Metal-oxides borate glasses doped with Nd^{3+} for photonic applications

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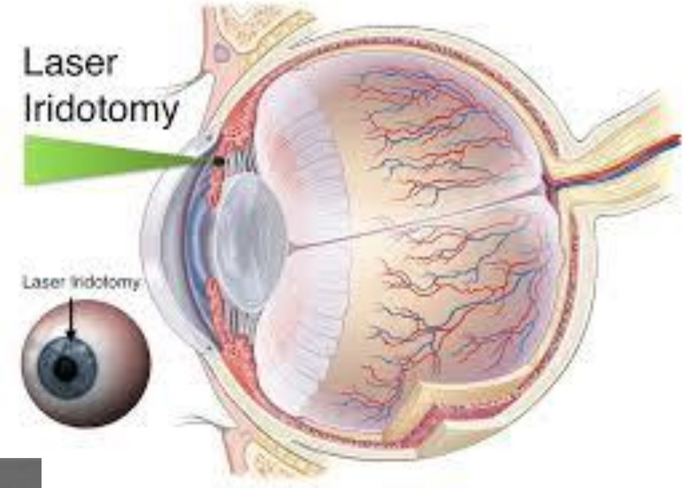
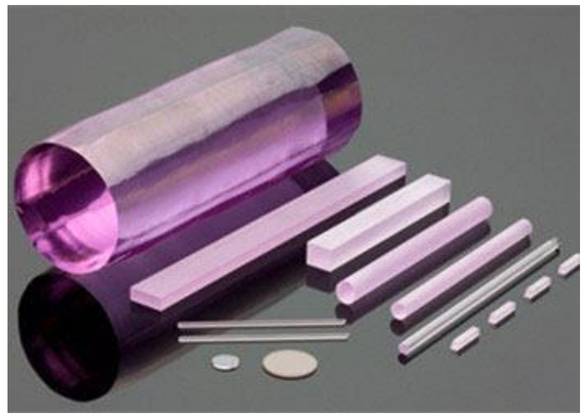
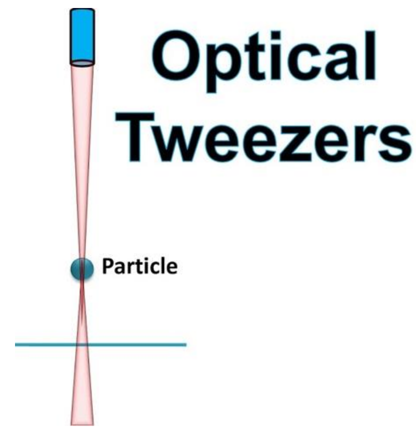
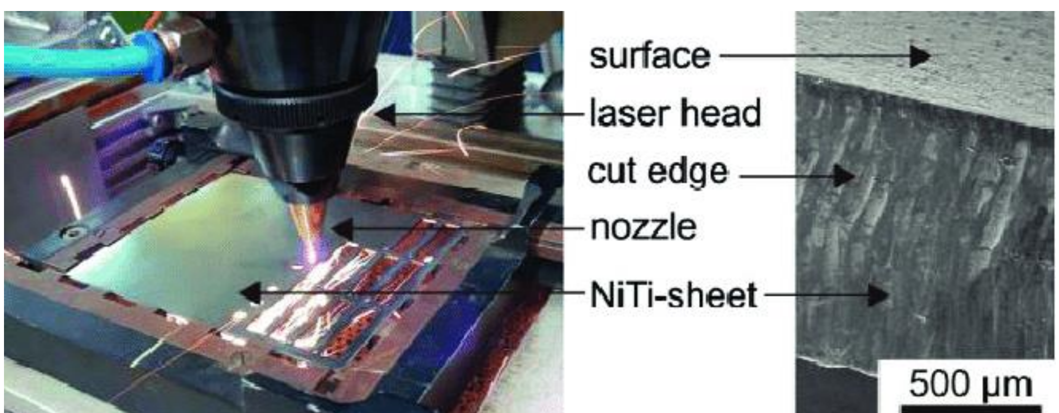


Nd:YAG laser



$Nd:Y_3Al_5O_{12}$





Aluminium garnet compound family

$Y_3Al_5O_{12}$ (YAG) : 1960s

↓

$Lu_3Al_5O_{12}$ (LuAG) : 1990s

↓

↓

↓

$A_3(B,C)_5O_{12}$: Until present

Possible A element = Y, Lu, Gd or mixing between them

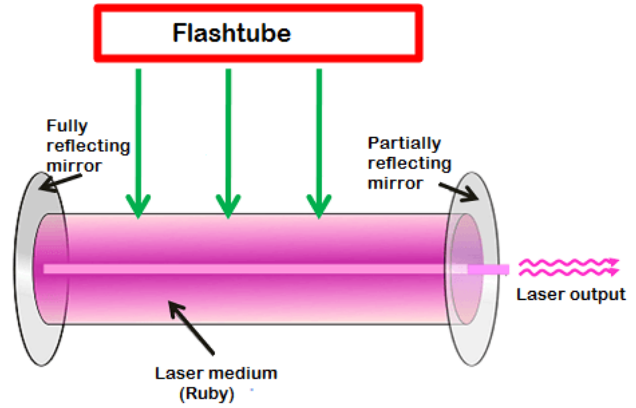
Possible B & C element = Al, Ga or mixing between them

Multi-component garnet

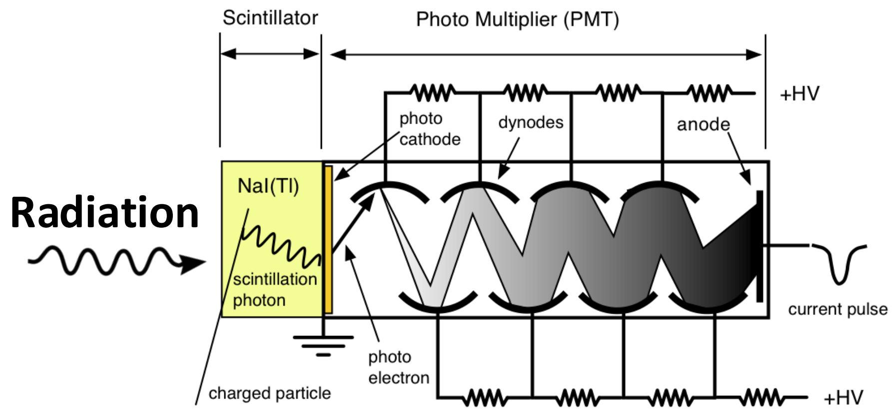
Ion	Ionic radius (Å)
Y^{3+}	0.900
Lu^{3+}	0.977
Gd^{3+}	1.053
Al^{3+}	0.535
Ga^{3+}	0.620

Aluminium garnet compound family

$Y_3Al_5O_{12}$ (YAG) : 1960s



$Lu_3Al_5O_{12}$ (LuAG) : 1990s



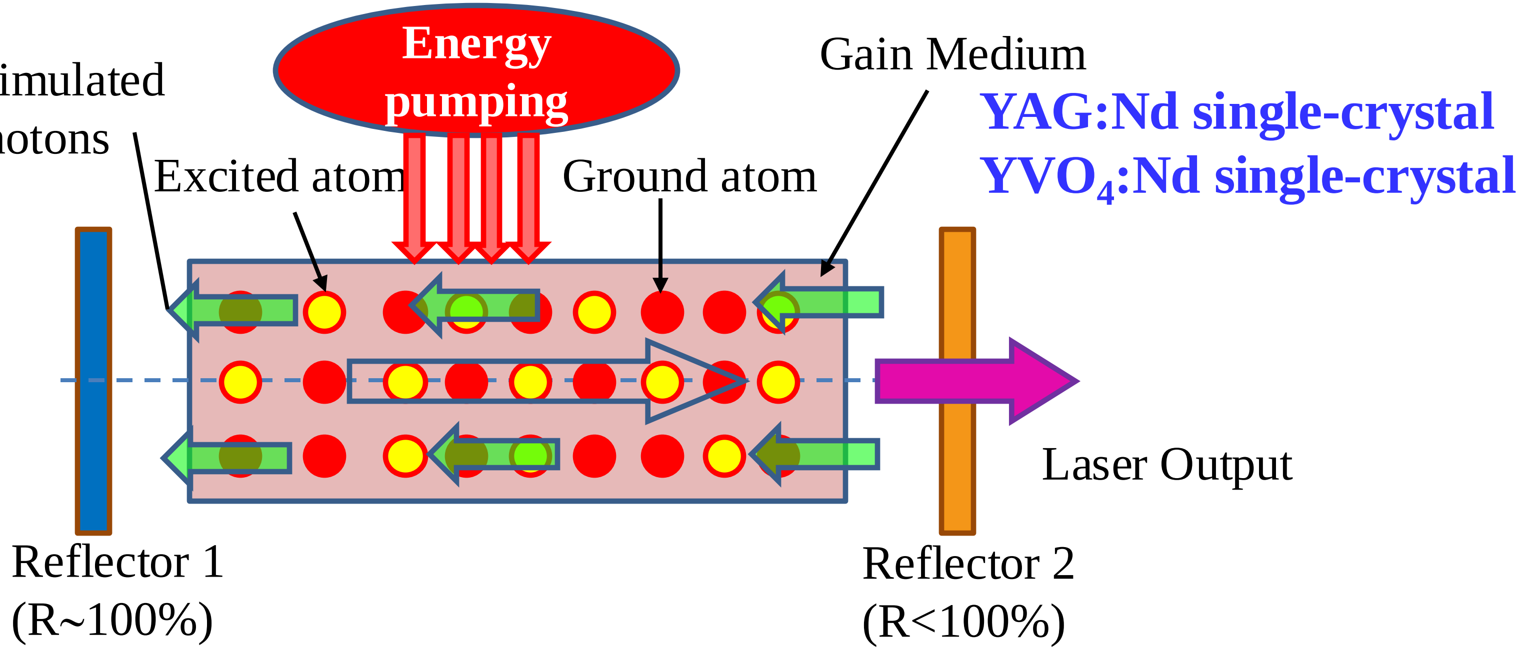
$A_3(B,C)_5O_{12}$: Until present

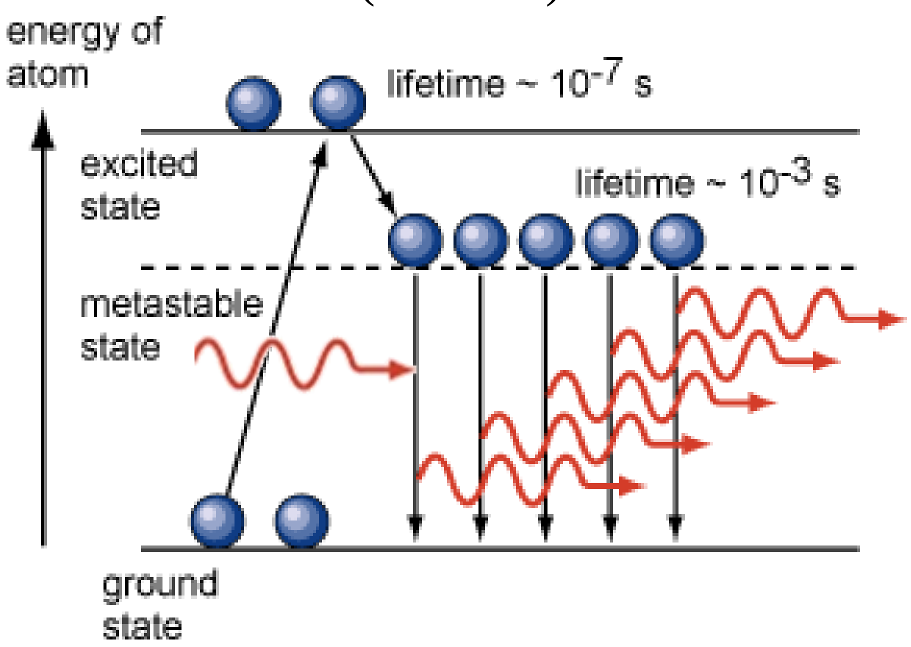
Possible A element = Y, Lu, Gd or mixing between them

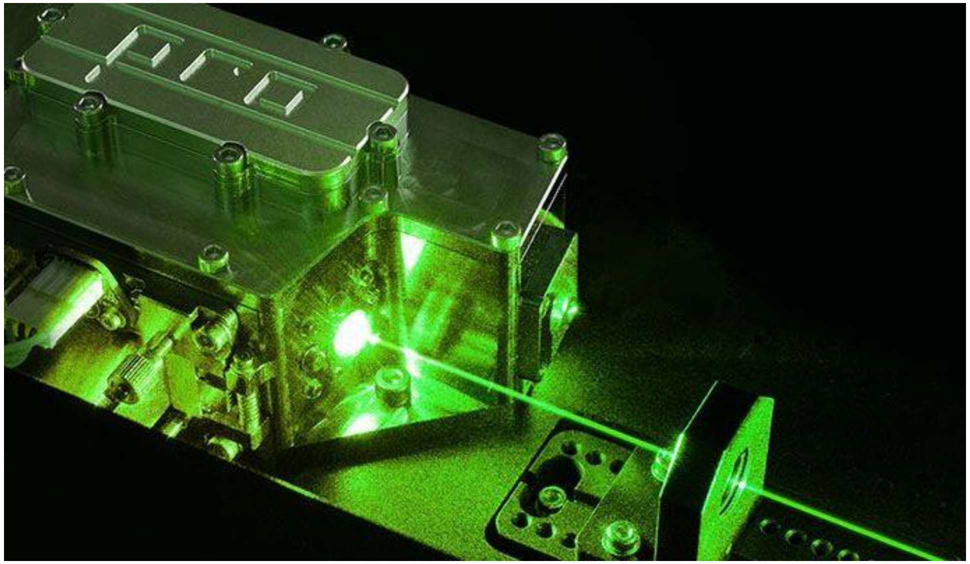
Possible B & C element = Al, Ga or mixing between them

