

Ultraviolet and Visible Upconversion Luminescence and Spectroscopic Properties in Neodymium Doped Soda Lime Silicate Glasses

Megha Agarwal, Beena Bhatia, Ajay Singh Gehlot
J.N.V. University, Department of Physics
Jodhpur, Rajasthan-342005 (India)

Abstract— Ultraviolet and Visible upconversion emission under UV, VIS and NIR excitation have been obtained in Nd³⁺ doped soda lime silicate glasses. The mechanism of the upconversion emission i.e. excited state absorption (ESA) and energy transfer (ET) have been analysed. An intense room temperature Yellow to Blue upconversion at 0.581 μm ($^4\text{G}_{5/2} \rightarrow ^4\text{I}_{11/2}$) and 0.458 μm ($^4\text{G}_{11/2} \rightarrow ^4\text{I}_{9/2}$) were measured. In addition to this, intense UV emission at 0.362 μm ($^4\text{D}_{3/2} \rightarrow ^4\text{I}_{9/2}$) was also observed. We have taken into account absorption spectra in visible region which help us in reporting Judd-Ofelt parameters Ω_{λ} ($\lambda=2,4,6$) so as to investigate the linear optical properties and to characterize the glass specimens.

Keywords : Silicate glasses, Upconversion luminescence, Rare earth doped glasses.

I. INTRODUCTION

Attention has been focused on the development of solid state laser materials in visible, near infrared and infrared region [1, 2]. These lasers are of interest for a wide variety of applications such as gas sensing, eye-safe lasers, infrared counter measures, medical procedures & spectroscopy [3]. Upconversion emission from high excited levels of lanthanides ions can be obtained via two distinct mechanism one of them is sequential absorption of two or more photons by a single ion ESA i.e. excited state absorption. The other one involves absorption of photons by different ions ET i.e. energy transfer mechanism [4].

Energy Transfer process among RE ions are important in solid state system because they can favour luminescence emission and therefore the reduction of laser threshold or enhancement of amplifier gain can be obtained. The donor ions are excited by the incident light source and transfer all or fraction of the absorbed energy to the acceptors [5]. Frequency upconversion can be realized into the glass with lower phonon energies [6,7] but it is difficult to be obtained in silicate glasses with higher phonon energies resulting in high optical gain in fiber amplifier[8].

Oxides are more useful than fluorides as host materials for practical applications due to their high chemical durability and thermal stability [9]. Among oxide glasses, phosphate and silicate glasses are the two most important hosts which can be used extensively for lasers and fiber amplifier [10, 11]. As compared to silicate glasses, phosphate glasses have their limited use because phosphate glasses are hygroscopic in nature and have low glass transition temperature [12]. On the other hand silicate glasses have superior chemical resistance and are optically transparent at the excitation and lasing wavelength [9]. Therefore they are more compatible with fabrication process in the development of optical devices. When neodymium ions are introduced in a glass material the energy levels and the spectral broadening are significantly affected by the glass host material as well as the co-doped ions [13, 14].

The present article reports the study of upconversion process and the Judd-Ofelt theory was applied to obtain, omega parameters which in turn decide the covalency in the neodymium doped soda lime silicate glasses prepared by melt-quenching technique.

