<u>**Optical and Photonic Glasses**</u>

Lecture 37:

Non-Linear Optical Glasses I - Fundamentals

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Non-linear optical glasses

Photonic devices like all-optical switches and modulators are examples of non-linear optic (NLO) devices which find application in optical communications or optical computing.

Optical non-linearities in glass materials may be divided into the main categories of resonant and non-resonant. *Non-resonant NLO* glasses are, e.g., high refractive index / high dispersion glasses like heavy flint optical glasses, or heavy metal oxide glasses, or chalcogenide glasses. *Resonant NLO* glasses include semiconductor or metal particle doped glasses.

Stimulated emission (or stimulated Raman scattering) is also an example of NLO behavior, which was treated separately before, when dealing with glasses for lasers and amplifiers.

NLO fundamentals

An optical non-linearity is a deviation from the linear relationship between a material's polarization response and the electric component of an applied electromagnetic field. Considering a non-magnetic medium ($\mu \sim \mu_o$) where the velocity of light is v, $n = (\varepsilon/\varepsilon_o)^{1/2} = c/v$ and the linear polarization is:

$$P = \varepsilon_o \chi E$$

where χ is the electric susceptibility (and $\varepsilon_o\chi$ is the polarizability per unit volume), such that:

$$\varepsilon = \varepsilon_o (1 + \chi)$$

$$n = (1 + \chi)^{1/2}$$

In the transparency region of a dielectric isotropic material (with no permanent electric dipoles) like most glasses, between the ionic (vibrational) and the electronic excitation processes, the light frequency is too high for the ionic polarizability to follow the electromagnetic field oscillations and too low to resonate with the electronic excitations. However, electronic transitions may still take place through multiphoton processes; e.g., the probability of *two-photon* absorption will increase proportionally to the *square* of the electromagnetic field intensity.

The intensity dependence of the absorption and the refractive index (corresponding to the *non-linear refractive index*) of the material is a NLO process.

Another type of NLO behavior is observed in anisotropic materials that have permanent electric dipoles, such as non-centrosymmetric crystals and unlike glasses.

In general, unless the motion of the charged particles in a dielectric medium is very small, the electric polarization (or dipole moment per unit volume) is given as a power series of E:

$$P = \varepsilon_o \chi^{(1)} E + \varepsilon_o \chi^{(2)} E^2 + \varepsilon_o \chi^{(3)} E^3 + \dots$$

with $\chi^{(2)}$, $\chi^{(3)}$, … being the non-linear electric susceptibilities of the medium.

If the alternating electric field of light is given by $E = E_o \exp(i\omega t)$, the second order term will give a polarization which varies with 2ω, enabling the phenomenon of Second Harmonic Generation (SHG), or *frequency doubling*, while the third order term will give rise to *frequency tripled* light, called third harmonic generation (THG).

In a centrosymmetric material, opposite directions about the inversion center are equivalent, so the polarization must change sign when the optical electric field is reversed, which implies that $\chi^{(2)}$ must be zero. Although **glass** is **not centrosymmetric**, it is **isotropic** and thus $\chi^{(2)} \sim 0$. Only $\chi^{(3)}$ is $\neq 0$ and may lead to NLO behavior in glass.

The second order, third order, etc., terms of the electric polarization only become significant under high intensity light such as that available from laser sources and the values of $\chi^{(n)}$ usually decrease rapidly as n increases. However, for centrosymmetric materials, or isotropic materials like glass, $\chi^{(2)} = 0$ and then only $\chi^{(3)}$ is significant.

The intensity dependent refractive index is generally given as:

$$n = n_o + n_1 E + n_2 E^2$$

where n_o is the linear refractive index, n_1 is the Pockel's coefficient (assumed negligible for glass, which is isotropic) and n_2 is the so called *non-linear refractive index* or Kerr coefficient (from the optical Kerr effect). Since the intensity of the electric field of the light is equal to the square of its amplitude, one can also write:

$$n = n_o + n_2'' I$$

In electrostatic units, one also has:

$$n_2 = 12 \pi \chi^{(3)} / n_o \quad (\text{or } n_2'' = \chi^{(3)} / (\varepsilon_o c n_o^2))$$

The dominant non-linearity, in this case, is at a frequency well below the glass bandgap and this effect is called *non-resonant*.