Doped with Nd^{3+} → Strong luminescence for laser / photonic

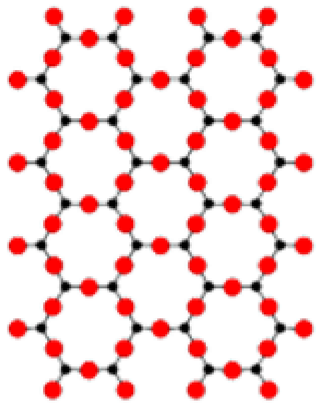
Light Amplification by Stimulated Emission of Radiation







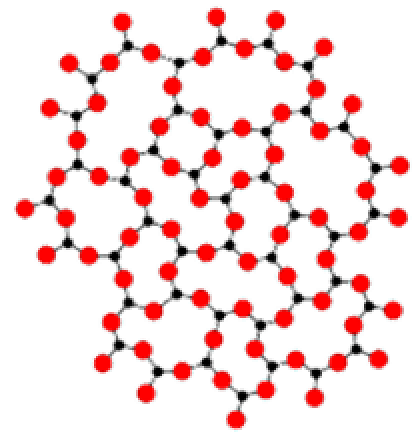
Bulk material



Crystalline A_2O_3

Convert

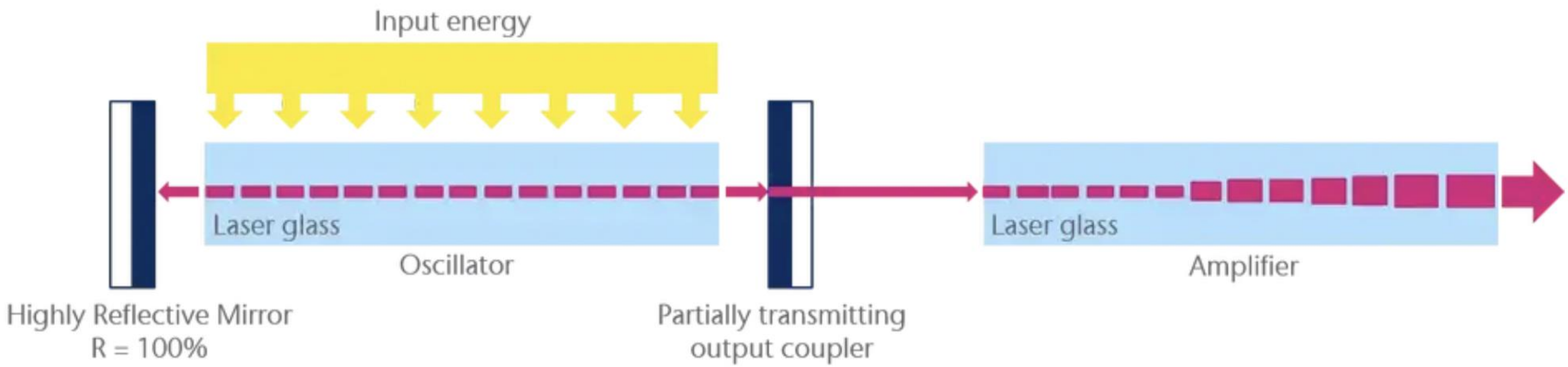
using base chemicals



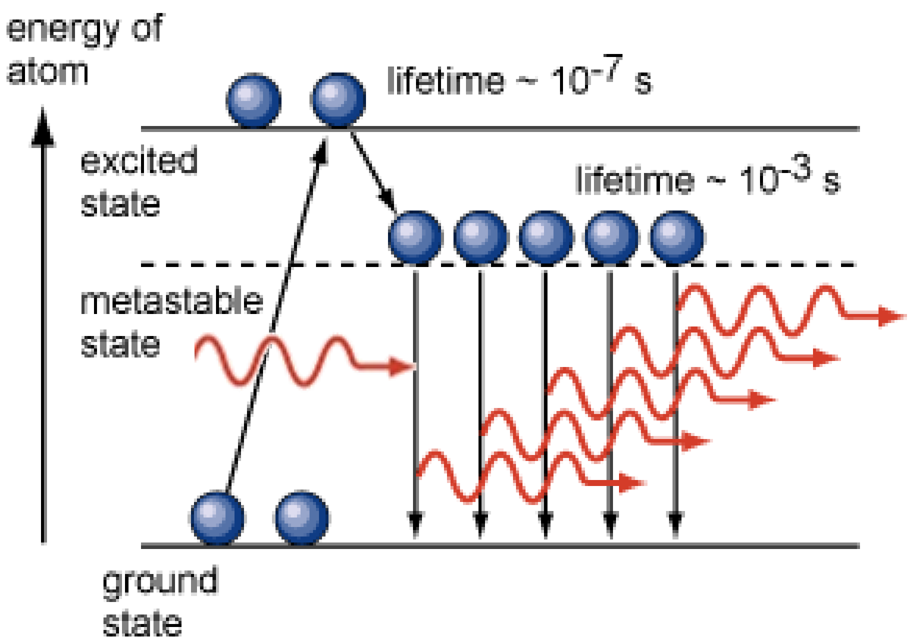
Glassy A_2O_3

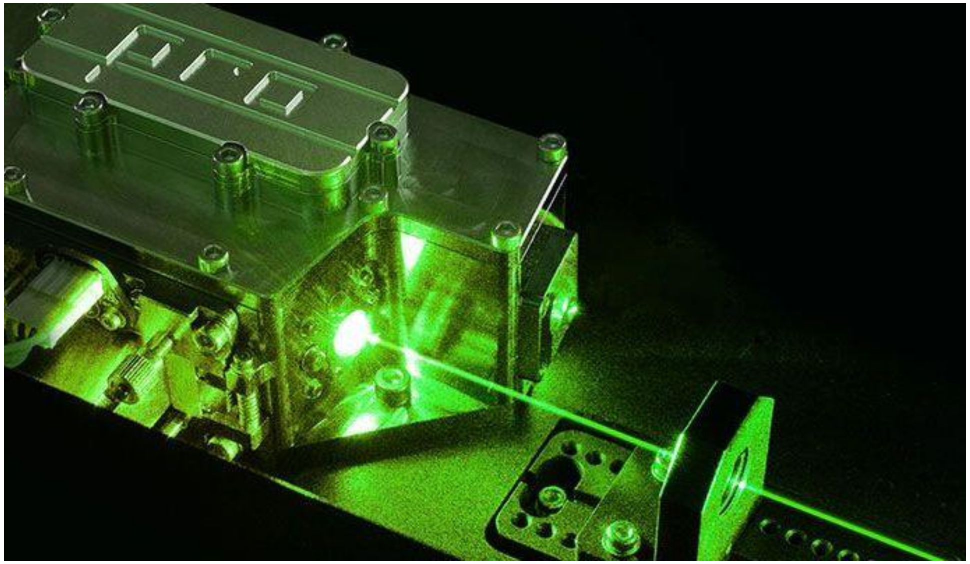
Single-crystal	Glass
Crystalline structure	**Amorphous** structure
Obvious electronic bandgap	**Unclear** electronic bandgap
Difficult for preparation	**Easy** for preparation
Can prepare in **limited size** and **shape**	Can prepare in **various sizes** and **shapes** with same properties
Chemical ratio is strict and **fixed**	**Wide range** of chemical ratio
High production cost	**Low** production cost

Light Amplification by Stimulated Emission of Radiation



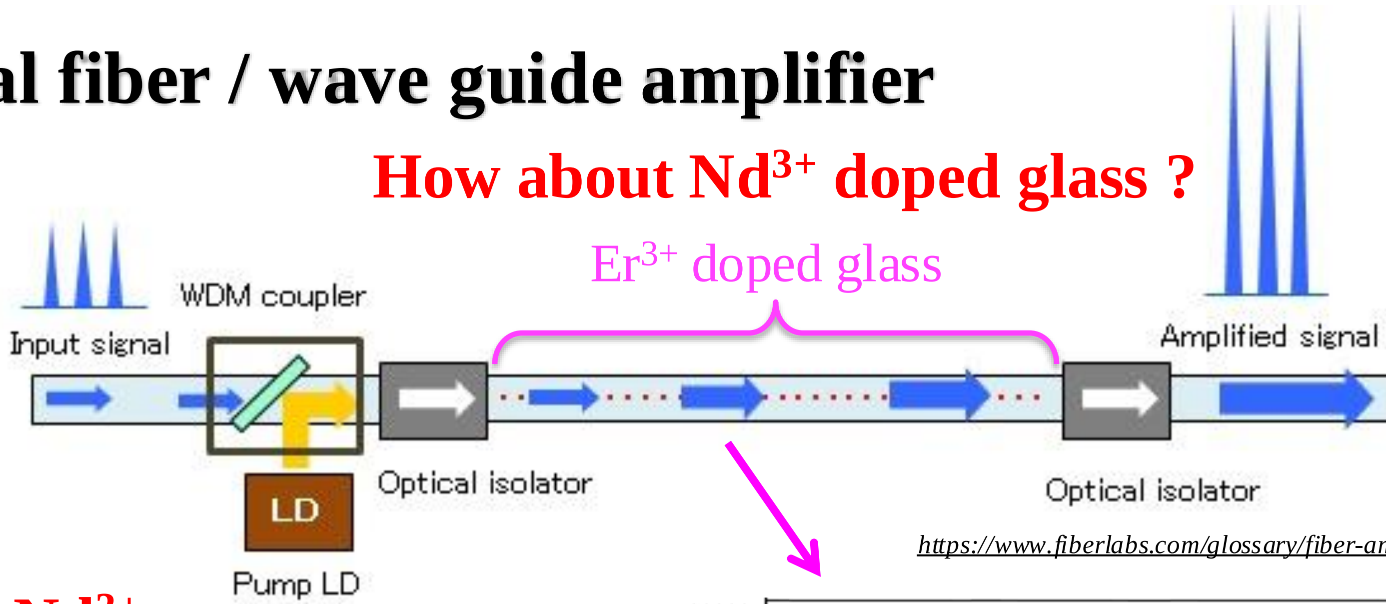
https://www.schott.com/en-gb/solutions-magazine/edition-1-2022/from-light-to-laser



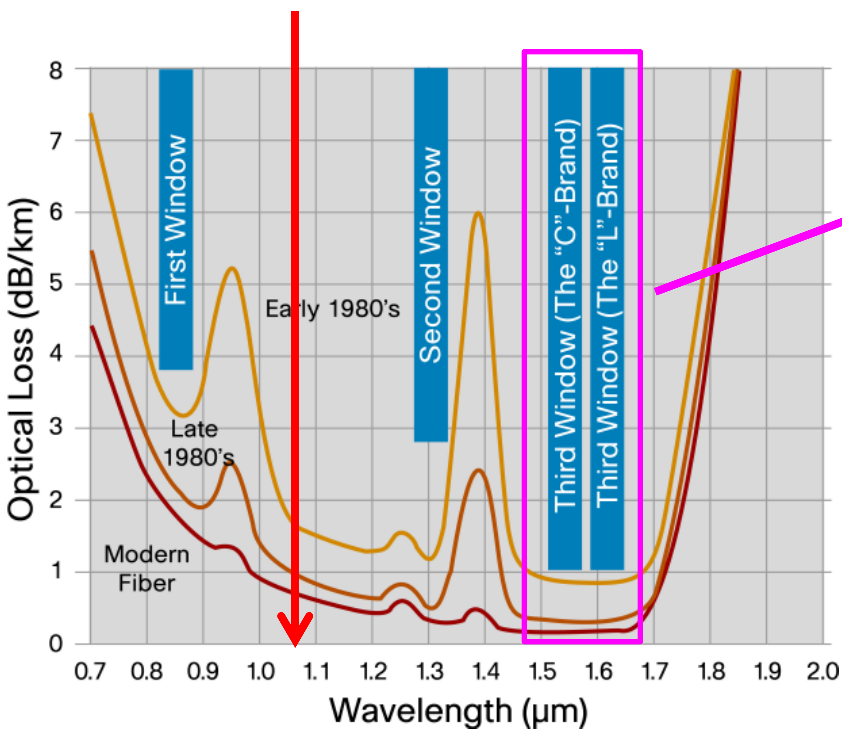


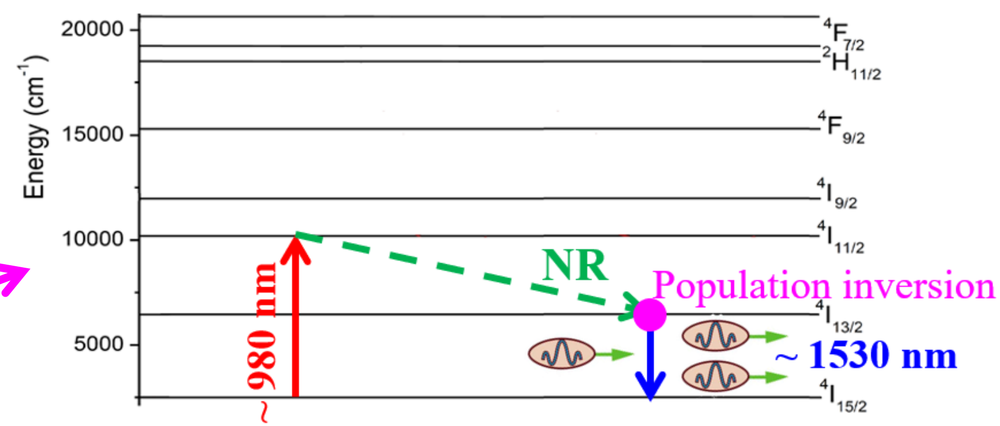
Optical fiber / wave guide amplifier

How about Nd^{3+} doped glass ?

