode: the spring is neither compressed nor expanded. (b) Asymmetrical Mode: the spring is expanded and compressed.

The initial presence of the signal pulse in channel 1 can be decomposed like the superposition of the two normal modes shown in Fig. 8a. As each mode propagates at different group velocity, the phase between the two modes changes as the pulse propagates, eventually reaching the π value. At this point, the two modes should be subtracted rather than added. This is the superposition shown in Fig. 8b where the light is totally contained in channel 2. The wave-guide channels in this device have exactly this size, so that an incoming signal by door 1 exits normally through door 3. However, the total light coupling of channel 1 and channel 2 is only total if the two wave-guides are identical and the distance where it occurs depends on the indexes of refraction, both inside and outside the channel, as well as on the channel dimensions and the gap between them. When the controlling pulse changes the index of channel refraction, this coupling no longer occurs and the light is kept in channel 1.

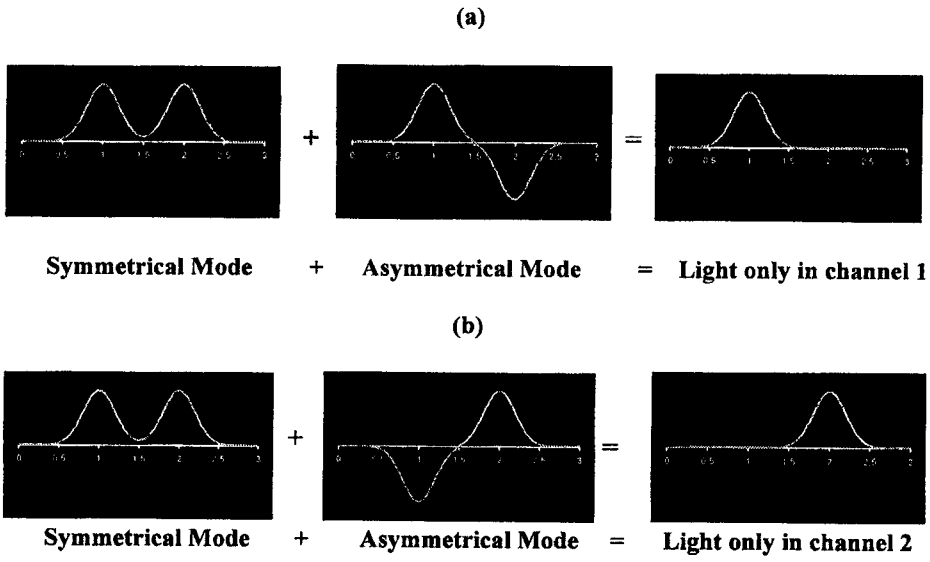

Fig. 8. Superposition of symmetrical and asymmetrical modes results in light in (a) channel 1 only (b) in channel 2 only.

rate. Tesunetomo et al. [134], using glasses with CdTe quantum dots, demonstrated a totally optical device operating in 250 G bit/second.

Concluding remarks

The oxide glasses have long been a matter of technological and scientific interest, but the peculiar difficulties of the amorphous systems have lagged the progress of the basic concepts as compared with the evolution of solid-state physics.

However, the development and characterization of thousands of different glass compositions has led to a very large number of applications, being photonics among of the most promising potentialities of the present day.

Although the glass structure is not repetitive, the comparative study of glasses having similar local structure as their crystalline counterparts, has given the means to the understanding of some basic regularities and to the building blocks of the glass network.

The basic structural study of the oxide glasses, together with new topological approach and the evolution of new theories about some universal characteristic properties are unique of the amorphous state.

New methods of preparation were developed and high performance oxide glasses were produced in order to attend the great demands related with the recent advances in science and technology.

The improvement of several optical functions of oxide glasses has opened a wide potential to the photonic applications.

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