# $Nd^{3+}$ Ions doped OxyChalcogenide Glass-Ceramics Containing Low-Phonon Energy Nano Crystals

**Dr. Sudhir Kumar Mishra,**

Principal,
S.S. College, Jehanabad,

*Abstract*: **OxyChalcogenide glass–ceramics containing rare earth have been studied. Photoluminescence of rare earth has been greatly increased in glass–ceramics. The frequency conversion phenomenon was observed for glass and glass ceramic samples with excitation using Nd:YAG laser operating at 1064 nm. the upconversion phenomena are expedited by the low multiphonon relaxation rate in oxychalcogenide antimony glasses owing to their low phonon energy.**

***Keywords: OxyChalcogenide Glass, Glass-Ceramic, Rare earth, Up-Conversion, Low-Phonon Energy***

## Introduction

The RE ions doped transparent glasses and glass-ceramics are One of the compounds which had used as active media of solid state lasers and optical fiber amplifier and other optical and laser components [1-4]. Among the rare earth ions, $Nd^{3+}$ ions in different host matrices widely have been studied and reviewed. Recent spectroscopy results show that $Nd^{3+}$ doped glass ceramics has become a good host for up-convertor lasers [5].

Chalcogenide glasses have been considered as promising hosts for rare-earth (RE) doped photonic devices such as lasers, optical amplifiers, up convertors and broad band sources [4] and for applications in the mid-infrared spectral range.[7], due to their low maximum phonon energy, and the resulting low non-radiative quenching of fluorescence transitions, high refractive index of sulphide-based glasses and IR transparency [8]. Antimony oxide ($Sb_2O_3$)-based glasses are also expected to have lower phonon energies due to lower stretching vibration of Sb–O–Sb bond ($605cm^{-1}$) [9]. The upconversion efficiency increases with decrease in nonradiative loss due to multiphonon relaxation. Improvement of the upconversion efficiency by employing different hosts has been subject of persistent research [10].

## Experimental

The base glasses was synthesized from high purity of $P_2O_5$ (Merk), $B_2O_3$ (Merk), $Sb_2O_3$ (Loba Chemie), $SbCl_3$ (Loba Chemie), $Na_2S_2O_3$, $Nd_2O_3$ (Merk) in its metallic form as starting materials. Appropriate quantities of each compound were weighed according to the glass formula and introduced into a alomina crucible. The mixture was heated (2 h) to 1100°C, cooled to room temperature and annealing near the glass transition temperature (350°C).

