Synthesis and optical characterization of Nd^{3+} doped $Na_2O–TeO_2–ZnO$ glass

M N Goswami
Department of Physics, Midnapore College, Midnapore-721 101, West Bengal, India**,** email:makhanlal@gmail.com

ABSTRACT

Nd_2O_3 was incorporated into $Na_2O–TeO_2–ZnO$ glass by a melting method in air atmosphere. The absorption and photoluminescence spectra of the transparent glasses, was studied. The measurement of optical properties was obtained by using a double beam optical spectrophotometer with an integrating sphere in the wavelength range 300 to 1100 nm. The absorption characteristics of Nd^{3+} doped samples clearly revealed the absorption due to Nd^{3+} ions. On the other hand the samples showed enhanced absorption due to ${}^4F_{7/2} \rightarrow {}^4F_{5/2}$ transition. The absorption and emission cross section for ${}^4F_{7/2} \rightarrow {}^4F_{5/2}$ of Nd^{3+} were estimated. Results of absorption, emission and fluorescence lifetime (for the ${}^4F_{3/2}–{}^4I_{9/2}$ transition) were presented for the prepared glass doped with 1 wt% concentrations of Nd_2O_3. Also the results of the investigations with essential discussions and conclusions have been reported here in this paper.

Introduction

Rare earth doped oxide glasses possessing high chemical durability and thermal stability are excellent materials for optoelectronics applications [1–4]. Silica bases glasses doped with rare-earth (RE) ions are of interest for various applications including solid state lasers, optical waveguides and fibre amplifiers. The main characteristics of spectroscopic transition involving RE ions are long lifetime of metastable states (ranging from

Advanced Journal of Basic & Applied Sciences,
Appearance Issue: Vol. 1, No.1
Published on 2nd August, 2022

tens of microsec to a few millisec) and narrow absorption and emission lines in the near infrared regions. They have a large potential for applications in some optical fields such as Faraday rotator, phosphors, electroluminescent, detectors of two-dimensional image of radio rays, tunable laser in the wavelength region from violet to blue and high-density optical storage [5-9]. It is to be mentioned that it is very difficult to prepare REs doped silica glass by the conventional technique involving the quenching of an oxide melt due to the high melting temperature of SiO_2. Not only have that, but also in the preparation glassed through sol-gel technique high concentration of hydroxyl groups that remain in sol–gel glasses is a disadvantage of the sol–gel method as it decreases the fluorescence efficiencies and shorten luminescent level lifetimes of dopant ions in glasses, adversely affecting optical device performance [10,11]. Techniques leading to the low hydroxyl sol–gel glasses include high temperature treatment in the presence of carbon tetrachloride [10], inclusion of hydrofluoric acid in the initial solution [12] and heat treatment in different atmospheres (oxygen, vacuum, carbon tetrachloride and helium) [13]. The other problem associated with sol–gel process is RE ions clustering [14], leading to concentration quenching of luminescence through cross-relaxation or energy transfer process. Glasses based on tellurite attract much attention from both fundamental and applied research. Unlike other oxide glasses such as silicate and borate ones in structure, tellurite glasses are composed of asymmetrical structural units, such as TeO_4 trigonal bipyramid, and TeO_3 trigonal pyramid [15,16]. Heavy metal oxide glasses and tellurite glasses are considered to be promising glass hosts for photonic devices [17,18]. Heavy metal oxide glasses and tellurite glasses are also considered to be better glass hosts for developing visible upconversion devices among oxide glasses [19,20]. Heavy metal oxide glasses and tellurite glasses may be better hosts because of their resistance to devitrification by absorbing moisture combined with high refractive index, which enhances radiative transitions in rare earth ions.

In the present work, Nd^{3+} doped Na_2O–TeO_2–ZnO glasses suitable for making optical devices has been fabricated and characterized.