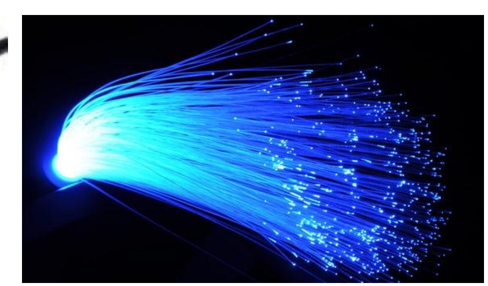


https://www.fiberlabs.com/glossary/fiber-amplifier/



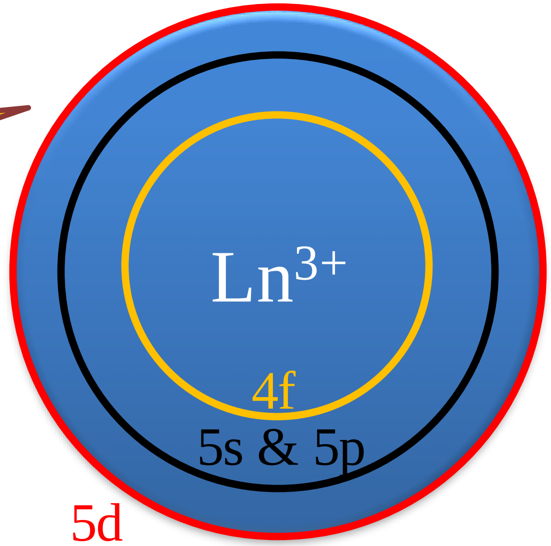


Stimulated emission of Er^{3+}



Strong luminescence properties of Ln^{3+}

- Photon
- Electric current
- Chemical reaction
- Neutron
- etc



- Intense emission
- Sharp emission band

Ln^{3+}	Emission	τ
Sm^{3+}	Red-Orange	ms
Dy^{3+}	Yellow-Blue, White	ms
Eu^{3+}	Red	ms
Nd^{3+}	NIR, λ/2 to Green	μs
Er^{3+}	NIR, Up-conversion to Red	ms
Tb^{3+}	Green	ms
Ce^{3+}	Blue	ns

Intra 4f-4f transition
Forbidden, but stable, Support by asymmetric ligand

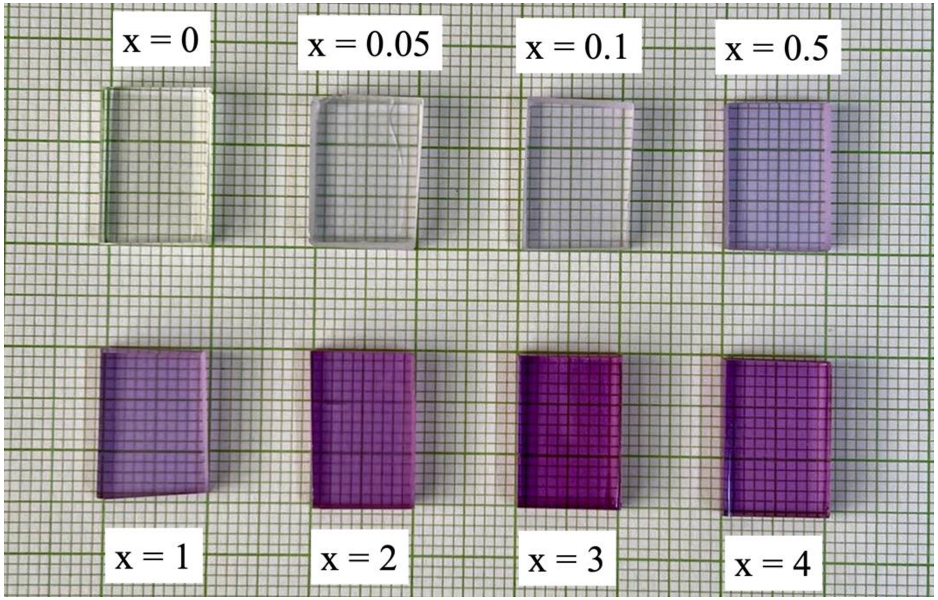
Inter 4f-5d transition
Allowed, but easy to disturb

GaLuAlYB:Ce glass composition

$10Gd_2O_3$-$15Al_2O_3$-$15Ga_2O_3$-$10Y_2O_3$-$(50-x)B_2O_3$-xNd_2O_3

Adapted metal oxide from multi-component garnet family

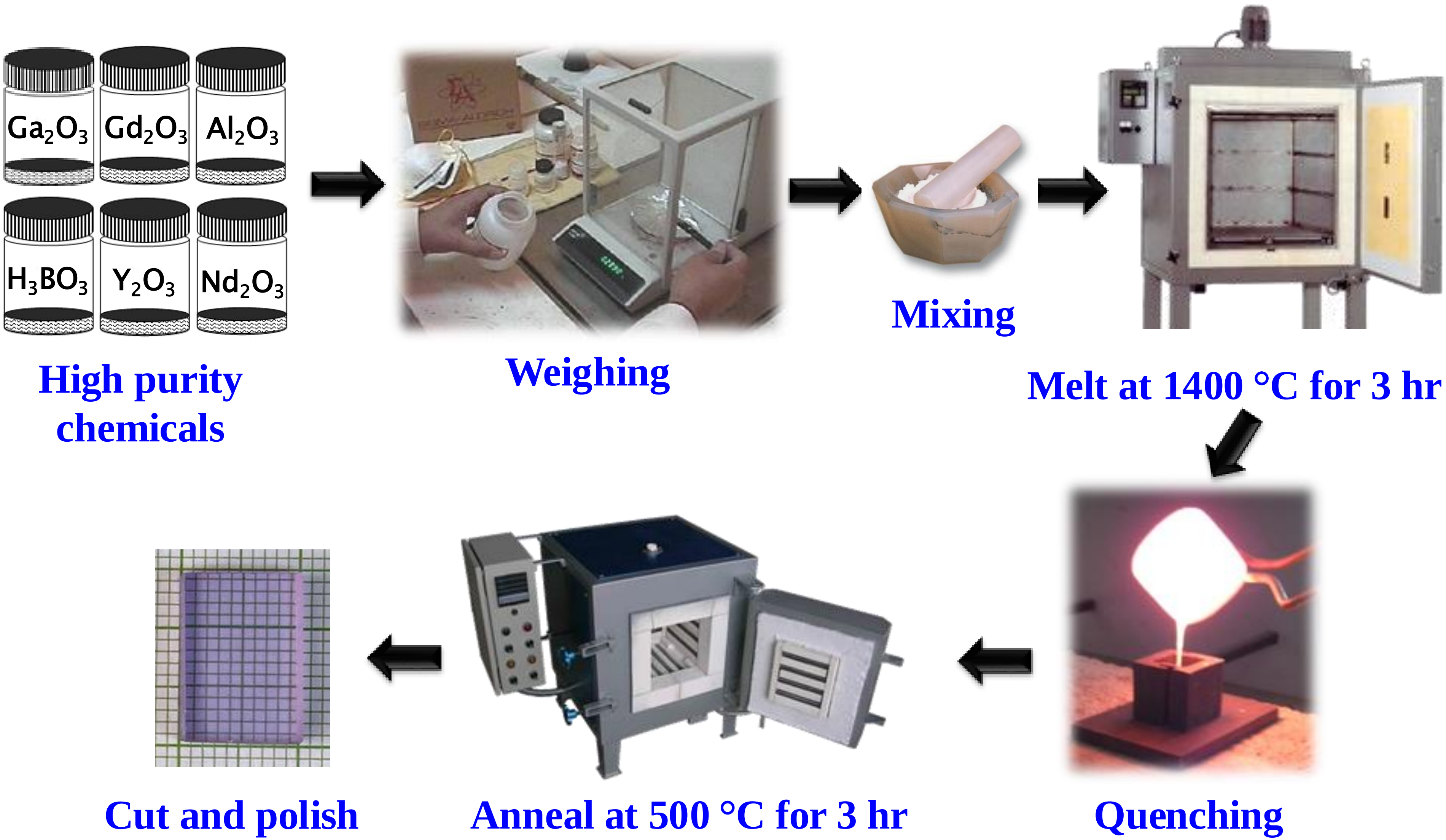
x = 0, 0.05, 0.1, 0.5, 1, 2, 3, 4 mol%



Excellent glass former
- High transparency
- High chemical durability
- Non-hygroscopic
- Easy to form network
- Good Ln^{3+} solubility

Strong NIR luminescence
- Popular in solid-state laser
- Can be converted to green laser
- Not fast decay time

Glass preparation (melt - quenching)



Characterization Instrument

Absorption spectra

UV-VIS-NIR Spectrophotometer
(UV-3600, Shimadzu)