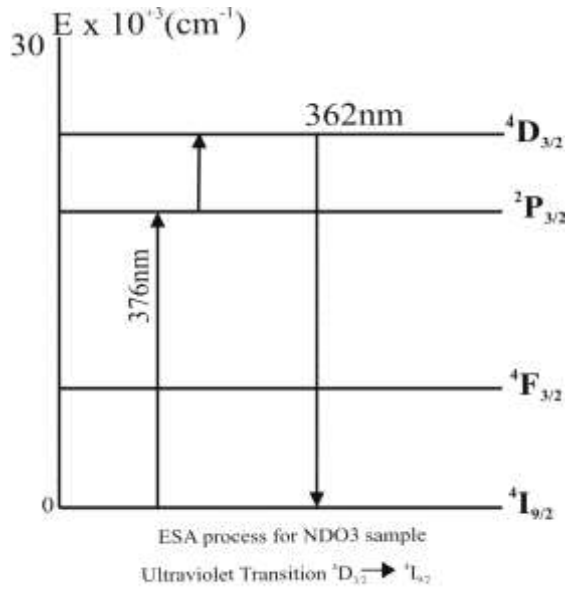


Fig. 1

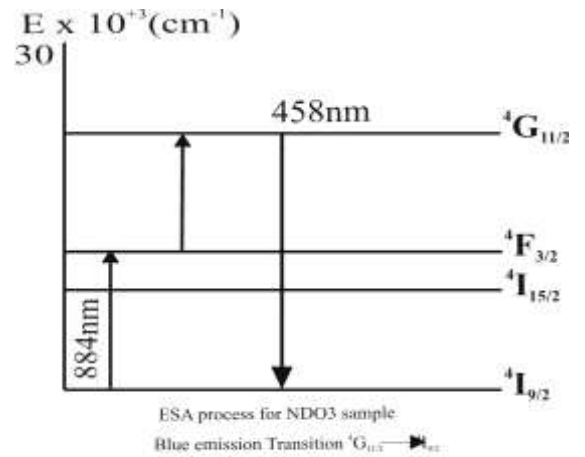
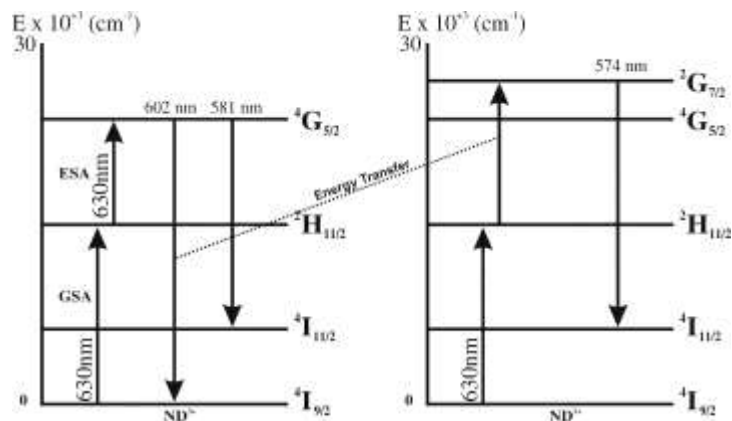


Fig. 2



(ESA + ET) process in NDO3 glass specimen
 Yellow emission for Transition 574 nm (${}^2G_{7/2} \rightarrow {}^4I_{11/2}$)
 581 nm (${}^4G_{5/2} \rightarrow {}^4I_{11/2}$) 602 nm (${}^4G_{5/2} \rightarrow {}^4I_{9/2}$)

Fig.3

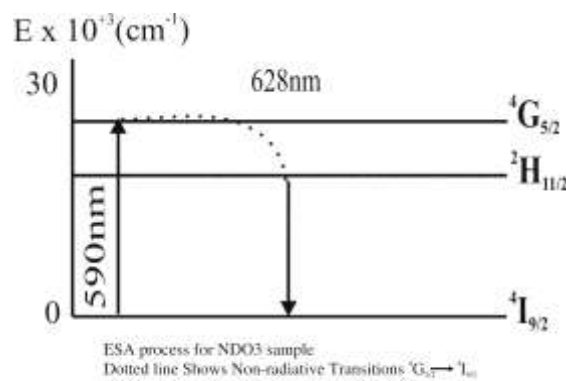
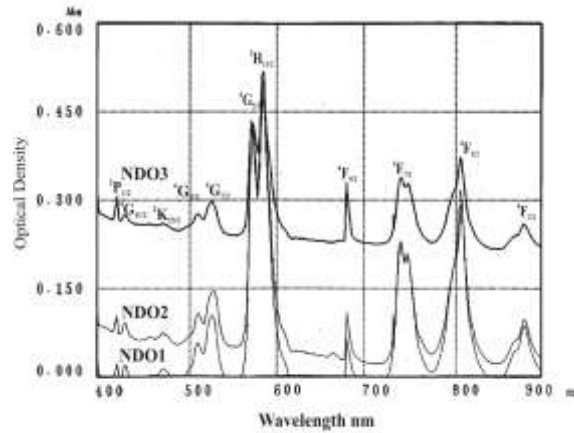