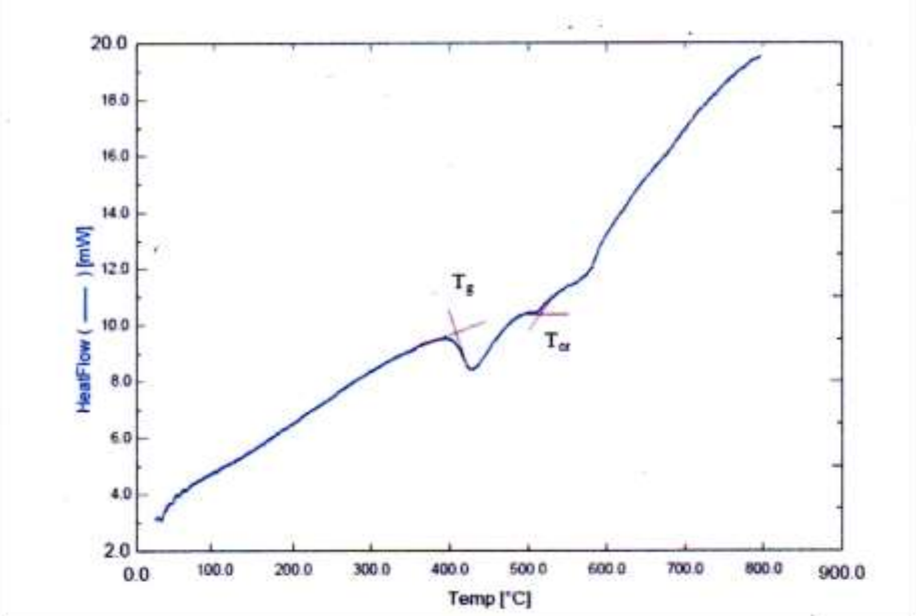


*Fig. 1. DTA curves of the base glass between 100ºC and 800ºC*

Glass samples were prepared by the melt-quenching technique. Compositions of the glasses were $40P_2O_5\text{-}12B_2O_3\text{-}27Na_2S_2O_3\text{-}20SbCl_3\text{-}1Nd_2O_3$ and $40P_2O_5\text{-}12B_2O_3\text{-}27Na_2S_2O_3\text{-}20Sb_2O_3\text{-}1Nd_2O_3$ in mol% for the PL measurements. The Glass transition temperatures that forecasted by experimental and (DTA) methods are about 420°C for chloride and oxide glasses. Fig. 1 shows the DTA curve of the base glass between 100°C and 800°C. The glass transition is observed at 420°C. crystallization temperature are located at 540°C. All ceramization tests have been done at temperatures below 540°C in order to avoid uncontrollable crystal growth. The chloride and oxide glass ceramics were obtained by heat treatment of initial glass at 490°C for 24h respectively. X-ray diffraction data of studied samples indicated the mean size of $Sb_2O_4$ crystals that had grown inside glass phase is 20 nm.

Optical transmission of glass–ceramics was measured by using a CARY5 double-beam spectrophotometer (Varian, Palo Alto, USA) that operates in the 200–1100 nm optical range. Emission spectra of samples were obtained with excitation at 265 nm, 353 nm and 531 nm. The emission spectra show emission band centered around 1060 nm corresponding to the electronic transitions from the 4F3/2 level to the level 4I11/2. It can be observed that the most intense emission band is located at 1060 nm for the glass–ceramics and for the base glass, but peak intensity in glass–ceramics are up to five times higher compared to the base glass.