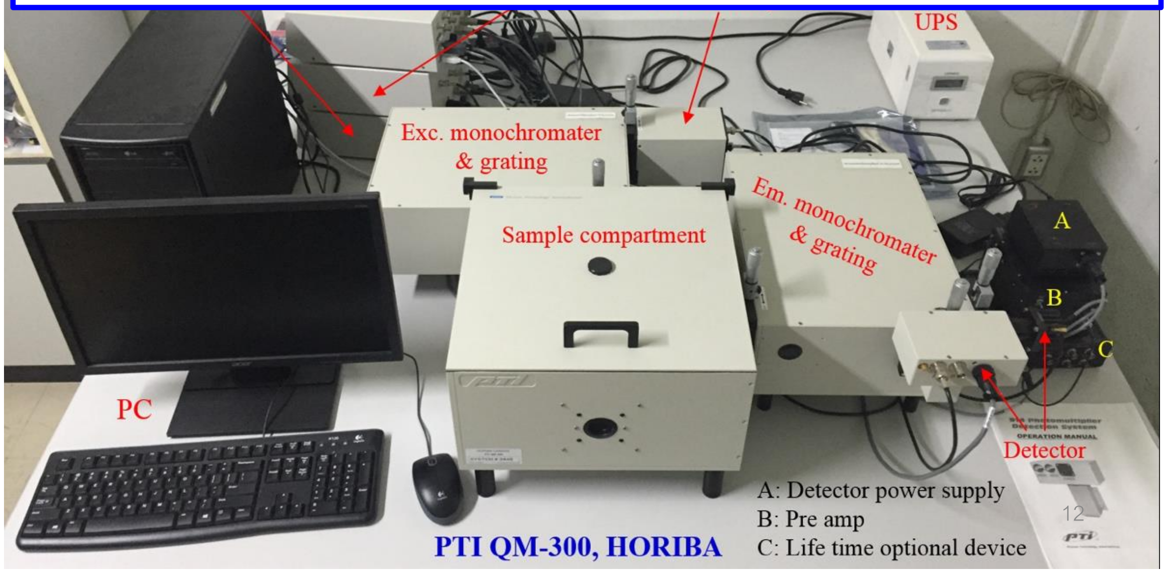
ρ; Archimedes principle

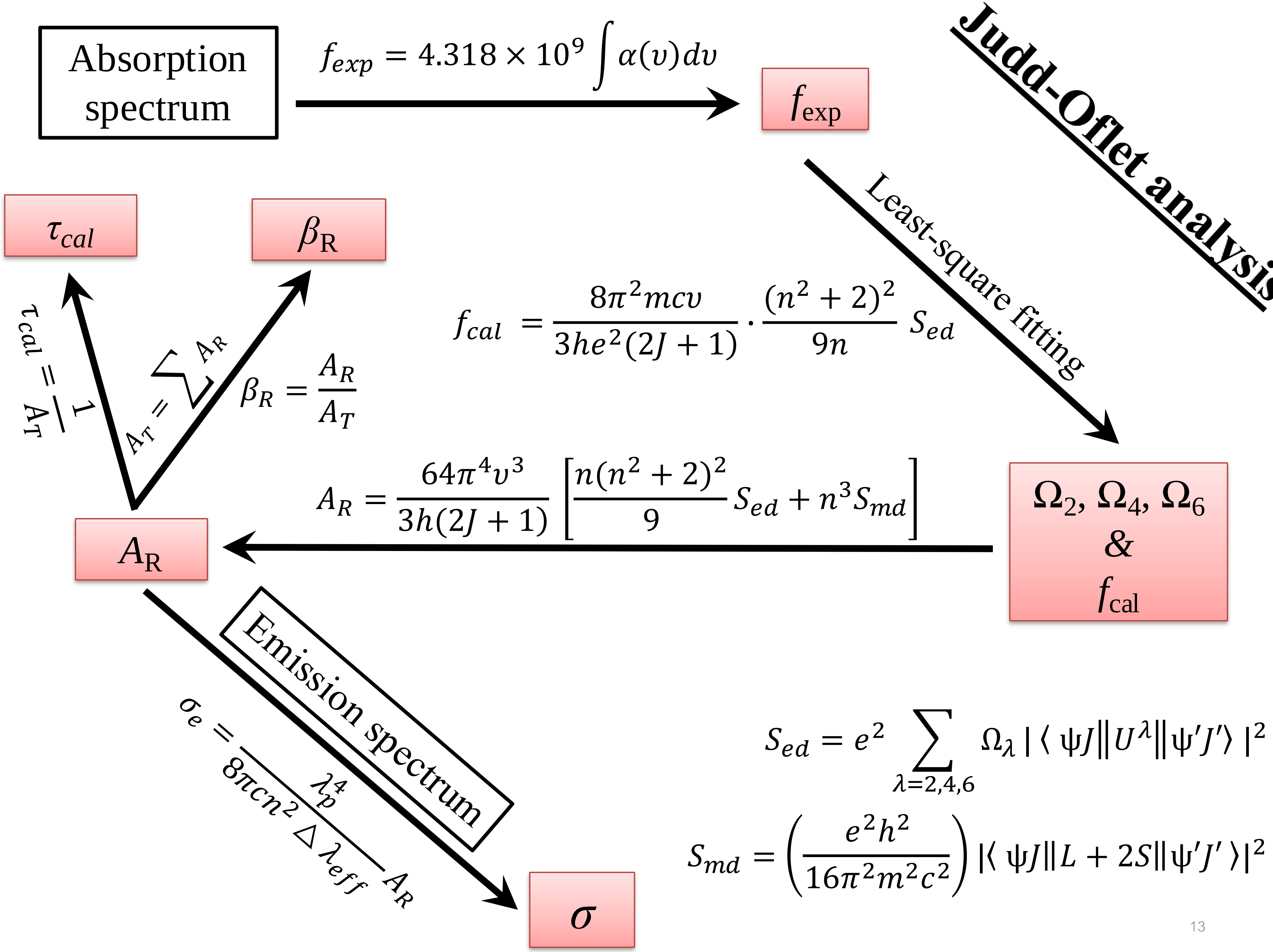
4-digit sensitive microbalance
(Denver, Pb214)

Refractive index

Abbe refractometer
(Atago, NAR-1T)

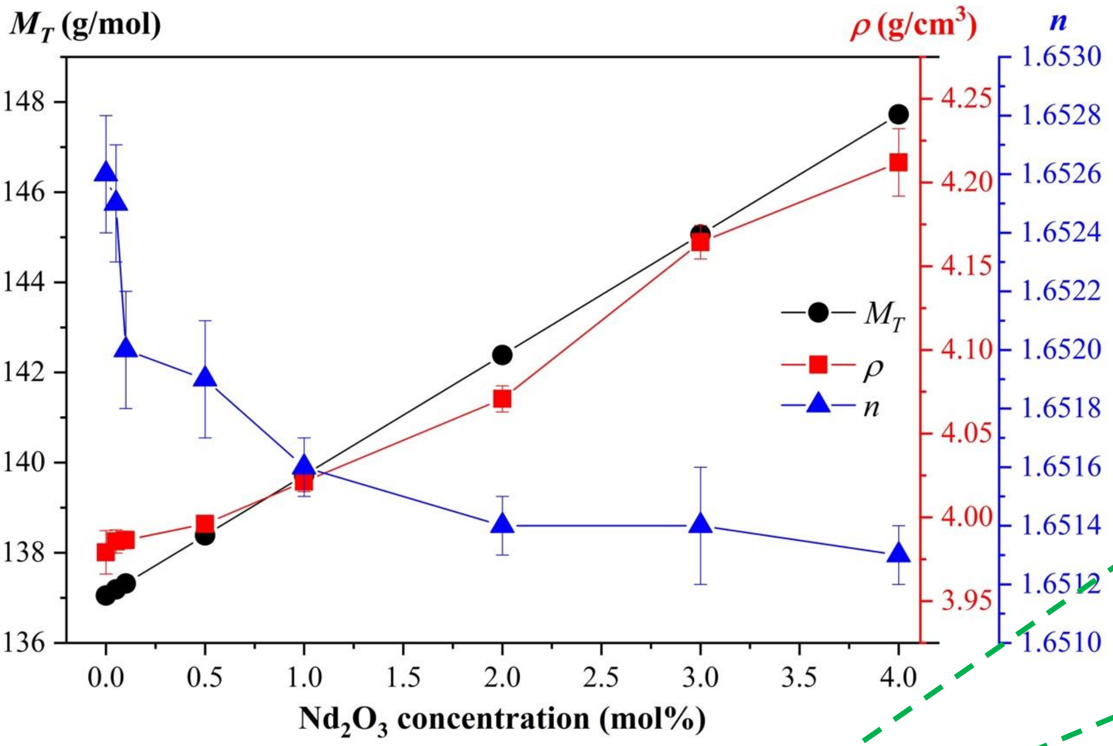
NIR PL spectra and decay curves




Judd-Oflet analysis
Absorption spectrum
$f_{exp} = 4.318 \times 10^9 \int \alpha(v) dv$
f_{exp}
Least-square fitting
$f_{cal} = \frac{8\pi^2 mcv}{3he^2(2J+1)} \cdot \frac{(n^2+2)^2}{9n} S_{ed}$
$\Omega_2, \Omega_4, \Omega_6$ & f_{cal}
$A_R = \frac{64\pi^4 v^3}{3h(2J+1)} \left[\frac{n(n^2+2)^2}{9} S_{ed} + n^3 S_{md} \right]$
A_{R}
τ_{cal}
β_{R}
$\tau_{cal} = \frac{1}{A_T}$
$A_T = \sum A_R$
$\beta_R = \frac{A_R}{A_T}$
Emission spectrum
$\sigma_e = \frac{\lambda_p^4}{8\pi c n^2 \Delta\lambda_{eff}} A_R$
σ
$S_{ed} = e^2 \sum_{\lambda=2,4,6} \Omega_\lambda \left| \langle \psi J \| U^\lambda \| \psi' J' \rangle \right|^2$
$S_{md} = \left(\frac{e^2 h^2}{16\pi^2 m^2 c^2} \right) \left| \langle \psi J \| L + 2S \| \psi' J' \rangle \right|^2$

Parameter	Name	Indication or meaning
$f_{exp/cal}$	Oscillator strength	The experimental/calculated transition strength of Ln^{3+} under photon absorption
Ω_2	J-O parameter	- Asymmetric environment surround Ln^{3+} - Covalency between Ln^{3+} and ligand
Ω_4 & Ω_6		Viscosity and rigidity of glass
A_R $\left(A_T = \sum A_R\right)$	Radiative transition probability	The transition probability (rate) of Ln^{3+} cause photon emission
β	Branching ratio	Emission ratio and lasing power
σ_{se}	Stimulated emission cross-section	- Stimulated emission probability - Laser threshold (energy used to start the lasing action) - Gain laser application (ratio of output/input energy)
τ_R	Radiative life time	Time of pure radiative transition
τ_{exp}	Experimental life time	Time of radiative combined with non-radiative transition

Molecular mass (M_T), Density (ρ) & Refractive index (n)



Mass of Nd_2O_3 > Mass of B_2O_3

….. -(50-x)B_2O_3-xNd_2O_3

B_2O_3 replacement by Nd_2O_3 make M_T of glass increase

ρ increased with addition of Nd_2O_3

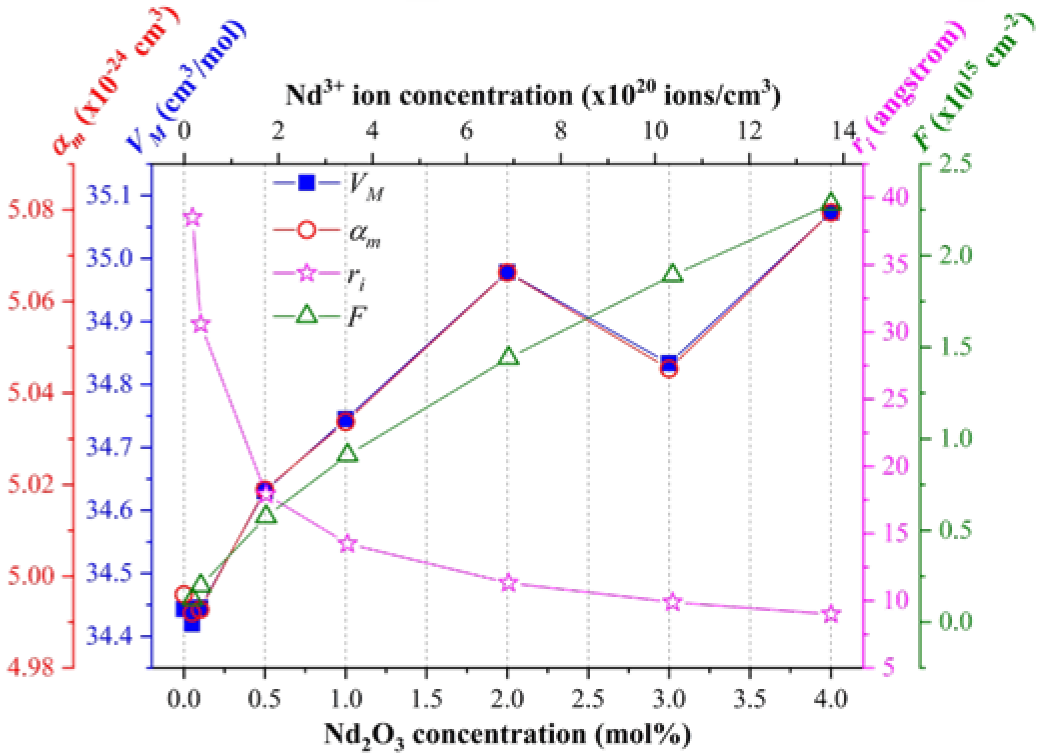
Lorentz – Lorentz relation

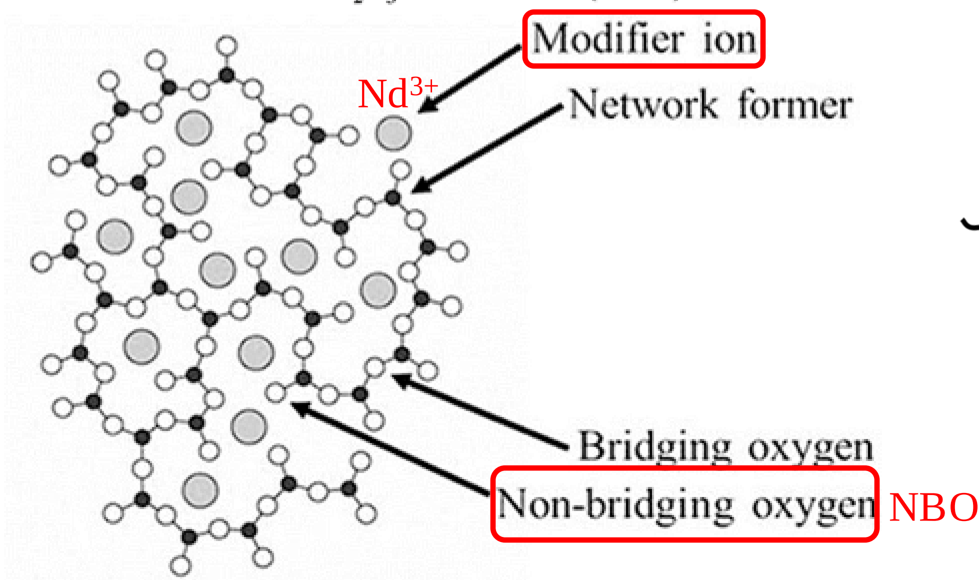
$$\frac{(n^2-1)}{(n^2+1)} = \left(\frac{\rho}{M_T}\right) R_m$$

n decreases via M_T addition

Change of M_T is more effective than that of ρ

Molar volume (V_M), polarizability (α_m), Nd-Nd distance (r_i) & Field strength (F)



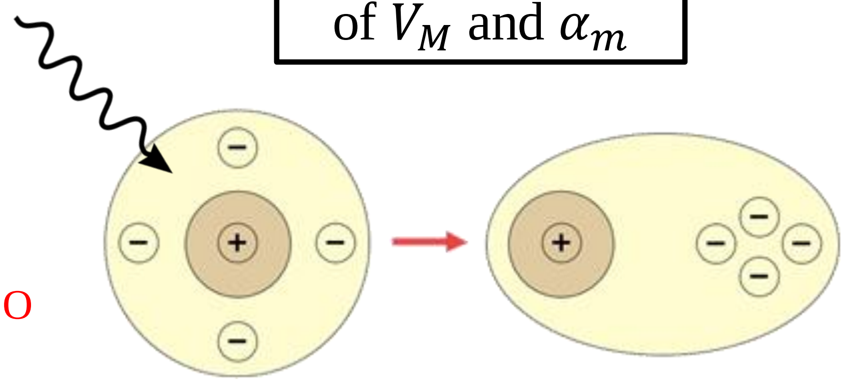


Overview
(compare to undoped glass)