Nonlinear refractive indices and nonlinear susceptibilities of optical glasses and special glasses for laser systems

Glass type	Refractive index n	Nonlinear refractive index n_2 (10^{-13} esu)	n_2'' (10^{-16} cm^2/W)	Nonlinear susceptibility $\lvert\chi^{(3)}\rvert$ (10^{-13} esu)
Optical glass				
Fused silica	1.456(d) [34], 1.458(D) [51] (d) [35] 1.452(d) [53]	0.99 [34], 0.95* [35, 41, 51], 0.85* [54]	2.73* [51]	0.28 [44, 59, 60]
FK 6	1.446(d) [34]	1.13 [34]		
BK 7 (borosilicate)	1.517(d) [34] (D) [51]	1.46 [34], 1.24* [35, 51], 1.30* [54]	3.43* [51]	
SF 7 (PbO-silicate)	1.640(d) [34]	5.83 [34]		
LaK-3	1.694(d) [34]	2.57 [34]		
LaSF 7	1.914(d) [34], 1.85(d) [58]	6.20 [34]		0.45 [58]
FK 5 (fluorosilicate)	1.487(D) [51] (d) [35]	1.07* [35, 51]	3.01* [51]	
FK 51 (fluorosilicate)	1.487(D) [51]	0.69* [35, 51]	1.94* [51]	
SF 59 (PbO-silicate)	1.953(d) [53, 56], 1.91* [55, 57] 1.97 [61], 1.917 [53]		68* [55], 32 [57], 67.6 [62] 90 [61]	0.78# [53] 1.11# [53], 0.75 [56, 57], 0.66 [58]
SF 57 (PbO-silicate)	1.8467(d) [53], 1.81* [55]		41* [55]	0.51# [53], 0.225 [58]
SF 6 (PbO-silicate)	1.8052(d) [53, 56], 1.77* [57]	8.0* [54]	22* [57]	0.45# [53], 0.44 [56, 57], 0.165 [58]
FD 60 (PbO-silicate)	1.8052(d) [53], 1.77* [55]		20* [55]	0.42# 53
LaSF 30	1.8032(d) [53]			0.12# [53]
SF 58	1.917(d) [56], 1.88* [55, 57]		49* [55], 23 [57]	0.52 [56, 57], 0.495 [58]
SF 56	1.75* [55]		26* [55]	
FDS-9	1.81* [55]		12* [55]	
FD6	1.77* [55]		31* [55]	
FDS 90	1.81* [55]		22* [55]	
8463 (Corning)	1.94 [57], 1.97(D) [58]		42* [57]	1.00 [57], 0.825 [58]
Special Oxide glass				
FR 5 (Tb_2O_3-aluminosilicate)	1.686(D) [51], 1.678* [52]	2.1* [35, 51], 1.93* [54]	5.2* [51]	
FR-4 (Ce_2O_3-phosphate)	1.556* [52]	1.95* [52]		