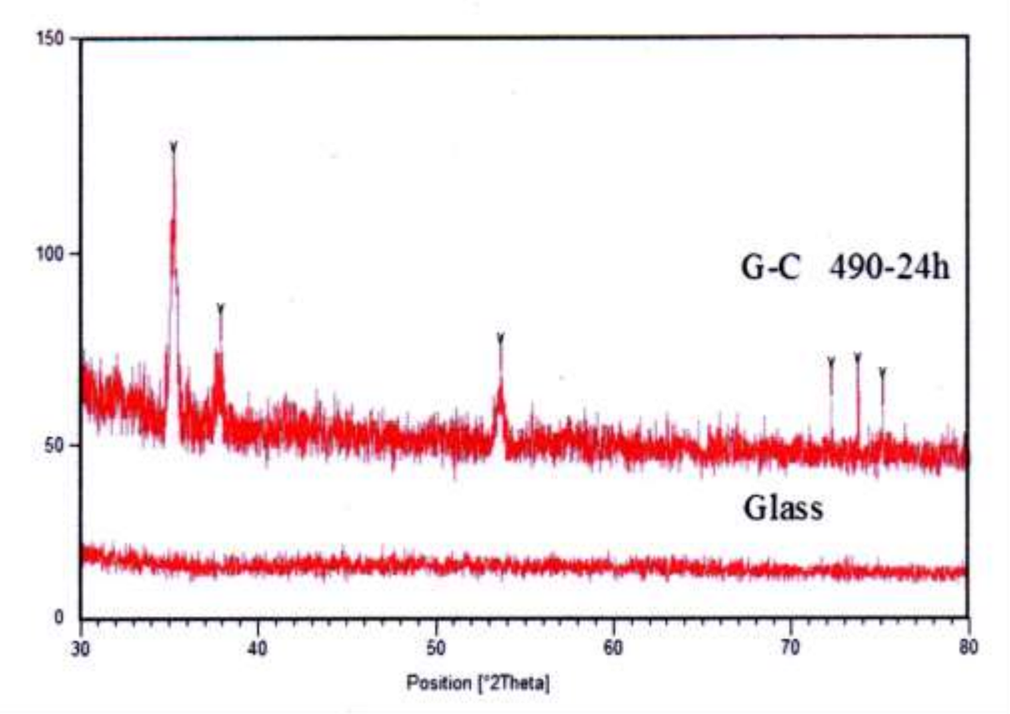


***Fig. 2. Patterns of Nd-doped glass and glass-ceramic treated at the $T_g$ temperature***

Fig. 3 presents the absorption spectrum of $Nd^{3+}$ ions doped base glass and glass ceramic. From this spectrum, absorption bands at 474, 514, 528, 585, 682, 748, 804 and 872 nm are observed, which could be ascribed to $Nd^{3+}$ transitions: ${}^4I_{9/2}\rightarrow{}^2D_{3/2} + {}^2G_{9/2}$,${}^4I_{9/2} \rightarrow {}^4G_{9/2}+{}^2K_{13/2}$ ‘ ${}^4I_{9/2} \rightarrow {}^4G_{7/2}$ ‘${}^4I_{9/2} \rightarrow {}^4G_{5/2} + {}^2G_{7/2}$ ‘ ${}^4I_{9/2}\rightarrow{}^4F_{9/2}$ ‘${}^4I_{9/2} \rightarrow {}^4F_{7/2} + {}^4S_{3/2}$ ‘${}^4I_{9/2} \rightarrow {}^4F_{5/2}+{}^2H_{9/2}$ ‘${}^4I_{9/2} \rightarrow {}^4F_{3/2}$.
Also, the absorption spectrum of $Nd^{3+}$ ions doped glass and glass ceramics showed that both glass and glass ceramic has nice transparency in near infrared and visible wavelengths. The maximum wavelength of absorption taken at 810 nm and 585 nm. As expected, the shapes and positions of the bands are similar to other $Nd^{3+}$-doped glasses. [11,12,13].

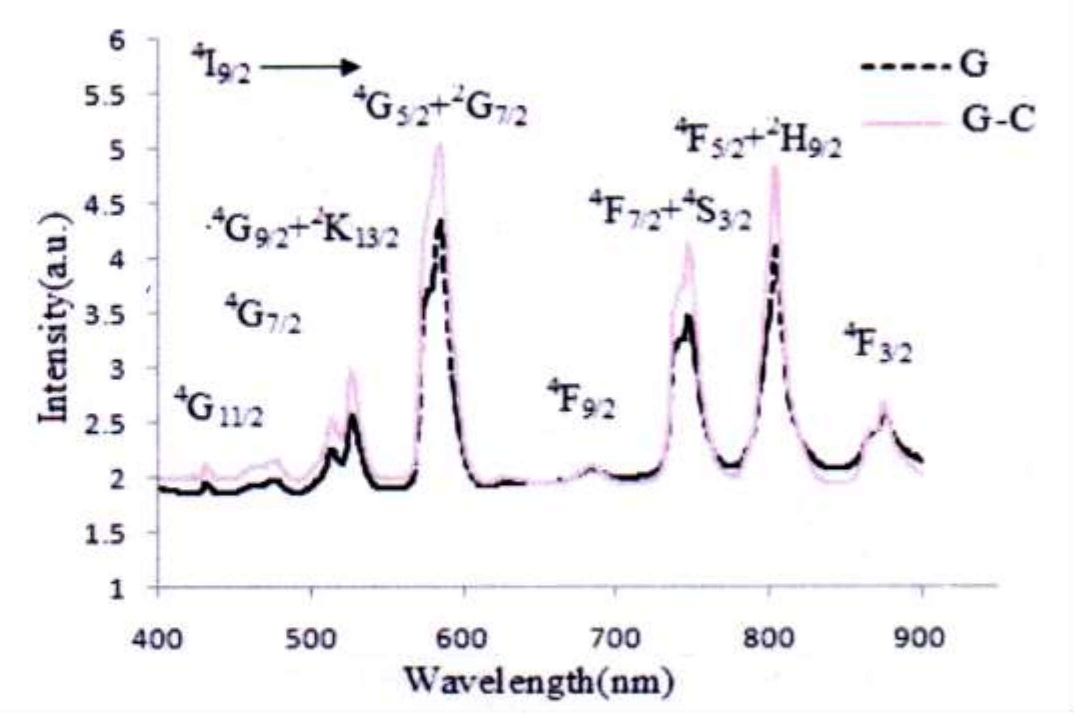


*Fig. 3. Absorption spectrum of 1mol% Nd$^{3+}$ ions doped glass ang glass ceramic.*

Fig. 4. shows the excitation spectrum of Nd$^{3+}$ ions doped glass, monitoring emission at 1064 nm. A sharp excitation peak at 353 nm has been obtained from the glass sample. This excitation band coincides with the absorption transition of Nd3+-doped glass. Two additional excitation bands at 265 and 531 nm have also been observed.