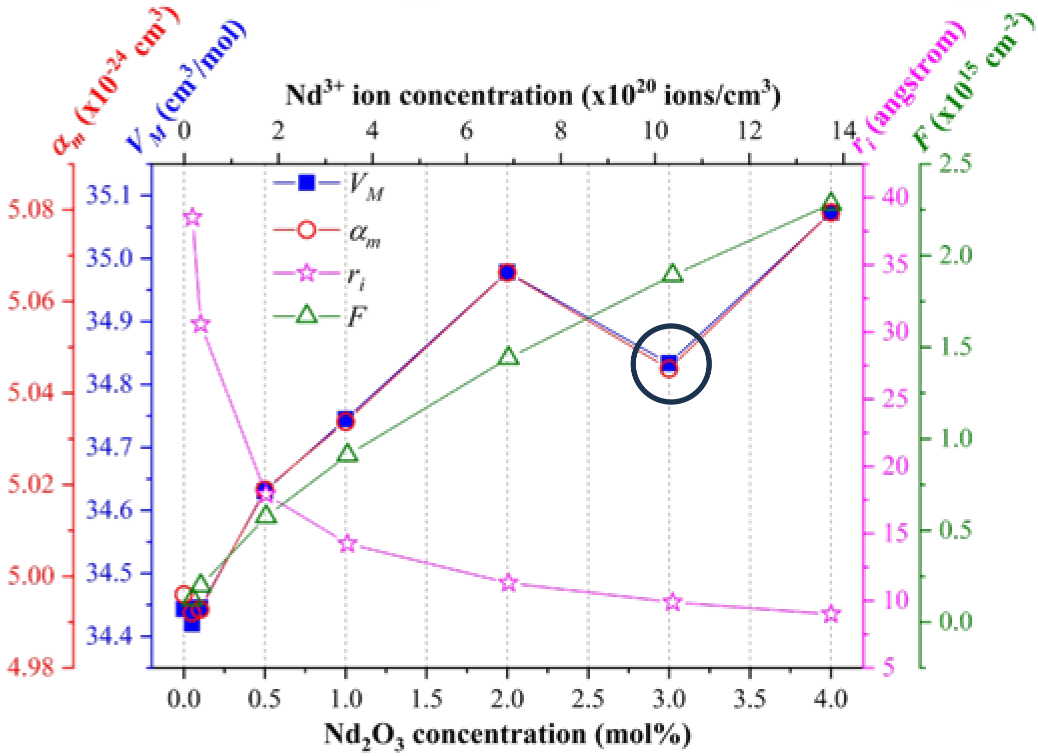
Nd_2O_3 act as glass modifier

Adding Nd_2O_3 create NBO and open space in glass network

Increasing trend of V_M and α_m



Molar volume (V_M), polarizability (α_m), Nd-Nd distance (r_i) & Field strength (F)

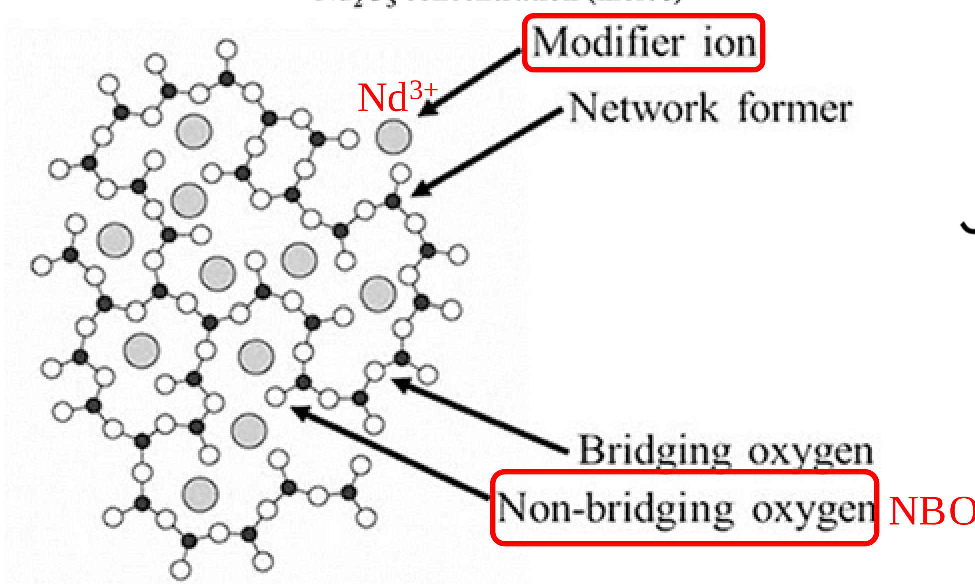


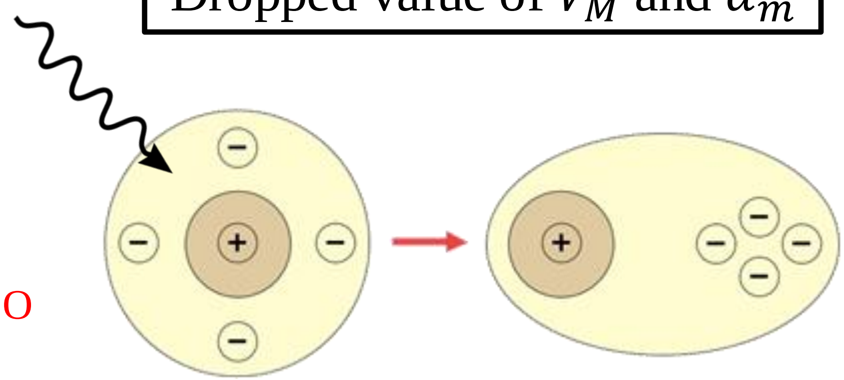
At x = 3 mol%

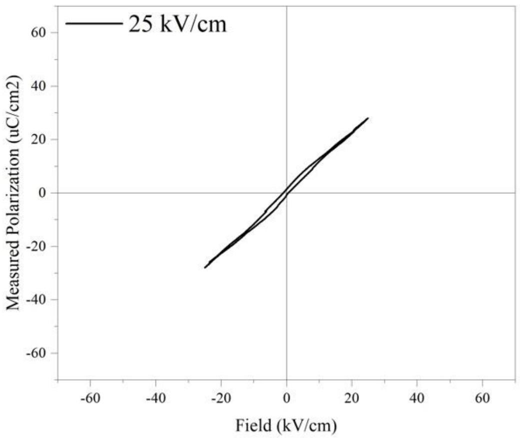
Nd$_2$O$_3$ acted as glass modifier but less effective than x = 2 and 4 mol%

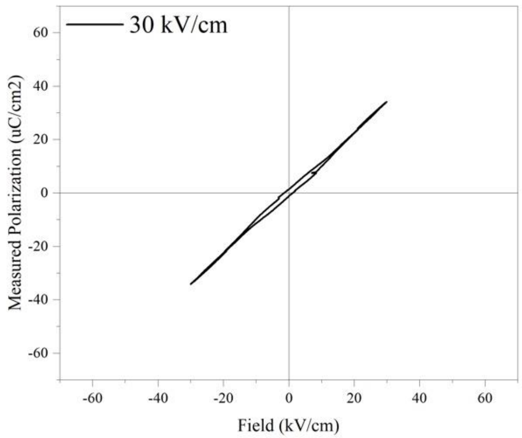
Less NBO and interstitial space in glass network than x = 2 and 4 mol%