Fig. 4

Fig. 1, Fig. 2, Fig. 3, Fig.4, shows energy level schemes for different transitions in ND03 sample

II. EXPERIMENTAL

The non-crystalline oxide glasses studied in this work were prepared with the following compositions in mol. wt% $(71-x)\text{SiO}_2-20\text{Na}_2\text{O}-6\text{CaO}-1\text{Al}_2\text{O}_3-2\text{B}_2\text{O}_3-x\text{Nd}_2\text{O}_3$ where $x=1,1.5,2$ mol. wt%. The three different glass specimens are termed as NdO1, NdO2 and NDO3 respectively and were prepared using melt quenching technique. The glass specimens were melted in platinum crucible at 1450°C for 4 hours to have maximum optical purity and proper homogeneity. Silicon carbide based globar furnace fitted with Pt-Rh thermocouple. The glasses were cast on to rectangular brass mould and annealed at 500°C to reveal the strain & finally the samples are grounded & polished. The refractive index for NDO1, NDO2, and NDO3 varies as 1.5278, 1.5278 and 1.5267 respectively. Thickness of samples varies between 0.255- 0.257 cm. Optical spectrum in visible region at room temperature was recorded using Sptro Scan 80D/80DV in UV-VIS spectrophotometer in the range 400-900nm.



Absorption spectra for NDO1, NDO2, NDO3 Glass specimens

Graph 3(a)

The fluorescence upconversion was recorded using Shimadzu RF-530 IPC instrument. The fluorescence spectrophotometer irradiates the sample with excitation light & measures the fluorescence emitted from the irradiated sample to perform qualitative and quantitative analysis.

Levels	ν (cm^{-1})	Oscillator Strength $\times 10^{-6}$		Line strength $\times 10^{-20}$	
		f_m	f_{cal}	S_m	S'_{cal}
$^4\text{F}_{3/2}$	11428	0.16	0.54	0.68	0.31
$^4\text{F}_{5/2}$	12391	1.56	1.56	0.30	0.33
$^4\text{F}_{7/2}$	13440	0.40	0.43	2.03	2.16
$^4\text{F}_{9/2}$	14705	2.22	2.21	1.01	1.03
$^2\text{H}_{11/2}$	16949	4.24	4.78	2.49	2.43
$^4\text{G}_{5/2}$	17241	3.52	2.12	1.59	1.47
$^4\text{G}_{7/2}$	19047	0.24	0.55	0.86	0.98
$^4\text{G}_{9/2}$	19417	0.89	0.23	0.35	0.37
$^2\text{K}_{15/2}$	21052	0.46	0.16	0.50	0.52
$^4\text{G}_{11/2}$	21739	0.48	0.24	1.49	1.97
$^2\text{P}_{1/2}$	22988	0.69	0.17	0.19	0.51

$$\sigma_{r.m.s} = \pm 0.45 \times 10^{-6}$$

Table 1 Experimentally calculated oscillator strength and line strength of different transitions for NDO3 glassy matrix

III. RESULTS

A. Spectroscopic Properties

The absorption spectra was recorded for all the three specimens and total eleven bands in range 400-900nm were studied. They have been assigned to various transitions in Graph1(a) by comparing them with the observed bands in the spectra of other oxide glasses[15,16] The position of the observed transitions in the absorption spectrum along with their assignments have been represent in Table1.