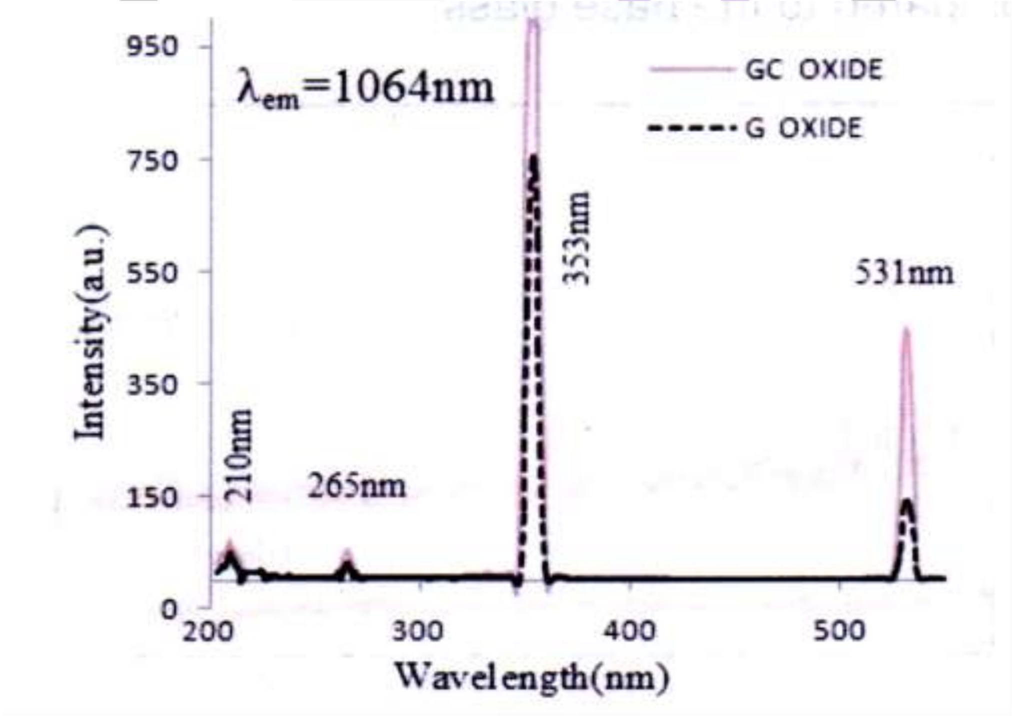


*Fig. 4. Excitation spectrum of 1mol% Nd3+ ions doped glass.*

Emission measurements, performed for the glass and glass–ceramics with excitation at 531 nm, are presented in Fig. 2.

It can be observed that the most intense emission band is located at 1064 nm for the two series of glass–ceramics and for the base glasses, but peak intensity in glass–ceramics are up to five times higher compared to the base glass.

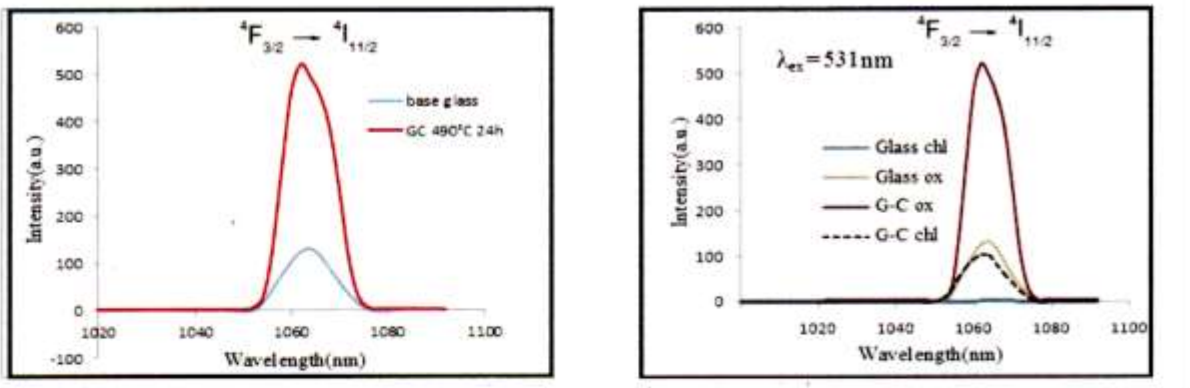
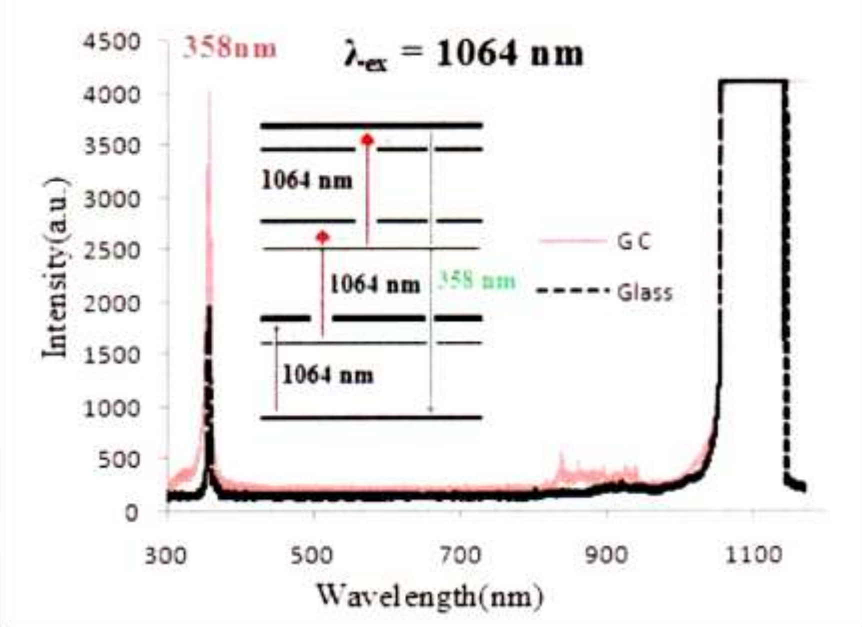