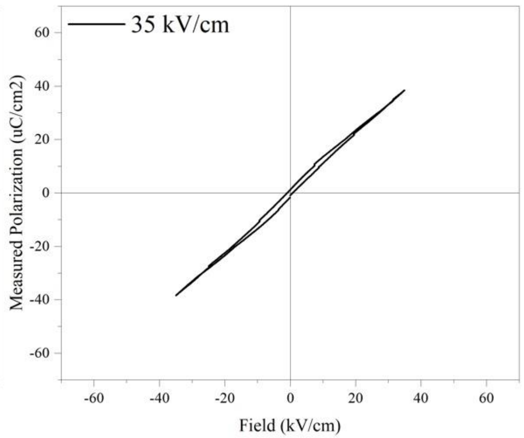
Dropped value of V_M and α_m

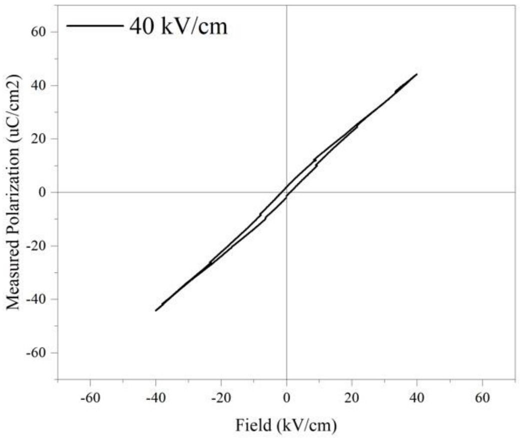


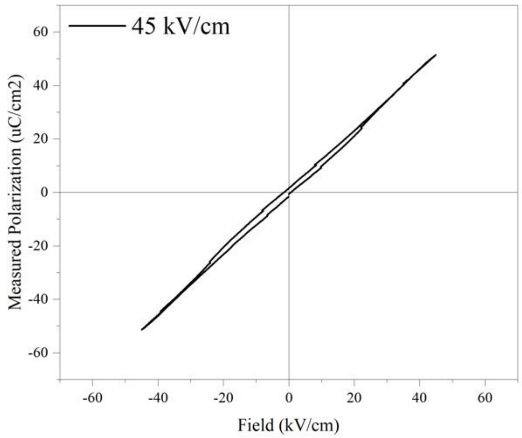


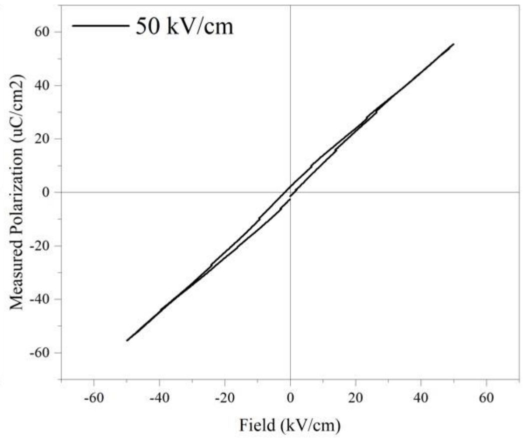


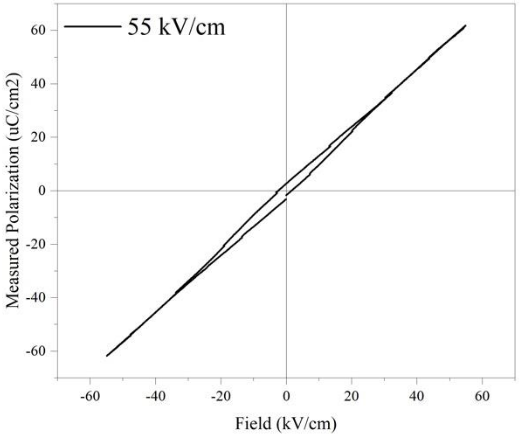




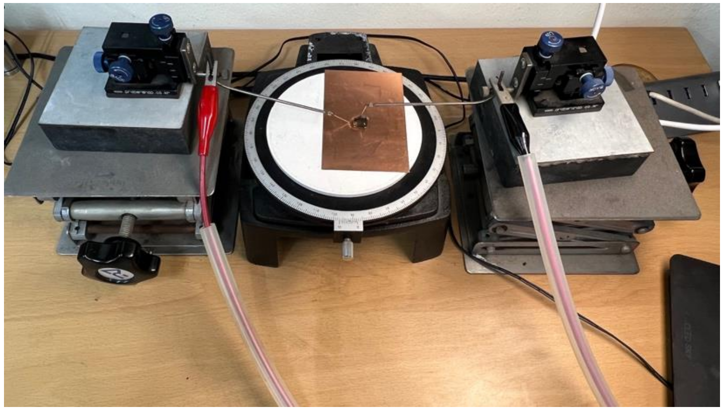






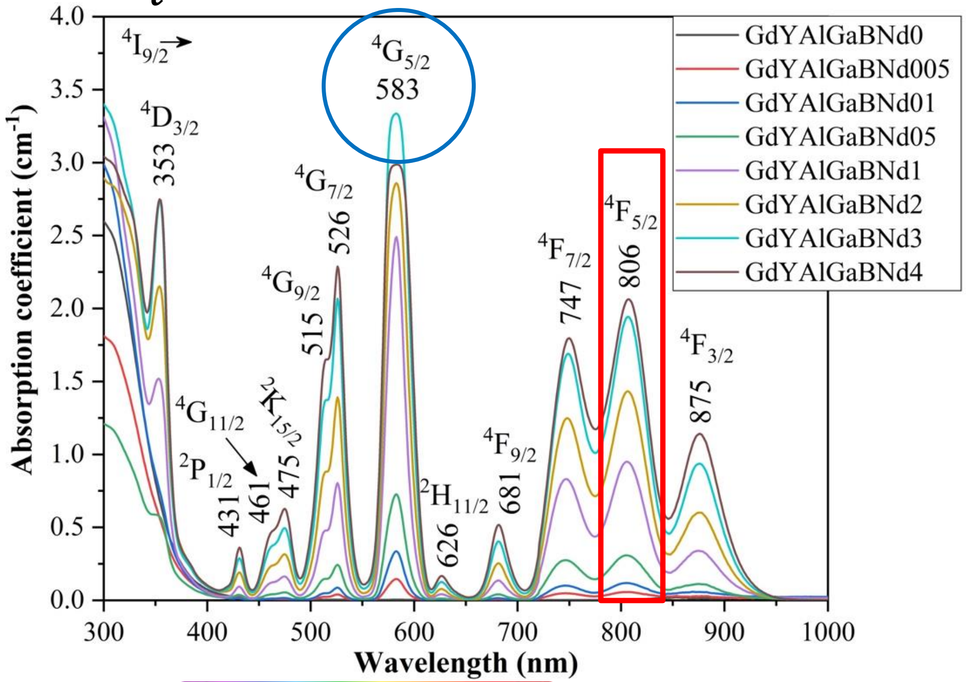


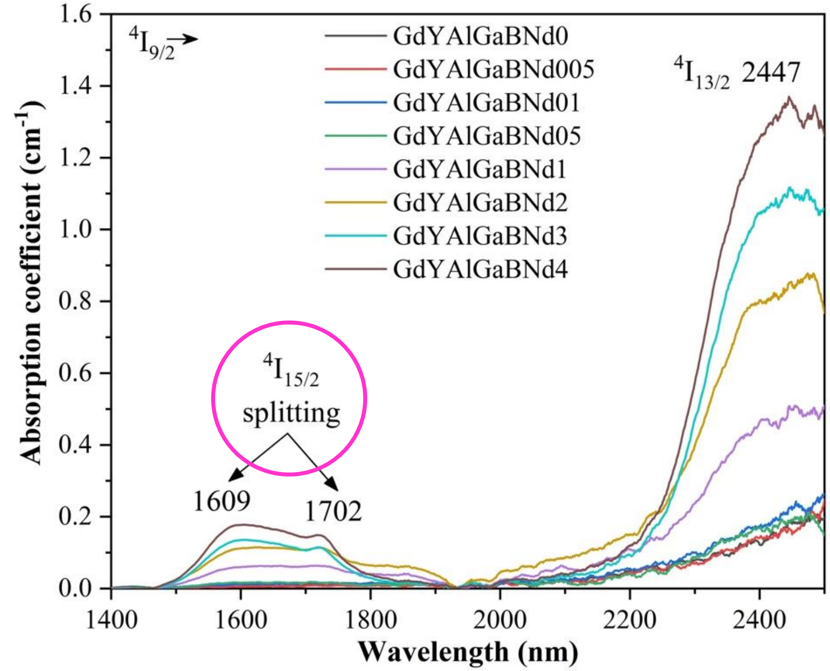
Hysteresis (P-E) loop of GdYAlGaBNd1

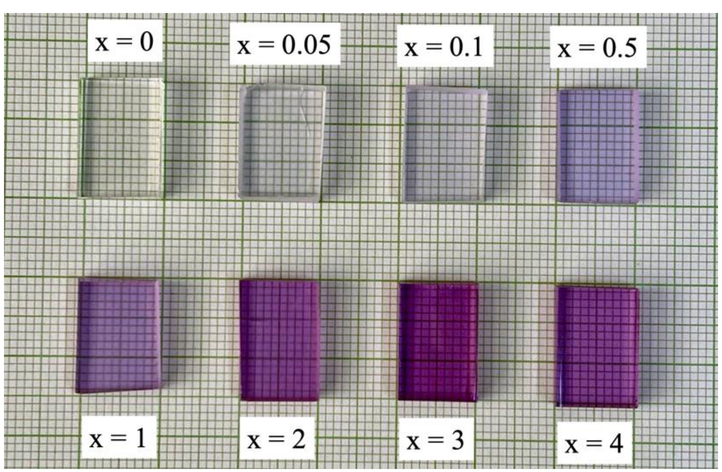


$$\frac{A}{l} = \varepsilon c$$

Absorption spectra







- 14 transitions from $^4I_{9/2}$, ground of Nd^{3+}
- The strongest $^4I_{9/2} \rightarrow {}^5G_{5/2}$ hypersensitive (HS) transition at x = 3 mol%

  ⬇

  Nd^{3+} environment is most asymmetry
- The ligand-field splitting for $^4I_{15/2}$ level in glass with x ≥ 1 mol%

J-O analysis of GdYAlGaBNd1 glass (Absorption spectra)

Absorption wavelength (nm)	Transition $^4I_{9/2} \rightarrow$	GdYAlGaBNd1	
		f_{exp} ($\times10^{-6}$)	f_{cal} ($\times10^{-6}$)
431	$^2P_{1/2}$	0.80	0.82
461	$^4G_{11/2}$	0.82	0.37
475	$^2K_{15/2}$	2.26	0.54
515	$^4G_{9/2}$	4.54	2.43
526	$^4G_{7/2}$	5.42	5.51
583	$^4G_{5/2}$	23.89	23.86
681	$^4F_{9/2}$	0.89	0.99
747	$^4F_{7/2}$	8.95	9.00
806	$^4F_{5/2}$	9.78	10.18
875	$_4F_{3/2}$	3.05	3.47
	σ_{rms}	0.89	

$\Omega_2 = 6.44 \times 10^{-20}\ cm^2$

$\Omega_4 = 5.91 \times 10^{-20}\ cm^2$

$\Omega_6 = 9.12 \times 10^{-20}\ cm^2$

$\chi = \Omega_4 / \Omega_6 = 0.65$

$^4F_{3/2} \rightarrow {}^4I_{11/2}$

$\lambda_{em} = 1064$ nm

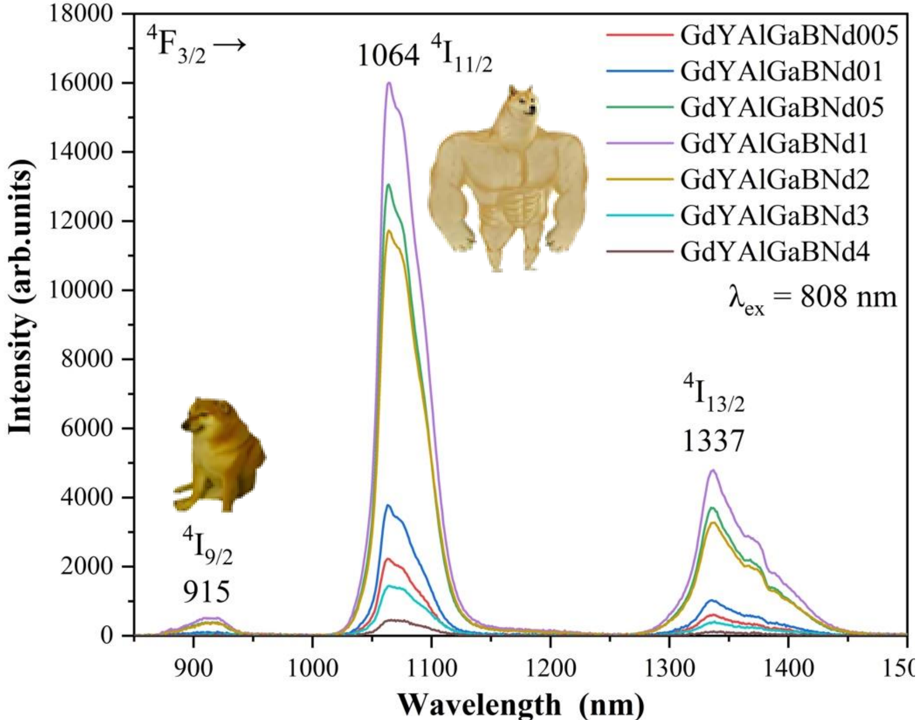
$^4F_{3/2} \rightarrow {}^4I_{9/2}$

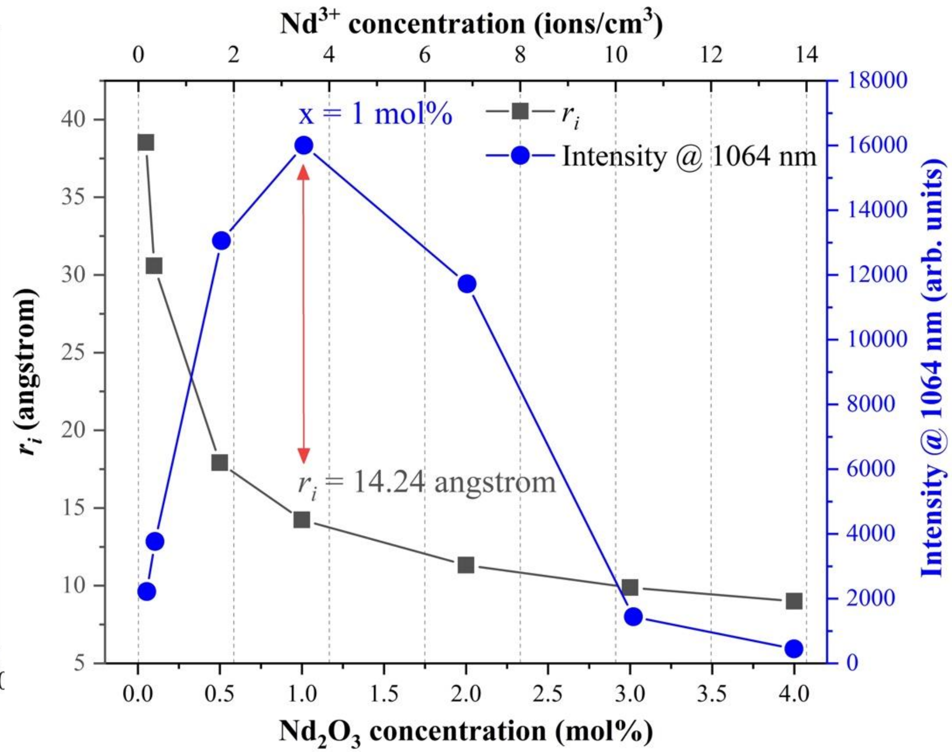
$\lambda_{em} = 915$ nm

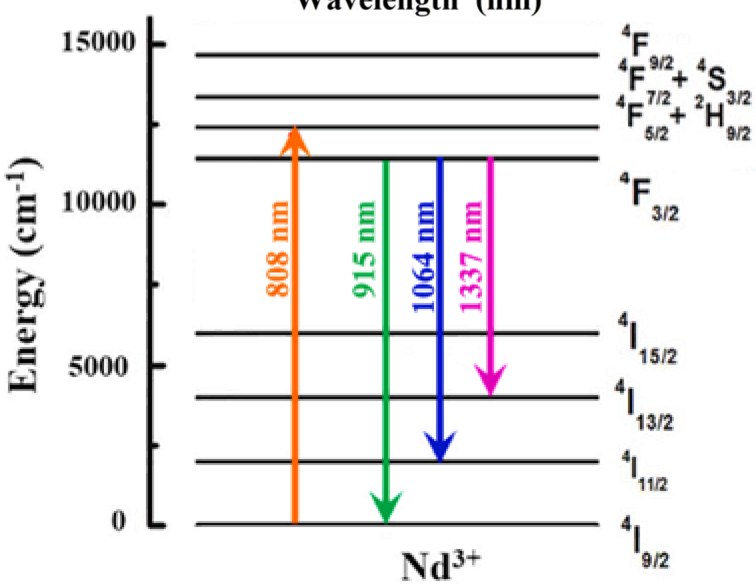
Comparison of J-O parameters

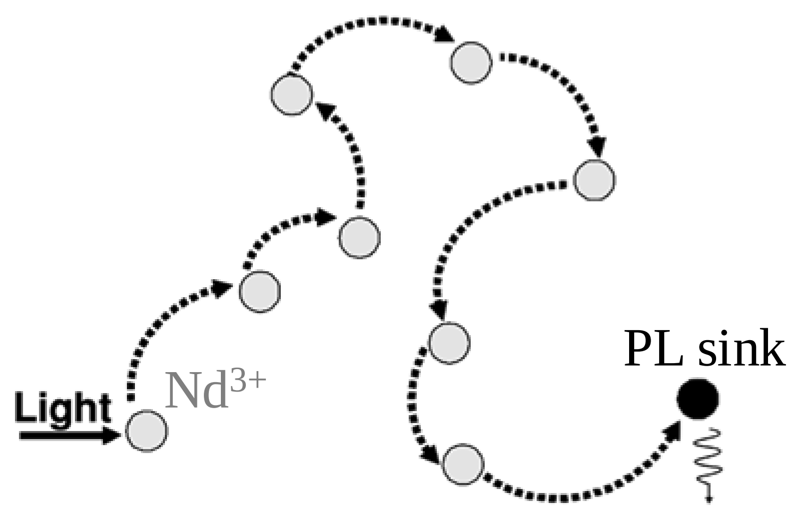
Glass	Ω ($\times 10^{-20}$ cm^2)			χ	Ref.
	Ω_2	Ω_4	Ω_6		
GdYAlGaBNd1	6.44	5.91	9.12	0.65	This work
Hoya LHG-80	3.60	5.00	5.50	0.91	A. Jose, et al. 2022
Schott LG-770	4.30	5.00	5.60	0.89	A. Jose, et al. 2022
Kigre Q88	3.30	5.10	5.60	0.91	A. Jose, et al. 2022
PbFBaFAlB:Nd	5.77	3.68	4.01	0.91	P.R. Rani, et al. 2021
PbGe:Nd	5.61	6.34	6.42	0.99	A. Herrera, et al. 2021
NaKFCaFAlCaP:Nd	7.35	6.89	9.70	0.71	J. Rajagukguk, et al. 2019
BaZnLiFNaFLiB:Nd	8.68	7.97	12.75	0.62	G. Lakshminarayana, et al. 2022
NbKZnFLiFSi:Nd	10.26	6.38	6.06	1.05	D. Ramachari, et al. 2014

