Progresses in Nonlinear Glass Research

Yuiko T. Hayden
Scott Glass Technologies, Inc.
400 York Avenue, Duryea, Pennsylvania 18642

Nonlinearity of glass had not been remarkably large among all the available nonlinear materials. However, its superiority in optical and mechanical properties has attracted much attention for the practical application. To this goal the recent interests in this field have been shifting from the understanding of nonlinear mechanisms to the improvements of nonlinear properties.

I. INTERDUCTION

The nonlinearity of optics has become a familiar terms as the level of available laser power has increased. In the early 1960's, research performed was mostly only theretical.[1-3]. Experimental work started in the late 1960's when the accessible intensity from pulsed lasers reached the multimegawatt level. At that time emphasis was on reducing nonlinear effects to maintain the beam quality of high power glass laser systems.

Advantageous application of nonlinear effects came under considerating with the successful discovery of optical bistability and phase conjugation in the latter 1970's. Today, potential applications for nonlinear materials include: image processing, recognition, correlation, targeting, optical limiting, adaptive optics, all-optical switching, modulation, and optical storage/memory systems etc.[4]

Literally and material could possess nonlinear effects, but to vastly different degrees. Materials with demonstrated nonlinearlity include gases, vapors, polymeric media, liquid crystals, biological systems, organic solutions, water, crystals, and glasses.[5] Among them, the solid state nonlinear materials are particularly attractive for their ease in handling.

Inorganic crystals and organic polymers are knwon for their large nonlinear effects. Their problems for practical application are, for example, cost, optical quality, and damage threshold etc. Glasses overcome these problems, but the magnitude of their nonlinear effects are, by comparision, not quite as large.

This paper reviews recent progresses in nonlinear glass research, with special emphasis on the improvements of the nonlinearity to reach the practical application. Most of the nonlinear examples discussed here are a results of the third order susceptibility, $\chi^{(3)}$ value, since glassay materials are in general isotropic and lack non-centrosymmetric structure, which is essential for the manifestation of $\chi^{(2)}$ processes.

II. HOMOGENEOUS GLASSES

2.1. Estimation of Nonlinear Index

Optical glass with a high linear refractive index usually has a high nonlinear refractive index and the nonlinearity of this type glass is attributed to non-resonance type electronic origin. Search for the empirical relationship between linear and nonlinear refractive indices has begun in 1970[6-8] and the equation widely accepted today is

$$n_2(10^{-13}\ \text{eus}) = \frac{68\ (n_d-1)\ (n_d^2+2)^2}{V_d\left[1.5+\frac{(n_d^2+2)(n_d+1)V_d}{6n_d}\right]^{1/2}} \qquad (1)$$

where V_d is the Abbe number at helium d line, n_2 and n_d are nonlinear and linear refractive indices respectively.

Actual measurement of nonlinear refractive index started in the 1970's using laser materials[10,11]. Weber et al[12] utilized time-resolved interferometry in order to obtain nonlinear indices for optical glasses and crystals at 1064 cm. Their work and studies by other groups[13,14] have proven the validity of the above empirical equation.

2.2. Ultrafast Photonic Switching

High index glasses were recently evaluated, for the real application, as a ultrafast photonic switching material[15-17]. Friberg and Smith[15] defined a figure of merit of material for this purpose as below.

$$F=\frac{n_2 C_p \rho}{a.\tau.\ dn/dT} \tag{2}$$

where dn is the index change induced by a temperature change dT, Cp is the specific heat, ρ is the density of material, α is the absorption coefficient of materials, and τ is the duration of the switching pulse. The defined figure of merit is expressed as the ratio of fast index change required to produce switching over resultant thermal index change. Value of F is a rough indication of the number of switching operations during the materials's thermal lifetime.