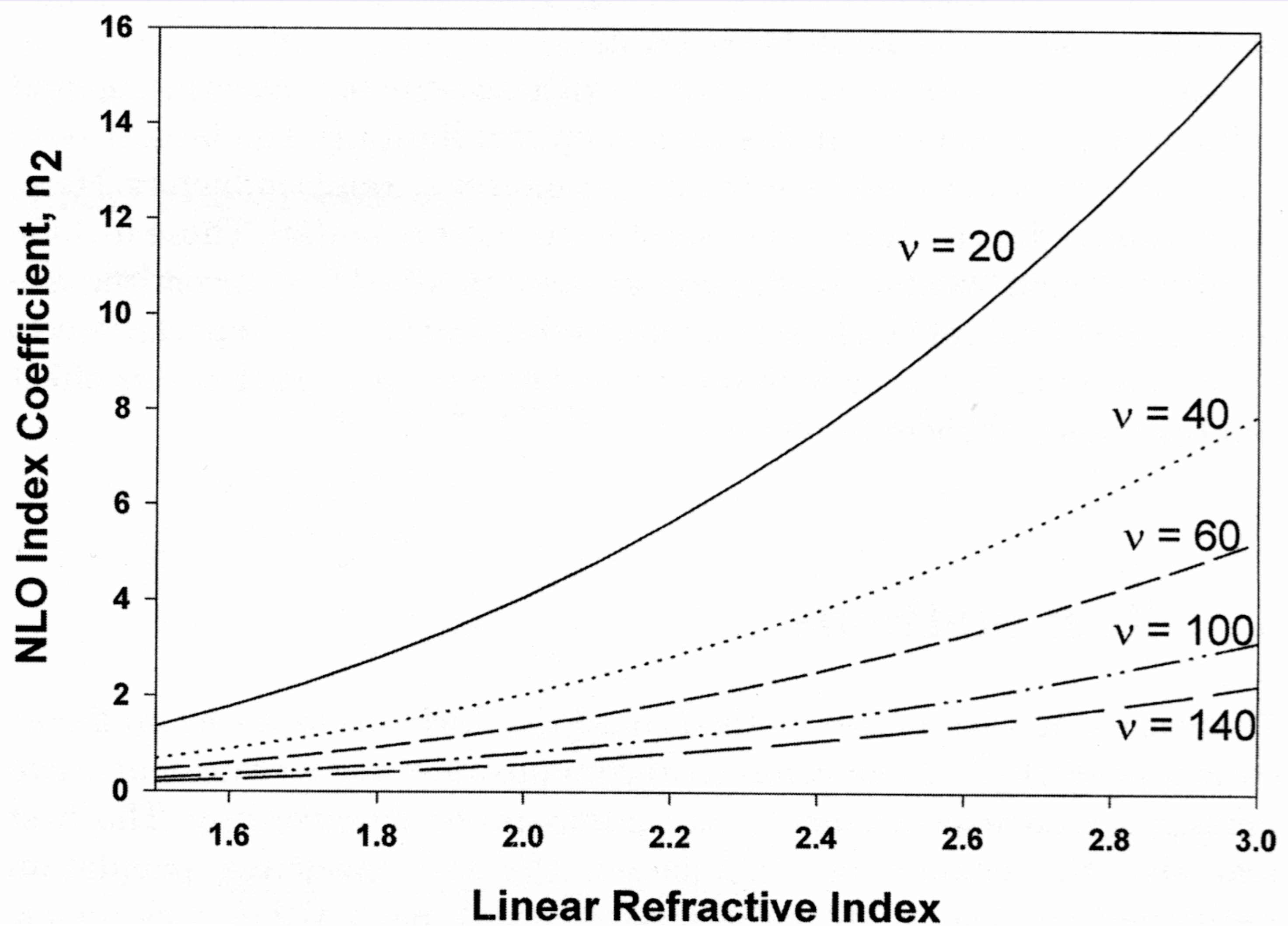
(d): d line; (D): D line; *: 1.06 μm; #: 0.65 μm.

(Adapted from: *Glasses for photonics*, M. Yamane and Y. Asahara, Cambridge Univ. Press, 2000)

It is interesting to note that n_o and n_2 are usually directly correlated, such that low index (n_o) glasses, like certain fluorides and phosphates, have also low n_2 and are usually important for high power applications like amplifiers in inertia confined fusion experiments, to minimize self-focusing and local damage to the optical glass.

On the other hand, for all-optical signal processing and switching devices, glasses with large n_o (thus large n_2) are desirable, including heavy flint optical glasses with high index and high dispersion.

ChG's appear to have the largest non-resonant third order optical non-linearities reported to date.



Variation in NLO index coefficient (in pico-esu) as a function of linear index and Abbe number, according to Eq. (7.61) (Boling, Glass, and Owyoung 1978).

(Adapted from: *Optical Materials*, J.H. Simmons and K.S. Potter, Academic Press, 2000)