*Fig. 2. Emission spectra under 531-nm excitation of glasses and glass-ceramics*



The frequency conversion phenomenon was observed for glass and glass ceramic samples with excitation using Nd:YAG laser operating at 1064 nm.

***Fig. 4. Upconversion fluorescence spectra of 1.0 (mol%) $Nd_2O_3$-doped glasses and glass ceramics upon excitation at 1064nm radiation.***

**Discussion**

In this work, a new oxychalcogenide antimony-based glass system doped with RE (here $Nd^{3+}$) ions has been developed and its fluorescence upconversion phenomenon in the visible region has been studied. Photoluminescence efficiency has been greatly improved in glass–ceramics by the presence of low phonon energy nano crystals and the narrowing of the $Nd^{3+}$ emission lines can suggest that the rare-earth ions are incorporated in the nano crystals.

**Acknowledgments**

The author would greatly like to thanks to Prof. R.P.S. Chauhan, Rtd. HOD, Deptt. Of Chemistry, M.U., Bodh Gaya, Prof. Sanjay Kr. Asso. Prof., Deptt. Of Chemistry, Jagdam College, Chapra, Prof. Rabindra Singh, HOD, Deptt. Of Chemistry, J.P.U., Chapra for their generous support and Technical helps accordingly.

**References**

1. Y. Hatefi, N. Shahtahmasebi, A. Moghimi and E. Attaran,"*Frequency-conversion properties of Eu3+ doped chlorophosphate glass ceramics containing CaCl2 nanocrystals*", Journal of Luminescence **131** (2011) 114–118.
2. Yunlong Yu, Daqin Chen, Yuansheng Wang, Feng Liu, En Ma., Journal of Non-Crystalline Solids **353** (2007) 405–409.
3. Y. Hatefi, N. Shahtahmasebi, A. Moghimi and E. Attaran,"*Ultraviolet to visible frequency-conversion properties of rare earths doped glass ceramics*", Journal of rare earthes, **29** (2011) 484-488.
4. Fu J. Parker J. M, Flower P. S , Brown R. M., Materials Research Bulletin **37**(2002) 1843-1849.

5. A. Wojciech, J. Pisarska, R. Lisiecki, L. Grobelny and G. Dominiak-Dzik and W. Ryba-Romanowski, Optical Materials **31** (2009) 1781–1783.
6. T. Schweizer, D.W. Hewak, D.N. Payne, T. Jensen, G. Huber,"*Rare-earth doped chalcogenide glass laser*", Electron. Lett. **32** (1996) 666.
7. T. Schweizer, B.N. Samson, J.R. Hector, W.S. Brocklesby, D.W. Hewak, D.N. Payne," *Infrared emission and ion–ion interactions in thulium- and terbium-doped gallium lanthanum sulfide glass*", J. Opt. Soc. Am. B **16** (1999)308.
8. N.F. Mott, E.A. Davis,"*Electronic Processes in Non-Crystalline Materials*", Clarendon, Oxford, 1979 (Chapter 9).
9. P.J. Miller, C.A. Cody, Spectrochim. Acta A 38 (1982) 555.
10. S. Tanabe, J. Non-Cryst. Solids 256/257 (1999) 282.
11. M.J. Weber, J.D. Myers, D.H. Blackburn, J. Appl. Phys. 52 (1981) 2944.
12. Z.H. Jiang, J.H. Yang, S.X. Dai, J. Opt. Soc. Am. B 21 (2004) 739.
13. K.U. Kumar, V.A. Prathyusha, P. Babu, C.K. Jayasankar, A.S. Joshi, A. Speghini, M. Bettinelli, Spectrochim. Acta A 67 (2007) 702.