They calculatd the above defined F values for representative nonlinear materials; GaAs, GaAs/GaAlAs multiple quantum well, an organic molecule PTS, semiconductor doped glasses, and SF-59. The result indicates that Schott SF-59 glass has the largest F than any other materials examined here, despite its nonlinear effect itself is the smallest. This result confirms that conditions to satisfy good optical properties, such as low absorptions and thermal stability, play significant roles in practical application.

In relation to this application, higher index glasses were also investigated for non-commercial composition. Such experimental compositions include high content of lead and bismuth oxides[18,19] and titanium and niobium oxidexs[19-22]. The degree of nonlinearity in these glasses would be useful when laser output becomes higher in the near future[23].

The efforts to fabricate, fibers and waveguides with these nonlinear glasses[24-26] brought out successful observation of special soliton[27,28] as well as newly discovered problems; two-photon absorption[28-30] and absorption by color center which mimics two-photon absorption[31]. both phnomena could place a fundamental limitation on waveguide all-optical switching devices, thus, Mizrahi et al.[29] formulted the criterion

$$\frac{2\beta\lambda}{n_2} < 1 \tag{3}$$

where β is a two photon absorption coefficient.

They experimentally evaluated β value for lead glass fiber, using SF-6 as a core and SF-56 as a cladding. The calculated criterion value is 1.4 at 1060 nm, which still violates the set criterion but only at marginal level, compared to the value of 1.3×10^3 at 532 nm. This trend suggests that opration at longer wavelengths may avoid excessive nonlinear absorption. Also DeLong et al. state that the same absorption can still be useful for optical limiting at milliwatt power levels at short wavelengths[31].

2.3. Third Harmonic Generation

Nasu et al.[32-34] have measured the non-resonant part of the third order susceptibility for some chalcognide glasses. Selected compositions are in combination of Ge-As-S-Se. Experimentals were carried out by third harmonic generation (THG) with IR region coherent wavelengths. The highest $\chi^{(3)}$ value is obtained for an As-S-Se composition in the renge of 10^{-11} esu, which is the three orders of magnitude larger than that of silicate type glass and is comparable with those of nonlinear organic compounds. This degree of nonlinear effect is large enough to operate an optical shutter of a semiconductor laser. Current empirical law suggests that high $\chi^{(3)}$ values are obtainable by combining heavy elements as glass constituents.

2.4. Second Harmonic Generation

Although glassy materials are usually centrosymetric, successful observations of second harmonic generation (SHG) have been reported in germania doped optical fibers[35-37]. The phenomenon has not fully understood, yet it is believed that there involves a symmetry-breaking organizational process which gives non-zero $\chi^{(2)}$ necessary for frequency doubling. Since the SHG is

the application which has been denied for glass, developments in this area will lead to new possibilities for nonlinear glasses.

III. HETEROGENEOUS GLASSES

3.1. Semiconductor Doped Glasses

Semiconductor doped glasses are known as colloidally colored, longpass filter glass in the glass industry and they are readily available from filter glass catalogues[38]. The colorants in thes glasses are rendered effective by a secondary heat treatment (striking process) of the initially colorless glass. CdSSe doped glasses present yellow, orange, and red with very steep absorption edge, of which wavelength strongly depend upon the thermal history during the secondary heat treatment, as well as on the characteristics and the concentration of colorants and base glass compositions.

The active research on this material started in the 1980's, at that time Lind and Jain measured nonlinear refractive index for this type glasses by their four-wave mixing experiments[39]. Other measurement techniques reported are direct interferometric method[40] and very simplified degenerate four-wave mixing setup[41] as some examples. Nasu et al[42] demonstrated theoretical calculations for this type of glass compositions.

The active research on this material started in the 1980's, at that time Lind and Jain measured nonlinear refractive inex for this type glasses by their four-wave mixing experimets[39]. Other measurement techniques reported are direct interferometric method[40] and very simplified degenerate four-wave mixing setup[41] as some examples. Nasu et al.[42] demonstrate theoreticl calculations for this type of glasses.