Nonlinear refractive indices of chalcogenide glasses

Glass type	Refractive index (λ, μm)	Nonlinear refractive index n_2'' (10^{-16} cm^2/W)	Nonlinear susceptibility $\lvert\chi^{(3)}\rvert$ (10^{-13} esu)	Nonlinear susceptibility $\lvert\chi^{(3)}_{1111}\rvert$ (10^{-13} esu)	Measurement (λ, μm)	Ref.
As_2S_3			14.8 (0.635)		DFWM	80
			22		THG (1.9)	80
	2.48 (1.06)			17.4	DFWM (1.06)	57
	2.53 (2)		72		THG (2)	81
	2.4 (1.06)	1400			Z (1.06)	82
			100		THG (1.9)	70
		420	120		KE (1.303)	83
	2.38	40 (1.3)				88
GeS_3			10		THG (1.9)	80
GeS_2-$10Tl_2S$			7		THG (1.9)	80
$90As_2S_3$ 10I			3		THG (1.9)	80
Ge S(NOG 1)	2.05 (1.9)		20		THG (1.9)	81
Ge–As S(NOG 2)	2.22 (1.9)		37		THG (1.9)	81
Ge–As S(NOG 3)	2.35 (1.9)		46		THG (1.9)	81
Ge As–S Se(NOG 4)	2.36 (1.9)		70		THG (1.9)	81
As–S Se(NOG 5)	2.55 (2.0)		141		THG (2)	81
As S Se	~2.47 (10.6)	~175 (1.55)				88
$Ag_2As_{39}S_{59}$	2.43 (1.06)	1.02×10^5			Z (1.06)	82
VA(La_2S_3 Ga_2S_3)	2.50			220 (0.6), 7.9 (1.25)		65
ACN(GeS_2–Ga_2S_3 BaS)	2.22			190 (0.6), 2.2 (1.25)		65
XT(GeS_2 Ga_2S_3)	2.19			300 (0.6), 2.7 (1.25)		65
$As_{40}S_{57}Se_3$	2.5 (0.656)		140		THG (1.9 ~ 2.2)	70, 85, 87
Na_2S GeS_2	2.03 ~ 2.08 (1.9)		~50		THG (1.9)	84
(PbS, Ag_2S, Na_2S) La_2S_3 Ga_2S_3	2.13 ~ 2.41 (0.633)		11.1 ~ 32.4		THG (1.9)	86
Ge As Se Te	2.50 (10.6)	140 (1.3)				88
Ge–As S Se	2.41 (10.6)	35 (1.55)				88
As–Se–Sb Sn	2.80 (10.6)	150 (1.33)				88
Ge–Sb Se	2.60 (10.6)	80 (1.3)				88
Ges_2 Ga_2S_3 CsI Ag_2S	1.99 ~ 2.16 (0.633)	165 ~ 750			Z (0.705)	89
As_2S_3		250			Z (1.00)	90
$GeSe_4$		800			Z (1.06)	90
$Ge_{10}As_{10}Se_{80}$		1020			Z (1.06)	90

THG, third harmonic generation; DFWM, degenerate four-wave mixing; Z, z scan; KE, optical Kerr effect.

(Adapted from: Glasses for photonics, M. Yamane and Y. Asahara, Cambridge Univ. Press, 2000)

If a complex non-linear susceptibility is introduced:

$$\chi^{(3)} = \text{Re}\,\chi^{(3)} - i\,\text{Im}\,\chi^{(3)}$$

the imaginary part of $\chi^{(3)}$ contributes to a change in the absorption coefficient, such that α becomes a function of the light intensity:

$$\alpha = \alpha_o + \beta I$$

where β is the non-linear absorption coefficient:

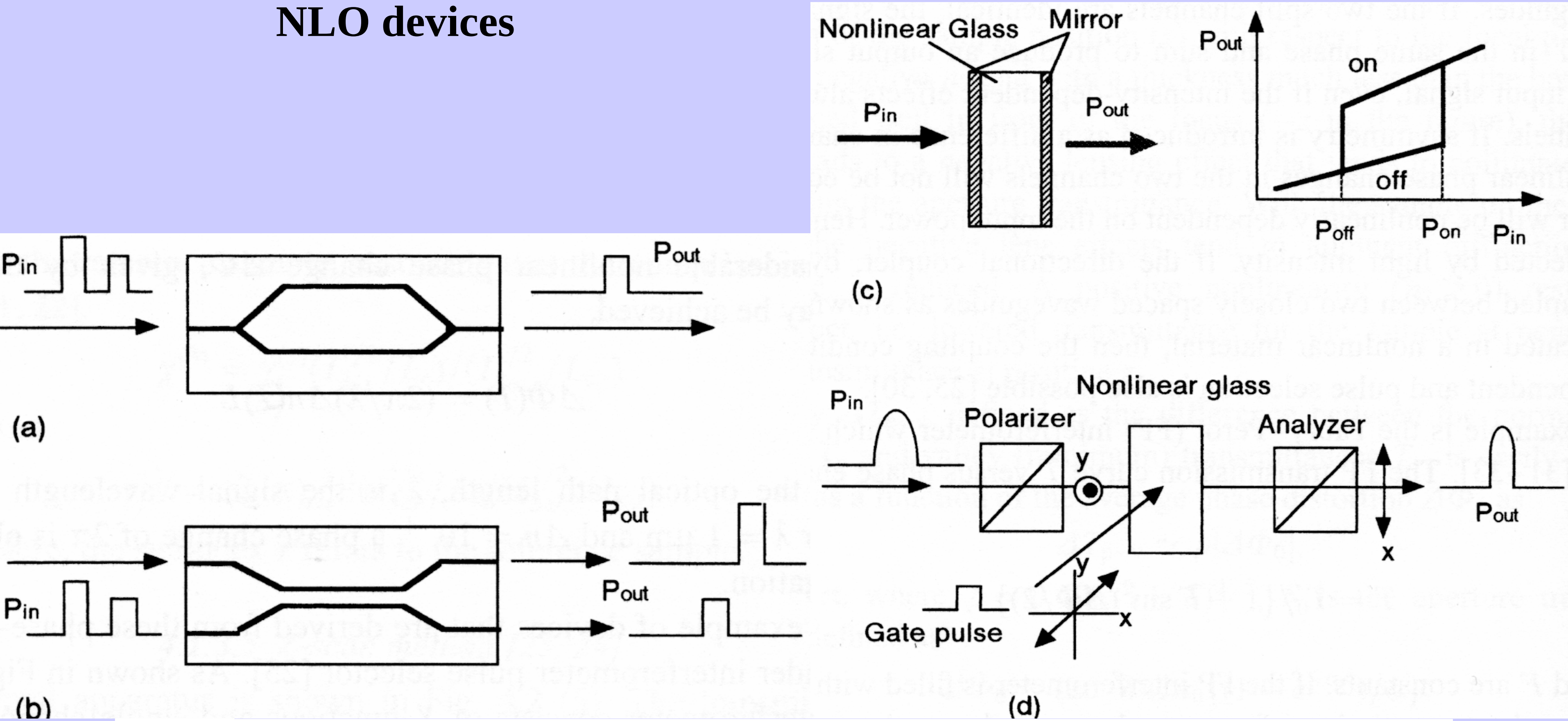
$$\beta = (32\,\pi^2\,\omega / c^2\,n_o{}^2)\,\text{Im}\,\chi^{(3)}$$

In this case, non-linearities are predominantly at frequencies above the electronic absorption edge and are thus called *resonant*.

The values of $\chi^{(3)}$ are usually measured by degenerate four-wave mixing (DFWM), by the Maker fringe method (THG method), or by the Z-scan method.

The third order non-linearity ($\chi^{(3)}$) may be explored in phase conjugate mirrors, in Mach-Zehnder interferometer pulse selectors or in Fabry-Perot interferometers filled with a non-linear medium. The optical Kerr effect can also be used in optical switches.

NLO devices



Standard nonlinear optical devices and their response to optical power, (a) Mach–Zehnder interferometer – pulse selector. (b) Nonlinear directional coupler. (c) Fabry–Pérot interferometer – bistable switching and (d) Optical Kerr shutter.

(Adapted from: *Glasses for photonics*, M. Yamane and Y. Asahara, Cambridge Univ. Press, 1960)

Non-linear response time

The measured response times of non-resonant NLO glasses have been measured between 100 fs and 1 ps.

The main practical application of non-resonant glasses is in ultra-fast all-optical switches, e.g., ChG fiber switches.

Nonlinear response times of nonresonant glass materials

Glass	λ (nm)	$\chi^{(3)}$ (esu)	n_2'' (cm^2/W)	τ (ps)	Ref.
SF59	650	$2.6 \sim 3.7 \times 10^{-14}$		0.17	53
SF59	1060		7×10^{-15}	1	55
As_2S_3	1319	1.2×10^{-11}	4.2×10^{-14}	5	83
As_2S_3	1552		2×10^{-14}	0.1	92
Bi_2O_3 Glass	810	$5.8 \sim 9.3 \times 10^{-12}$		0.2	70
$As_{20}S_{80}$	810			0.2	87

(Adapted from: *Glasses for photonics*, M. Yamane and Y. Asahara, Cambridge Univ. Press, 2000)