Experimental

The glasses were prepared from high purity chemicals sodium carbonate (Na_2CO_3), tellurium oxide (TeO_2), zinc oxide (ZnO) and Neodymium oxide (Nd_2O_3) powders according to the molar composition: 10%Na_2O, 70% TeO_2, 20% ZnO. The glasses were doped with 1.0 wt% of Nd_2O_3. The well-mixed raw materials were melted at 910℃ in a platinum crucible for 1hr using an electric furnace, and then the melts were poured onto a smooth surfaced stainless steel plate and pressed with another similar plate in order to obtain a few circular glass discs of 3 cm in diameter with a thickness of 0.2 cm each and quenched to room temperature. These samples were annealed at 450 ^{0}C for 4 h and cooled down slowly to the room temperature to remove internal stresses present in the glass samples.

Transparent, crack and bubble free rare-earth doped glasses were thus prepared reproducibly. Optical measurements of the doped glass sample were carried out using the sample dimension 1.5 cm x 1.2 cm x 0.2 cm. The density of the sample was measured to be 4.76 gm/cc; hence the number density of Nd^{3+} ions in this doped glass was 2.08 x 10^{20} cm^{-3}. The measurement of optical absorption spectrum was obtained by using with a Perkin–Elmer UV/VIS/NIR (Lambda -35) a double beam optical spectrophotometer with an integrating sphere in the wavelength range 300 to 950 nm. Photoluminescence (PL) spectra of samples were recorded using 325 nm He-Cd laser source with a power density of 1.5 W/cm^2. All measurements were made at room temperature.

Fig.1 Photograph of melt calcined sample

Results and Discussions

Visual Characteristics

All the doped glass samples were transparent (Figure-1). The color of the samples depends mainly on the concentration of dopants.

Absorption Spectra

Figure 2 shows the absorption spectra (300–1100 nm range) of 1.0 mol% Nd_2O_3 doped Na_2O–TeO_2–ZnO glasses annealed at 450°C. All the absorption peaks correspond to the atomic transitions of Nd^{3+} ions. The spectrum is similar to the one reported earlier [21] for Nd^{3+} doped glass sample. The different transitions of Nd^{3+} from the ground state $^4I_{9/2}$ to excited states are given in Table-1.

From the Lambert-Beer dependency, the absorption cross-section of the $^4F_{7/2} \rightarrow {}^4F_{5/2}$ transition of Nd^{3+} ions have been determined from the

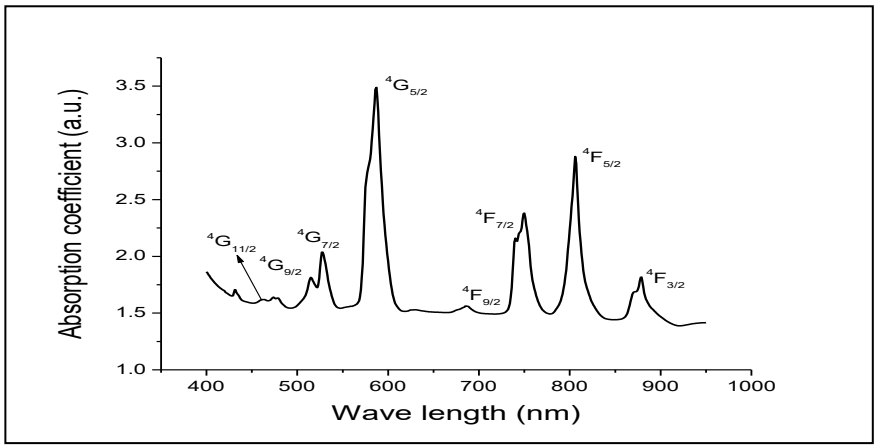

Fig. 2 The variation of optical absorption coefficient versus wavelength for the transparent Nd^{3+} doped Na_2O–TeO_2–ZnO glass material

absorption spectra using the formula:

$$\sigma_{ab}(\lambda) = 2.303 \log(I_0/I)/(Nt), \quad (1)$$

where $\log(I_0/I)$ is absorbance, t the sample thickness, and N the Nd^{3+} ion (ions/cm^3) concentration. There are number of ways [22-24] by which

emission cross sections can also be determined. According to MaCumber theory [23], for a two-level system imbedded in a medium at temperature *T*, typical equations connecting stimulated-emission and absorption cross sections $\sigma(\lambda)$to the rate $f(\lambda)$ of spontaneous emission of photons per unit solid angle per unit frequency interval are:

Table 1. Absorption band positions of Nd^{3+} ions in the wavelength range 300–950 nm

Level transition from the ground state, $^4I_{9/2}$ to	Wavelength (nm)
$^4G_{11/2}$	430
$^4G_{9/2}$	514
$^4G_{7/2}$	527
$^4G_{5/2}$	585
$^4F_{9/2}$	686
$^4F_{7/2}$	748
$^4F_{5/2}$	806
$^4F_{3/2}$	878

$$\sigma_{em}(\lambda) = \sigma_{ab}(\lambda) \exp[(E - hc/\lambda)/kT], \quad (2)$$

where, E is the net free energy required to excite one Nd^{3+} from $^4F_{7/2}$ to $^4F_{5/2}$ state at temperature *T*, *h* the Planck's constant, and *k* the Boltzmann constant.

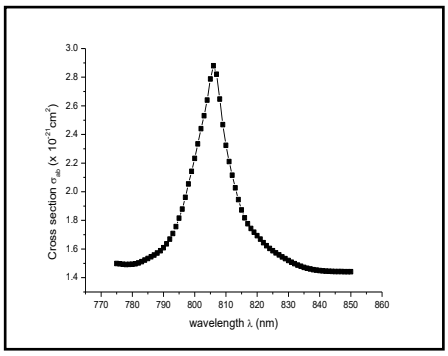

Fig.3 The absorption cross-section spectra for 1.0 mol% of Nd_2O_3 doped Na_2O–TeO_2–ZnO

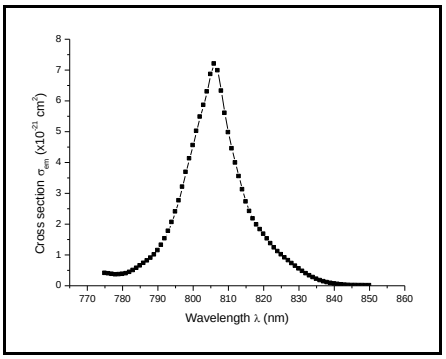

Fig.4 The emission cross-section spectra for 1.0 mol% of Nd_2O_3 doped Na_2O–TeO_2–ZnO glass

Figures 3 and 4 illustrate the calculated absorption and emission cross-sections for the $^4F_{7/2} \rightarrow {}^4F_{5/2}$ transition of Nd^{3+} ions in Na_2O–TeO_2–ZnO glasses. The calculated absorption and emission cross-section values of $\sigma_{ab}(\lambda)$ and $\sigma_{em}(\lambda)$ are shown in figures 3 and 4. The values of cross-

sections are larger than the previously reported fluoride glasses [21] and zinc boro-silicate glass [25].