Photoluminescence (PL) spectra

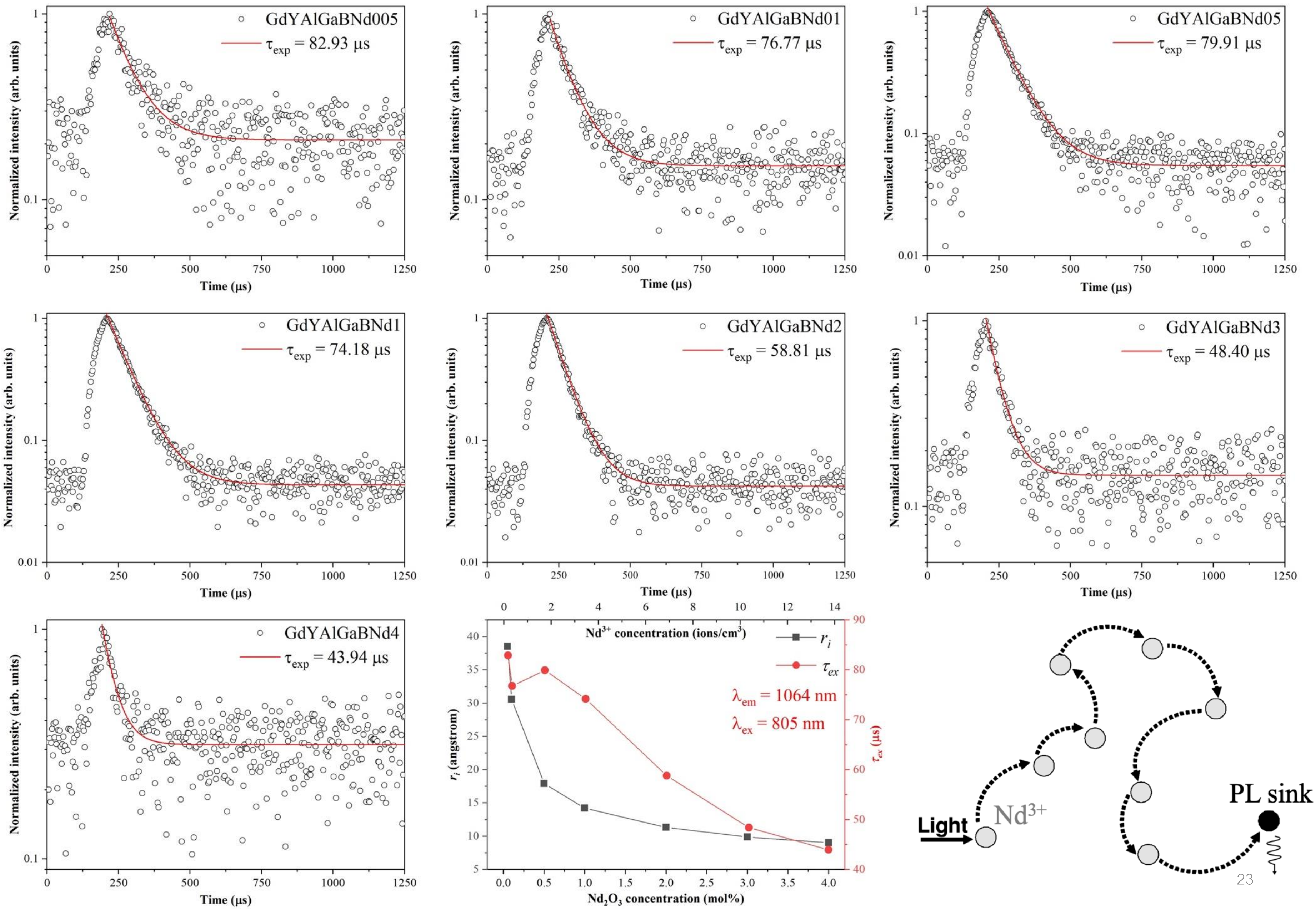








PL decay time



J-O analysis of GdYAlGaBNd1 glass (Emission spectra)

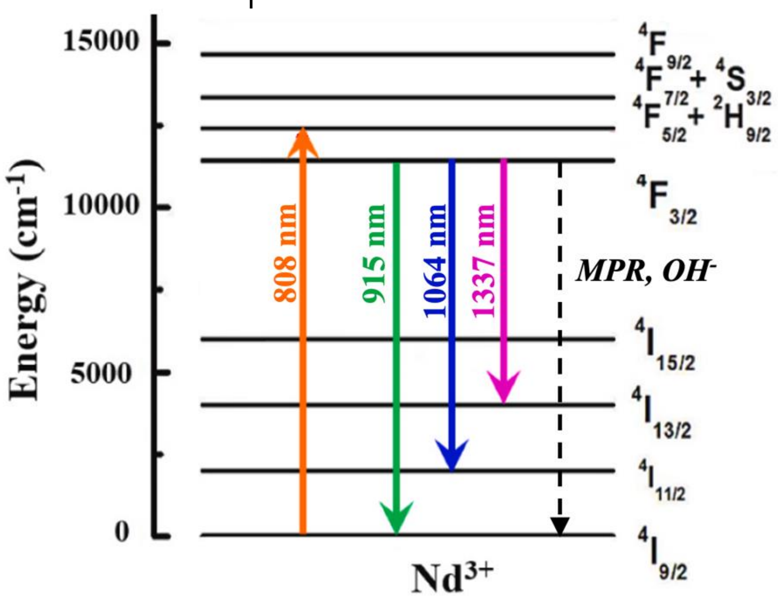
λ_{em} (nm)	Transition $^4F_{3/2} \rightarrow$	GdYAlGaBNd1			
		A_R (s^{-1})	$\Delta\lambda_{eff}$ (nm)	σ_{se} ($\times 10^{-20}$ cm^2)	β_{exp}
915	$^4I_{9/2}$	2052	42.31	1.65	0.02
1064	$^4I_{11/2}$	**2948**	**45.39**	**4.05**	**0.69**
1337	$^4I_{13/2}$	606	63	1.48	0.29
τ_R for $^4F_{3/2}$ level = 177.40 μs					

Highest probability for stimulated emission

Winner for competitively emission transition

Quantum efficiency (η)

$$\eta = \frac{\tau_{exp}}{\tau_R} \times 100 = \frac{74.18}{177.40} \times 100 = 41.82\ \%$$



Comparison of radiative parameters

Glass	$\Delta\lambda_{eff}$ (cm)	σ_{se} ($\times 10^{-20}$ cm^2)	$\Delta\lambda_{eff} \times \sigma_{se}$ ($\times 10^{-25}$ cm^3)	τ_{exp} (μs)	I_s ($\times 10^8$ W/m^2)	η (%)
GdYAlGaBNd1	45.39	4.05	1.84	74.18	6.22	41.82
Hoya LHG-80	23.90	4.20	1.00	-	-	-
Schott LG-770	25.40	3.90	0.99	-	-	-
Kigre Q88	21.90	4.00	0.88	-	-	-
PbFBaFAlB:Nd	34.80	7.23	2.52	245	1.04	90.00
PbGe:Nd	37.33	4.52	1.69	88	4.64	64.00
NaKFCaFAlCaP:Nd	33.22	4.92	1.63	200	1.87	98.92
BaZnLiFNaFLiB:Nd	32.46	2.60	0.84	62	11.44	17.00
NbKZnFLiFSi:Nd	38.00	4.30	1.63	135	3.18	78.00

Character of GdYAlGaBNd1 glass

- Wide $\Delta\lambda_{eff}$ and $\Delta\lambda_{eff} \times \sigma_{se}$
- Fair σ_{se} and I_s
- Quite Short τ_{exp}

Approach to applications

- Potential optical amplifier
- Interesting laser medium

Point to improve

- Upgrade η

Conclusion

- Nd_2O_3 addition → more density but less refractive index
- Overview behavior: Nd_2O_3 is glass modifier for GdYAlGaB glass
- GdYAlGaBNd glass is weak paraelectric material
- The optimum Nd_2O_3 concentration : 1 mol%
- Strong absorption at 806 nm produces the strong luminescence at 1064 nm with decay time ~74 μs
- Judd-Ofelt analysis: potential amplifier for laser and optical telecomunication

Acknowledgement

- Muban Chombueng Rajabhat University (MCRU)
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Thank you

Luminescence materials for photonics

Excitation energy → Materials → Photon

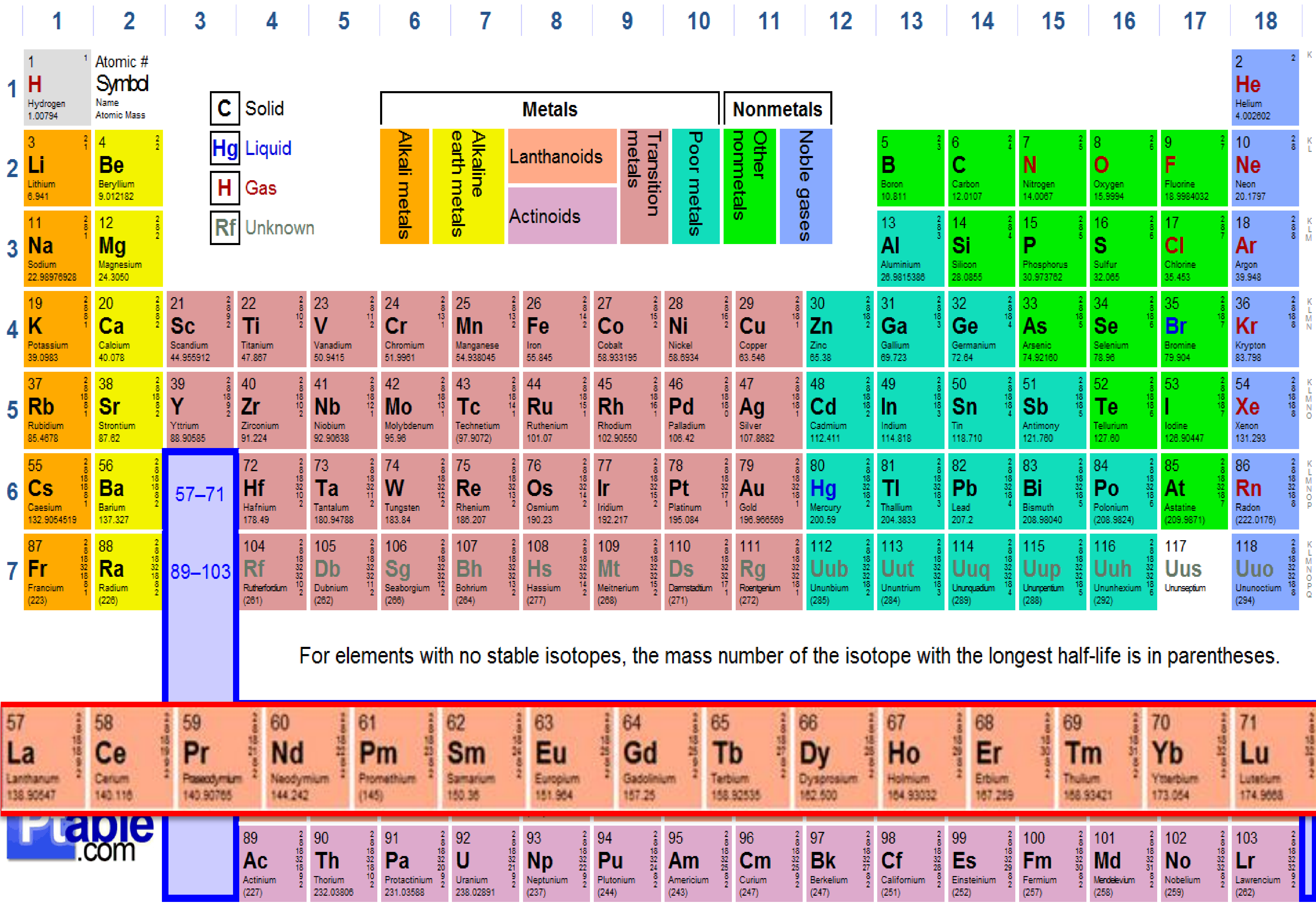
- Photons / Radiation
- Electric current
- High energy particles
- Chemical reaction
- Mechanical action
- etc