The high nonlinearity in this type glass is now attributed to electronic resonance within semiconductor microcrystallities, which are isolated by insulator, i.e., glass matrix. Two different nonlinear mechanisms have been proposed depending upon microcrystalline particle sizes; band-filling effect for larger particles and quantum confinement effect when particle size is smaller than its Bohr radius. More detaild review for these two mechanisms was given in the previous paper[43]

3.1.1. Ultrafast All-Optical Switching

When semiconductor-doped glasses are evaluated for a ultrafast all-optical switching material, their figure of merit value was not quite as large as those for high index glasses, as discussed in section 2.2. The smallr F value, despite the larger nonlinearity, is caused by high absorption due to the nature of resonance nonlinearity.

Fabrication of semiconductor-doped glass waveguides started in 1986[44,45] Ion-exchange is the effective method to increase refractive index[44-50] and it is applied to both bulk and thin-filmed glass samples. Cotter et al.[51] successfully fabricated fibers from CdSSe-doped glasses, however, the demonstration of complete optical switching was prevented by the saturation of index change near the band gap energyy region.

They recently shifted their attention to the off-resonance regime for photon energies well below the band gap[52]. This is based on their discovery that certain seiconductordoped glasses display substantial refractive nonlinearity (up to 40 times greater than silica) even at 1 μm wavelength. In order to utilize this off-resonance nonlinearity, optical fiber must be prepared with sufficiently long path lengths while controlling microcryystallite size.

3.1.2. Other Semiconductor Dopants

Semiconductor dopants other than CdS and CdSe have been studied in search of higher nonlinearity. These dopants are; Bi_2S_3, PbS, HgSe, In_2Se_3, and AgI[53, 54]. Stegeman et al.[55] presented all-optical switching material figure of merit for this type of glasses and they calculated material figures of merit for several semiconductors and identified ZnTe, CdTe, and GaAs as better materials.

Researchers in University of Arizona[56] reported optical nonlinearity of CdTe quntum dots in glass since CdTe has the largest Bohr radius of any semiconductor successfully grown as quantum dots in glass. Therefore quantum confinement effects can be seen in larger dots making CdTe dots especially sensitive to electric fields.

The next generation of nonlinear optical mateirial project in Japan disclosed[57] of CuCl and CuF doped glasses as new materials, which have, 1000 times larger

light sensitivity than insufficiently slow response time. Ruller et al.[58] are investigating the CuCl doped glasses; metal halides dispersed glasses have been known to show photochromism. This may relate to photodarkening, which has shon to affect the speed of nonlinear response.

Increased nonlinearity is reported by Omi et al.[59] who doped glass with 100 times higher concentration CdSe than that of conventional filter glass. Such high concentration doping became possible by employing low melting glass matrix. Their degenerated four wave mixing experiment showed $\chi^{(3)}$ of such a glass to be in the order of 10^{-6} esu near the resonance.

3.2. Other Types of Heterogeneous Glass

Metallic particles doped glasses[60-65] and organically doped glasses[66-68] are also known as nonlinear materials. The nonlinearity of the former is assigned to the local field effect enhanced near the surface plasma resonance. This type of nonlinear material became even interesting since Neeves and Birnboim[65] showed theoretical calculation for the model composites of nanospheres with a metallic core and nonlinear shell or vice verse. The result indicated possible enhancement in nonlinearity by 10^8 times.

The nonlinearity of the latter type relies on doped organics. This type material takes advantages of high nonlinearity from organic materials and stability and optical quality of glass. When organic compounds are doped into molten glass, low melting glass matrix must be developed[66,67]. Glass-organic compound composites are also being prepared by a solgel method[69]. Organic polymer film on glass substrate[70] is also in progress with electric field to pole polymer molecules for maximum nonlinearity.

IV. CONCLUSIONS

Nonlinearity of glasses has been known for more than a quarter of century. After years of basic research accumulation, the research interests in this field are now apparently focusing on practical application. This review showd the recent advancemments in the area particularly increasing nonlinear effects in various types of glass materials. In several situations the nonlinear effects in glass are being sufficiently large enough to fabricate functional devices.

