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FABRICATION AND CHARACTERIZATION OF NONLINEAR OPTICAL GLASSES

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Advent of lasers offering high intensity beam has opened the glass to the nonlinear optic (NLO). The high electric field associated with such laser beams can be so large that high order components of the glass polarization can be measured. Such development is of scientific and technological interests in particular in systems involving an intensity-dependent refractive index and/or ultra-fast response ($<10^{-12}$s). From a scientific viewpoint the NLO response intensity must be understood as a function of the glass composition. On the other hand, large family of applications are presently under investigation in various fields of optical materials or systems e.g. laser glasses for fusion energy, soliton propagation for ultra-long distances, ultra-fast-switching, optical storage etc...

Usually NLO is introduced by considering the dielectric susceptibility χ in term of the oscillating optical electric field : the $\chi^{(1)}$ term is the susceptibility measured at low power, the $\chi^{(2)}$ term is at the origin of the second harmonic generation and the $\chi^{(3)}$ term leads to the third-harmonic generation and/or the refractive index change. The object of the presentation is :

(i) to analyze the dependence of the glass composition and of the glass structure on the magnitude of the nonlinear index n_2 ($\chi^{(3)}$) in a non resonant configuration,

(ii) to review the more recent results related to the second-order nonlinearity ($\chi^{(2)}$) induced by electro-thermal poling on glasses.

The determination of precise n_2 is a complex problem and the different techniques vary in their sensitivity accuracy. Recently was developed a sensitive method based on a Mach Zehnder interferometer using a cw mode-locked Ti:sapphire laser generating 100 femtosecond pulses at 800nm with a repetition rate of 80Mhz to time resolve all the relevant non linearities and to measure the nonlinear index n_2. All the relevant parameters such as optical power, beam profiles, time delays and interferometry sensitivity can be precisely measured. For non-oxide glasses, n_2 depends on the network former anion and increases within the series F<Cl<Br<I or O<S<Se<Te. In oxides the lowest n_2 are obtained for the silica. Higher nonlinear index results from the introduction of d^0 cations such as Ti^{4+}, Nb^{5+} which is consistent with the bond orbital theory. The largest nonlinear responses are generated by heavy cations having an electronic configuration with ns^2 lone pairs (Te^{4+}, Bi^{3+}, Tl^{+}).

The role of d^0 ions has been investigated by increasing proportions of TiO_2 or Nb_2O_5 in borophosphate glasses [1]. The n_2 values are located between those of silica and of the standard SF 59 (lead silicate Schott glass). The nonlinear behavior has been analyzed in the context of the bond orbital theory previously introduced by Lines for optically transparent transition metal ions. This model allows to conclude to the explicit influence of the empty d orbitals on the intensity of the NLO response. Actually experimental and calculated n_2 are in

fair agreement when the titanium or niobium concentrations remain low. For the richest titanium and niobium glasses larger experimental values than those predicted are measured.
The nonlinear indices of tellurium glasses are approximately 50 to 100 times higher than the n_2 of silica. The origin of the optical nonlinearity in tellurite glasses is attributed to the Lewis $5s^2$ free doublet of tellurium [2]. Both Raman and EXAFS investigations shows that the introduction of additional cations (e.g. Al^{3+}, Nb^{5+}, Tl^{+}) in TeO_2 glass leads to a progressive transformation of disphenoid TeO_4 groups into a TeO_3 trigonal pyramids trough an intermediate TeO_{3+1} asymmetric polyhedron. Theoretically the polarizability of the two first groups can be understood by their molecular diagram analysis. The molecular orbital correlated to the $5s^2$ non-bonding doublet of Lewis governs the polarizability which can be estimated 20% higher for the TeO_4 group than for the TeO_3 one.
The nonlinearity of sulfide glasses is about 100-400 higher than the n_2 obtained for the silica [3]. The results obtained are strongly dependent on the materials optical bandgap located in the visible and near infra-red. Nevertheless, correlation has been established between the glass composition, the entities present and the linear and nonlinear optical properties. In these materials nonlinear absorption has been also clearly evidenced.
Since the observation reported by Myers et al. [4] in 1991v of a second-order nonlinearity of a thermally poled commercial fused silica the mechanism responsible for such phenomena is still discussed. It is generally admitted that the $\chi^{(2)}$ can be due to chemical bonds orientation or due to the creation of frozen - in space charge field. Similar question is also opened for photoinduced second harmonic generation in fibers. As a contribution to tentatively clarify this problem XPS and XANES spectrocopies have been used to characterize cathodic and anodic surfaces of borophosphates glasses before poling and after poling and depoling treatments [5]. An accumulation of Na^{+} cations is clearly evidenced at the cationic surface of the glass after high dc field treatment. Moreover some breakage of the phosphate chains were detected during the poling treatment. Conversely bridging bonds are partly restored after thermal depoling. More recently it was demonstrated that such induced 2^{nd}-order nonlinearity can be erased by a prolonged exposure to IR radiation which obviously opens the possibility to write " active " zone in optical devices.

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