Materials:
- Photons production
- Photons conversion
- Photons guide

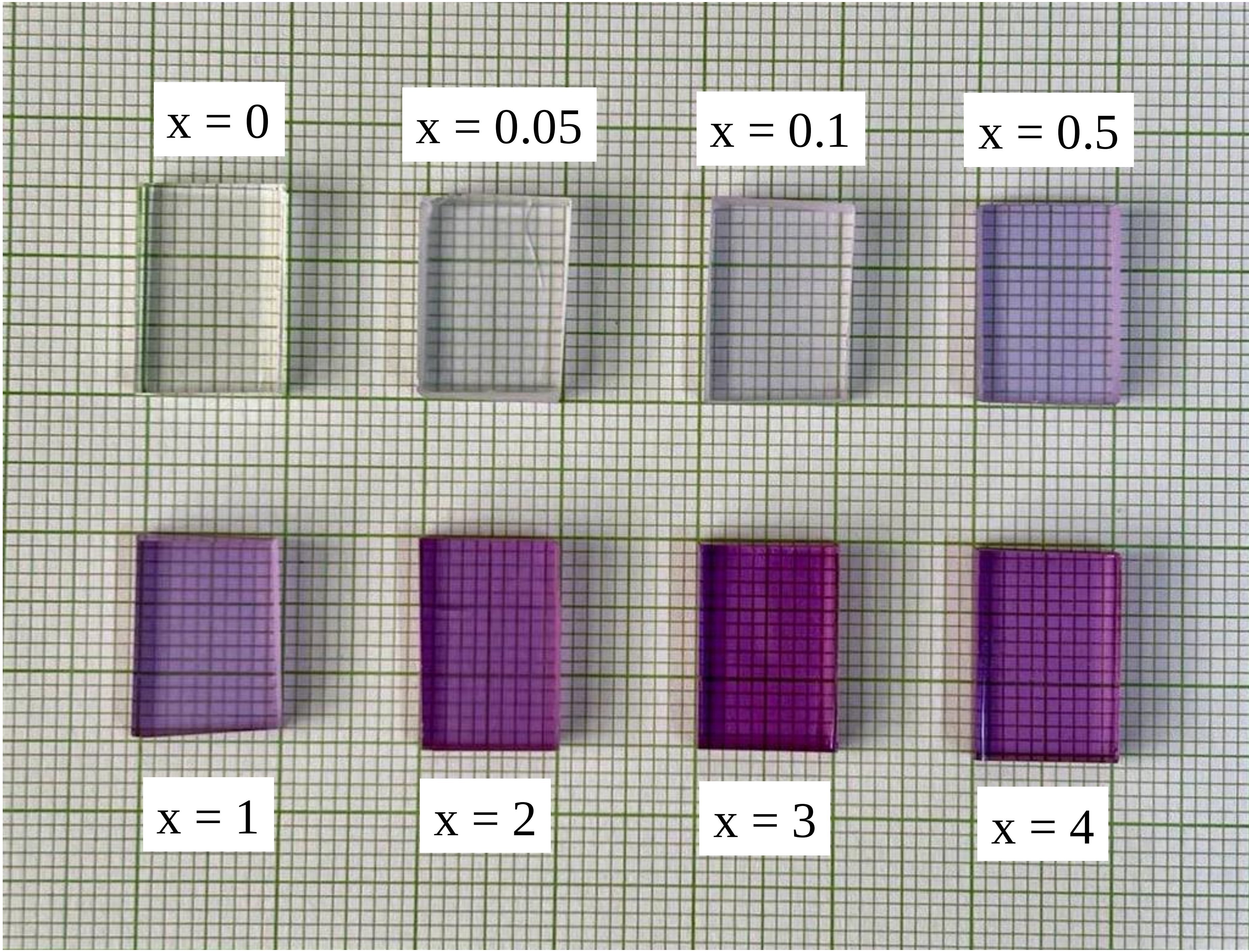
Luminescence Bulk materials

Well-known and widely used: Single-crystal, Transparent Ceramics

Challenge to develop: Glasses


Atomic #
Symbol
Name
Atomic Mass
C Solid
Hg Liquid
H Gas
Rf Unknown
Metals
Nonmetals
Alkali metals
Alkaline earth metals
Lanthanoids
Actinoids
Transition metals
Poor metals
Other nonmetals
Noble gases
57–71
89–103
For elements with no stable isotopes, the mass number of the isotope with the longest half-life is in parentheses.
Ptable.com

[1]

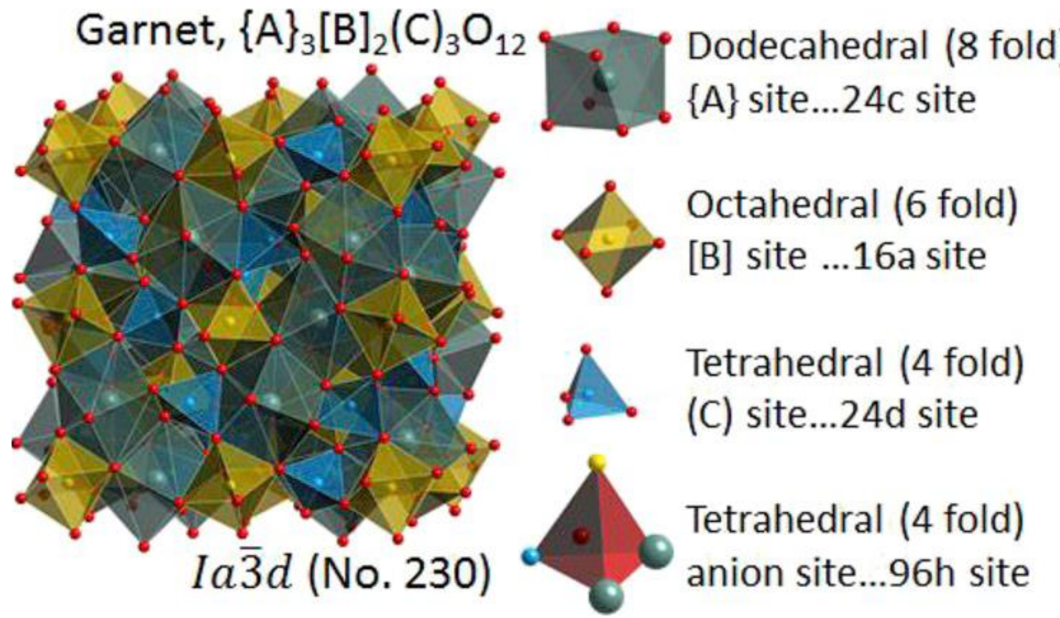

x = 0
x = 0.05
x = 0.1
x = 0.5
x = 1
x = 2
x = 3
x = 4

Aluminium garnet compound family

$Y_3Al_5O_{12}$ (YAG) : 1960s

$Lu_3Al_5O_{12}$ (LuAG) : 1990s

Cubic crystalline structure



Ueda, J., Tanabe, S. (2019). Optical Materials: X, 1, 100018

$A_3(B,C)_5O_{12}$: Until present

Possible A element = Y, Lu, Gd, Sc or mixing between them

Possible B & C element = Al, Ga, Sc or mixing between them

Multi-component garnet

Luminescence glass material

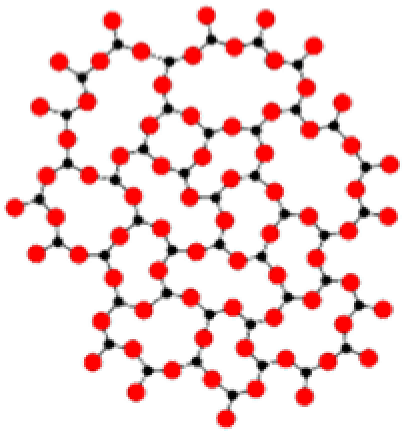
Ln^{3+}

↑

Require
the excellent luminescence center

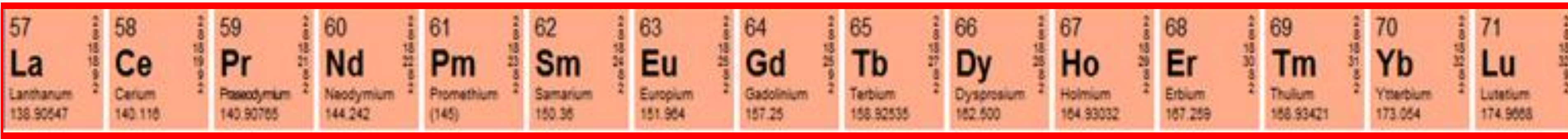
↑

Difficult for self-emission
with strong light signal ←



Glass
Amorphous structure
Unclear electronic bandgap
Easy for preparation
Can prepare in **various sizes** and **shapes** witch same properties
Wide range of chemical ratio
Low production cost

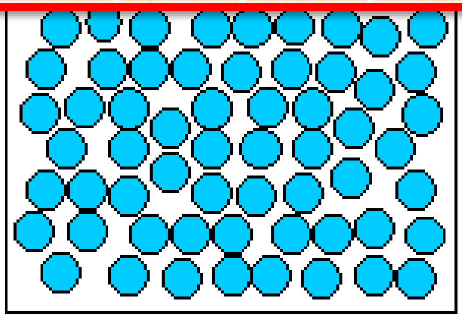
Luminescence glass material



Ln^{3+}

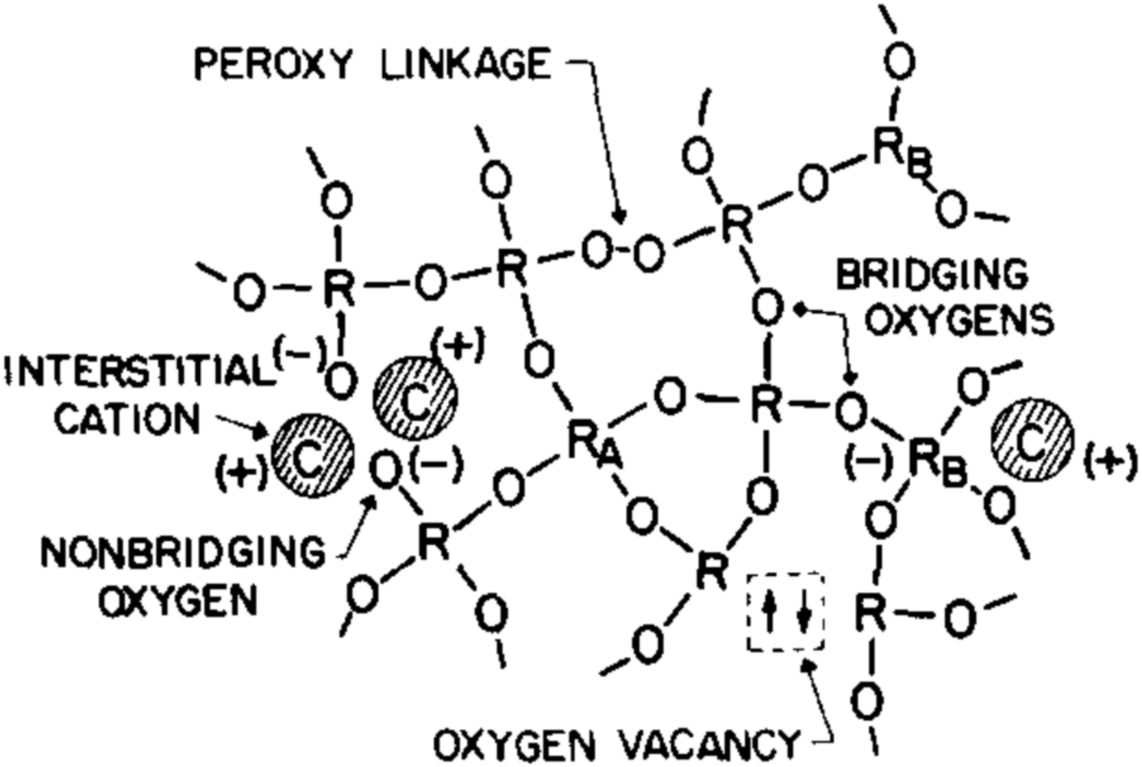
Require
the excellent luminescence center

Difficult for
intrinsic luminescence



Glass
Amorphous / Random structure
Unclear electronic bandgap & center
Easy for preparation
Can prepare in **various sizes** and **shapes** which the same properties
Wide range of chemical ratio
Low production cost

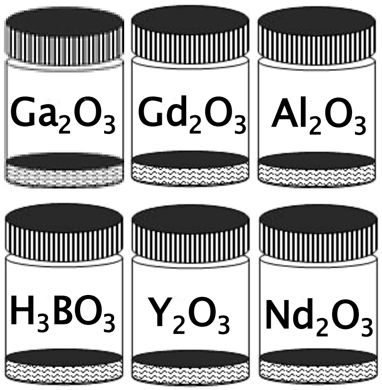
Glass defect



R, R_A, R_B = Network Formers = Si, B, P, Ge, Al, ...

C = Monovalent Network Modifying Cation = H, Li, Na, K, ...

Glass preparation (melt - quenching)



High purity chemicals

Weighting

Mixing

Melt at 1400 °C for 3 hr

Quenching

Anneal at 500 °C for 3 hr

Cut and polish