V. ACKNOWLEDGEMENT

The author would like to thank Dr. J. S. Hayden for many helpful discussions.

REFERENCES

[1] R. Braunstei, Phys. Rev., **125**, 475 (1962).
[2] J. A. Armstron, et al., Phys. Rev., **127**, 1918 (1962).
[3] N. Bloembergen and P. S. Pershan, Phys. Rev., **128**, 606 (1962).
[4] R. W. Bryant, *Nonlinear Optical Materials: New technologies, Applications, Markets,* Business Communications Co. Inc., Norwalk, 1989.
[5] W. L. Smith, *Handbook of Laser Science and Technology,* M. J. Weber Volume III, CRC Press, Boca Rayton, 1986.
[6] C. C. Wang, Phys. Rev., **B2**, 2045 (1970).
[7] J. T. Fournier and E. Snitzer, IEEE J. Quant. Electro., **QE10**, 473 (1974).
[8] N. L. Boling, A. J. Glass and A. Owyoung, IEEE J. Quant. Electro., **QE14**, 601 (1978).
[9] R. Hellwarth, et al., Phys. Rev., **B11**, 964 (1976).
[10] E. S. Bliss, D. R. Speck and W. W. Simmons, Appl. Phys. Lett., **25**, 728 (1974).
[11] M. J. Moran, C-Y She and R. L. Carman, IEEE J. Quant. Electro., **QE11**, 259 (1975).
[12] M. J. Weber, D. Milam and W. L. Smith, Optc. Engi., **17** 463 (1978).
[13] D. Heiman, R. W. Hellwarth and D. S. Hamilton, J. Non-Crys. Solids, **34**, 63 (1979).
[14] L. B. Al'tshuler, U. V. Nazarov, et al. Sov. J. Opt. Technol., **54**, 528 (1987).
[15] S. R. Friberg and P. W. Smith, IEEE J. Quant. Electro., **QE23**, 2089 (1987).
[16] P. W. Smith, SPIE Proc., **881**, 30 (1988).
[17] E. M. Vogel, J. Am. Ceram. Soc., **72**, 719 (1989).
[18] D. W. Hall, M. A. Newhouse, N. F. Borreli, et al. Appl. Phys. Lett., **54**, 1293 (1989).
[19] Mir Akbar Ali and R. L. Ohlhaber Glass Tech., **26**, 186 (1985).
[20] N. F. Borreli, et al., SPIE Proc., **1128**, 246 (1989).
[21] E. M. Vogel, S. G. Kosinski, D. M. Krol, et al.,