These values serves as basis for calculation of line strength and omega parameters. The experimentally determined electric dipole transitions can be related to the integral absorption coefficient by following Eqⁿ (1) as

$$F(J, J') = \frac{8\pi^2 m c v}{3h(2J+1)} \left[\frac{(n^2 + 2)}{9n} \right] \times \sum_{\lambda=2,4,6} \Omega_{\lambda} (\psi J \parallel U^{\lambda} \parallel \psi' J') \quad (1)$$

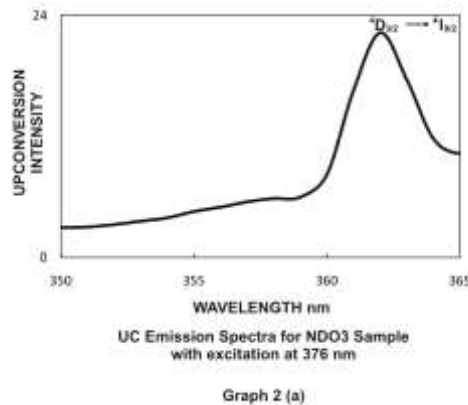
In the above equation m is electron mass, c is velocity of light, h is plank's constant, n is refractive index, v is energy of transition, Ω_{λ} is the Judd-Ofelt intensity parameter to be determined $\|U^{\lambda}\|$ are the doubly reduced squared matrix elements of the unit tensor operator of rank $\lambda= 2,4,6$ calculated from the intermediate coupling approximation of the transition [$\psi J \rightarrow \psi' J'$] where ψJ is the wave function of the ground state represented by $|4 f^n (S, L) J \rangle$ and $\psi' J'$ is the wave function of the corresponding excited state represented by $|4 f^n (S', L') J' \rangle$. Since intensity of various absorption bands in glasses is expressed generally in terms of line strength. Experimental oscillatory strength (f_m) and theoretical oscillatory strength (f_{cal}) have also been expressed in terms of experimental line strength (S_m) and theoretical line strength (S'_{cal}) can be given by Eqⁿ (2)

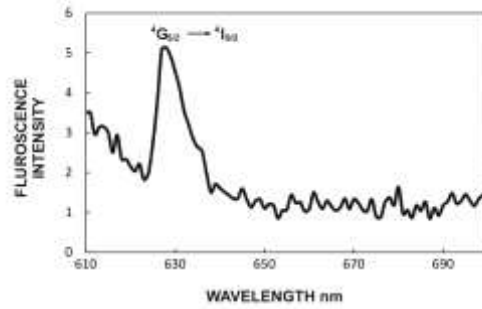
$$S'_{cal} = \sum_{\lambda=2,4,6} \Omega_{\lambda} |4f^n (S, L) J \parallel U^{\lambda} \parallel 4f^n (S' L') J'|^2 \quad (2)$$

In the glass samples studied by us maximum variation is seen in Ω_6 parameter and least variation is seen in Ω_2 parameter (Table 2) when concentration of Nd^{3+} is gradually increased.

λ	NDO1	NDO2	NDO3
2	1.45±0.15	1.72±0.21	2.58±0.21
4	2.38±0.26	3.79±0.38	3..18±0.32
6	4.38±0.23	5.42±0.33	3.79±0.19

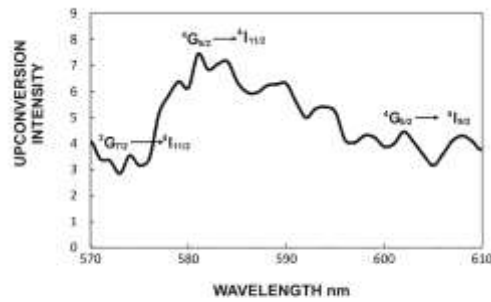
Table 2 Judd-Ofelt intensity parameter of different doping concentration of soda lime silicate glass specimen's $\Omega_{\lambda} \times 10^{-20} \text{ cm}^2$





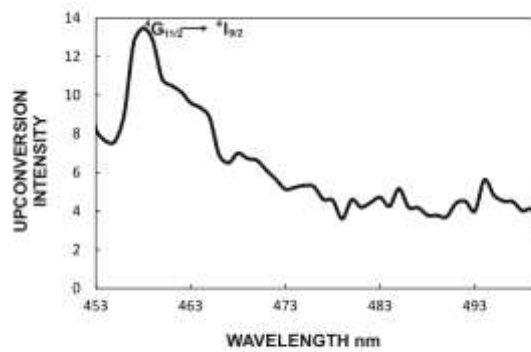
Excitation Spectra for NDO3 Sample at wavelength 590 nm