J. Non-Crys. Solids, **107**, 244 (1989).
[22] E. M. Vogel, et al. Mat. Res. Soc. Symp. Proc., **152**, 83 (1989).
[23] E. M. Vogel et al., Presented at Am. Ceram. Soc., Electronic Div. Meeting, Orland FL. Nov, 1990.
[24] E. R. Taylor, et al., presented at Mat. Res. Soc., Fall Meeting, 1989.
[25] E. M. Vogel, S. R. Friberg, J. L. Jackel and P. W. Smith, Mat. Res. Soc. Symp. Proc., **88**, 101 (1987).
[26] E M. Vogel, E. W. Chase, J. L. Jackel and B. J. Wilkens, Appl. Optc., **28**, 649 (1989).
[27] J. L. Jackel, E. M. Vogel and J. S. Aitchison, Appl. Optc., **29(21), 3126 (1990).**
[28] J. S. Aitchison, et al., Optc. Lett., **15**(9)U, 471 (1990).
[29] V. Mizrahi, K. W. DeLong, G. I. Stegeman, et al., Opt. Lett., **14**, 1140 (1989).
[30] Y. Silberberg Opt. Lett., **15**(18), 1005 (1990).
[31] K. W. DeLong, et al., Appl. Phys. Lett., **56**(15), 1394 (1990).
[32] H. Nasu, Y. Ibara and K. Kubodera, J. Non-Crys. Solids, **110**, 229 (1989).
[33] H. Nasu, New Glass, **4**(4), 13 (1990).
[34] H. Nasu et al., J. Am. Cer. Soc., **73**(6), 1794 (1990).
[35] U. Osterberg and W. Margulis, Opt. Lett., **12**, 57 (1987).
[36] R. H. Syolen and H. W. K. Tom, Opt. Lett., **12**, 585 (1987).
[37] J. K. Lucek et al., J. Modern Opt., **37**(4), 533 (1990).
[38] Schott optical filter glass catalog.
[39] R. K. Jain and R. C. Lind, J. Opt. Soc. Am., **73**, 647 (1983).
[40] G. R. Olbright and N. Peyghambarian, Appl. Phys. Lett., **48**, 1184 (1986).
[41] P. Horan, et al. Appl. Opt., **29** 31 (1990).
[42] H. Nasu and J. D. Machenzie Opt. Engi., **26**, 102 (1987).
[43] Y. T. Hayden and A. J. Marker, SPIE Proc., **1327**, 132 (1990).
[44] T. J. Cullen, C. N. Ironside, C. T. Seaton and G. I. Stegeman, Appl. PHys. Lett., **49**, 1403 (1986).
[45] P. Sergiusz, H. Jerominek, et al. J. Appl. Phys. **60**(5), 1591 (1986).
[46] H. Jerominek, et al., J. Appl. Phys., **63**(3), 957 (1988).
[47] A. Gabel, K. W. Delong, C. t. Seaton and G. I. Stegeman, Appl. Phys. Lett., **51**(21), 1682 (1987).
[48] C. N Ironside, W. C. Banyai, et al., J. Opt. Soc. Am., **B5**, 492 (1988).
[49] N. Finlaysonn, et al. J. Opt. Soc. Am., **B6**, 675 (1989).
[50] W. C. Banyai et al. Appl. Phys. Lett., **54**(6), 481 (1989).
[51] D. Cotter, et al., Opt. Lett., **14**, 317 (1989).
[52] D. Cotter, et al., to be presented at CLEO, May 1991.
[53] T. Rajh, et al., Chem. Phys. Lett., **143**, 305 (1988).
[54] L. Weigo, et al., J. Non-Cryst. Solids, **95&96**, 601 (1987).
[55] G. I. Stegeman, et al., New Glass Forum, Tokyo, 1989.
[56] V. Escher, et al., Phys. Rev., **B42**(12), 7450 (1990).
[57] Japan New Mat. Rep., **V**(2), 4 (1990).
[58] J. A. Ruller, et al., SPIE Proc., **1327**, 125 (1990).
[59] S. Omi, et al., to be presented at CLEO, May, 1991.
[60] D. Ricard, P. Roussignol and C. Flytzanis, Opt. Lett., **10**, 511 (1985).
[61] F. Hache, D. Ricard and C. Flytzanis, J. Opt. Soc. Am., **B3**, 1647 (1986).
[62] P. Roussignol, F. Hache, D. Ricard and C. Flytzanis, SPIE Proc., **1128**, 238 (1989).
[63] M. Bertolotti, et al., SPIE Proc., **1128**, 252 (1989).
[64] J. W. Haus et al., J. Opt. Soc. Am., **B6**, 797 (1989).
[65] A. E. Neeves and M. H. Birnboim, J. Opt. Soc. Am., **B6**, 787 (1989).
[66] W. R. Tompkin, R. W. Boyd, D. W. Hall and P. A. Tick, J. Opt. Soc. Am., **B4**, 1030 (1987).
[67] P. A. Tick and D. W. Hall, Diffusion and Defect Data, **53-54**, 179 (1987).
[68] C. Capozzi, Alfred University, Private communication.
[69] P. N. Prasad, SPIE Proc., **1328**, (1990).
[70] S. Yitzchaik, et al., Opt. Lett., **15**(20) 1120 (1990).