Graph 2 (b)



UC Emission Spectra for NDO3 Sample with excitation at 630 nm

Graph 2 (c)



UC Emission Spectra for NDO3 Sample with excitation at 884 nm

Graph 2 (d)

B. Fluorescence Properties

Up conversion and emission spectra obtained at different excitation wavelength are shown in the Graph 2(a),2(b),2(c),2(d) respectively. Fig.1, Fig.2, Fig.3, Fig.4 shows energy level diagrams of ND03 sample and the main pathways responsible for upconversion processes.

In the ND03 sample (Graph2 (d)), with excitation at near infrared region $\lambda=884\text{ nm}$ we get peak at 458nm. The mechanism involves absorption of two photons in NIR with blue emission before coming to ground state. Thus the UC process involved here is an ESA i.e. excited state absorption Fig.2 and transition assigned to it is (${}^4G_{11/2} \rightarrow {}^4I_{9/2}$).

The observed UC emission in ND03 sample (Graph 2(c)) is simply due to sequential two photon absorption plus energy transfer between Nd^{3+} ions. Fig3, depicts initial ground state absorption (GSA) of 630nm photon (${}^4I_{9/2} \rightarrow {}^2H_{11/2}$), the electron has a chance to absorb a second photon via. (ESA) and get excited to ${}^4G_{5/2}$ state and the electron then decays radiatively to ${}^4I_{11/2}$ with 602nm emission and an additional 581nm

emission (${}^4G_{5/2} \rightarrow {}^4I_{9/2}$) takes place. Now that the level ${}^2H_{11/2}$ is much more populated, so energy transfer between two Nd^{3+} ions to ${}^2G_{7/2}$ levels with yellow emission at 574nm to ${}^2I_{11/2}$ level takes place.

Another upconversion, with excitation spectra at $\lambda=376nm$ corresponds to emission centered at 362nm (Graph 2(a)) in the ultraviolet region (Fig.1). The transition assigned for NDO3 sample is (${}^4D_{3/2} \rightarrow {}^4I_{9/2}$), with two photon absorption and emission in UV region.

As it is seen in (Graph 2(b)) excitation spectra at $\lambda=590nm$ we get a weak non-radiative transition with emission in visible region at 628 nm. In this respect the transition (Fig.4) assigned to it is (${}^4G_{5/2} \rightarrow {}^4I_{9/2}$) for NDO3 glassy matrix. Though the absorption band of Nd^{3+} around 680 nm does not appreciably interact with the incident light at 590nm so, this confirms the spectrum to be an ESA. It is seen that the emission intensities first increase with increase in doping concentration and then decrease for all the excitation wave length.

DISCUSSIONS

Line strength, r.m.s. deviation and omega parameter were calculated, value of omega parameter $\Omega_{\lambda} (\lambda=2,4,6)$ shows variation as $\Omega_6 > \Omega_4 > \Omega_2$ in all the three glass specimens. Minimum value of r.m.s. deviation indicates the validity of our calculations.

Optical absorption and fluorescence spectra of Nd^{3+} doped sodalime silicate glass with Na_2O as primary modifier, CaO as secondary modifier and Al_2O_3 as an intermediate have been studied in the UV/VIS/NIR region. Addition of Al_2O_3 in the present glass specimens decreases covalency of Nd-O bond indicated by increase [17] in the coulomb interaction between the central rare earth ion and its surrounding oxygen made available by $[SiO_4]$ tetrahedral. Further more Al_2O_3 improves the quality of glassy matrix and also increases its conductivity [18,19].

Energy transfer rates among different concentration of Nd^{3+} ions were estimated from the analysis of temporal behavior of the frequency up conversion process. In the low doping level glasses it is seen that upconversion emission involving two photons can be observed but processes with three photons are negligible [4], similar results have been obtained in our case.

IV. CONCLUSION

The analysis of data reveals the fact that observed increase in value of Ω_6 parameter shows decrease in the covalency between Nd^{3+} ions surrounding oxygen atoms provided by $[SiO_4]$ tetrahedral. The reason for this being the presence of $[AlO_4]^{3-}$ tetrahedral in the second coordination sphere of the central Nd^{3+} ion. In conclusion, we observe that ET plus ESA is responsible for yellow emission and ESA for UV and blue emission under laser excitation. The result were described using transition rate equations for different levels. The upconversion emission in visible region at 574nm transition (${}^2G_{7/2} \rightarrow {}^4I_{11/2}$) in yellow spectral region and emission at 458nm in blue spectral region transition (${}^4G_{11/2} \rightarrow {}^4I_{9/2}$) in all the three doping concentration indicates suitability of the material for its use in the development of laser and EL devices.

ACKNOWLEDGEMENT

Our sincere thanks to Dr. R.P. Tripathi, Head, Deptt. of Physics J.N.V. University, Jodhpur for his guidance and Dr. K.V.R. Murthy, Faculty of Technology & Engineer M.S.University, Baroda for providing the fluorescence spectra measurement facilities.

REFERENCES

- [1] A.A. Kaminskii, V.S. Mironov S.N. Bagaev, Phys. Status solidA. 48, K107(1995).
- [2] A. Biswas, G.S. Maciel, R. Kapoor, C.S. Friend, P.N. Prasad Appl. Phys. Lett. 85, 2389 (2003).
- [3] E. Brown, U. Hommerich, A.G. Blwiett, S.B. Trivedi J.M. Zavadar J. of Applied physics 101, 113103(2007).
- [4] J. Mendez-Ramos, M. Abrill, I.R. Martin U.R. Rodringez-Mendoza, V. Lavin, and V.D. Rodrignez, P. Nunez and A.D. Lozano-Gorin, J. of Applied Physics 99, 113510(2006).
- [5] Marconi J.S. Brandao and Cid B. de Araeyo Gael Poirier and Younes Messaddeq. M. Poulain J. of Applied physics 99,113525 (2006).
- [6] X. Zou, T. Lzumitani, J.Non Crystalline Solids 162,68(1993).
- [7] H. Yamada, K. Kojima, J. Non-Crystalline solids 259,57 (1999).
- [8] Y.K. Sharma, S.S.L. Surana, R.K. Singh, R.P. Dubedi, Optical Materials 29 (2007) p.598-604.
- [9] H. Lin. E.Y.B. Bun, X.R. Liw, J. Non Crystalline Solids 283, 27 (2001).

- [10] S. Jiang, T. Luo, B. Hunng, G. Nunzi Conti, M. Mycrs D. Rhonehouse, S. Honhanen, N. Peyghambarian, *Opt. Eng.* 37,3282 (1998).
- [11] D.L. Veasey, D.S. Funk., N.A. Sanford, J.S. Hayden *Appl. Phys. Lett.* 74,789 (1999).
- [12] J. Yang, S. Dai, N. Dai, L. Wen, L. Hu, Z. Jiang, *J. Lumin* 106 ,9(2004).
- [13] H. Takebe, Y. Nageno, and K. Marinaga, *J. Am. Ceram. Soc.* 78 ,1161(1995).
- [14] M.B. Sai Sudha and J. Ramakrishna, *Phys. Rev. B* 53, 6186 (1996).
- [15] M.J. Weber, D.C. Ziegler and C.A. Anjell, *J. Appl. Phys.*, 53 , 4344(1981).
- [16] R. Reisfeld, M. Eyal and D. Brusilovsky, *Chem. Phy. Lett.* 153 ,210(1988).
- [17] A. A. Dymnikov, O.S. Dymshits, A.A. Zhilin, V.A.Savostjanov, T. I. Chuvaeva, *J. Non-Cryst. Solids* 196 ,67(1996).
- [18] Naftaly M and Jha A, *J. Appl Phys* 87 ,2089(2000).
- [19] Yasi J., Shibin J., Yanyan J, *J. of Non- Cryst. Solids* 112, 28 (1989).