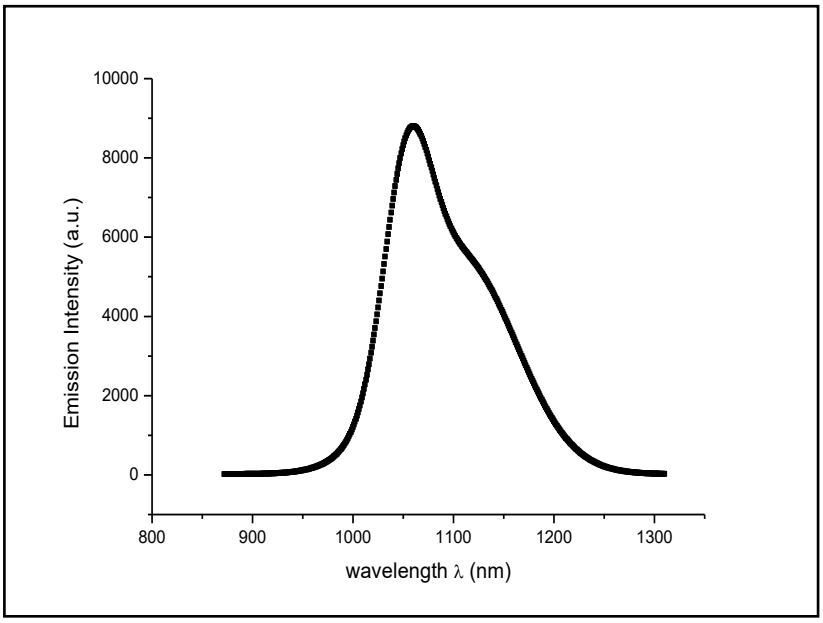

Fig. 5 The plot of Photoluminescence (PL) intensity versus wavelength of the transparent Nd^{3+} doped $Na_2O–TeO_2–ZnO$ glass

Room temperature photoluminescence spectra of the Nd^{3+} doped glass sample are presented in figure 5. A strong and sharp PL peak around 1.06 μm is observed for the sample. The intensity of 1.*06* μm luminescence due to Nd^{3+} ions is strongly enhanced in the presence of Na_2O. It is known that the emission at 1.06 μm originates from the transition of the excited $^4F_{3/2}$ to the ground state $^4I_{11/2}$. The strong enhancement of Nd-induced PL emission can be attributed to the absorption by TeO_2 semiconductor may be followed by an energy transfer from a trapped exciton to a nearby Te atom. The origin of 1.06 μm luminescence may be attributed to a mechanism that involves energy transfer from the excited Te atom to the rare earth ions. The mechanism of energy transfer from Te atoms to rare earth ions may be due to non-optical dipole–dipole interaction, similar to Forster mechanism applied in energy transfer from nanocrystals to rare earth ions in silica matrix [26]. The results strongly support the assertion

that indirect excitation via Te atoms plays a significant role in the luminescence due to Nd ions in an oxide glass matrix. The appearance of a shoulder around 1.12 μm in the emission spectra is not clear at this moment.

Conclusion

The possibility of synthesizing optical quality crack and bubble free Nd^{3+}: Na_2O–TeO_2–ZnO glasses doped with rare-earth ions by melting oxide melting technique have been demonstrated. Optical properties of the prepared glasses have been investigated from the measurement of absorption, emission spectra. A prominent and strong emission at 1060 nm has been observed from it with an excitation at 325 nm He-Cd laser source with a power density of 1.5 W/cm^2. From our results, we found that the Neodymium doped tellurite based glass has a good potential application as laser materials of NIR luminescent optical glass. It can also be concluded that that the high concentration of Na_2O is a benefit to developing waveguide device from the glass for the particular application of emitted wavelength 1060 nm.

Acknowledgements

This work was supported by the University Grant Commission of India as minor research project (Grant No. PSW-129/13-14).

References

1. M L Baesso, A C Bento, L C M Miranda, D F de Souza, J A Sampaio and L A O Nunes, *J. Non-crystal. Solids* 276[2000] 8
2. R Rolli, K Gatterer, M Wachtler, M Bettinelli, A Speghini and D Ajo, *Spectrochim. Acta* A 51[2001] 2009
3. Hai Lin, Shibin Jiang, JianfengWu, Feng Song, Nasser Peyghambarian and E Y B Pun, J. *Phys. D: Appl. Phys*. 36 (2003) 812–817
4. D Mandal, H D Banerjee, M N Goswami and H N Acharya, *Bulletin of Material Science* 27(4) (2004) 367 - 372

5. J Qiu, N. Sugimoto, K Hirao, J. *Appl. Phys. Lett*. 71 (6) (1997) 759.
6. J Qiu, K. Miura, N Sugimoto, K Hirao, *Phys. Chem. Glasses* 38 (2) (1997) 66.
7. M Nogami, Y Abe, *Appl. Phys. Lett*. 69 (1996) 3776.
8. R A Hewes, M V Hoffman, *J. Luminescence* 3 (1971) 261.
9. M Nogami, T Yamazaki, Y Abe, *J. Luminescence* 78 (1998) 63.
10. J Phalippou, T Woignier and J Zarzycki, 1984 *Ultrastructure processing of ceramics, glasses and composites* (eds) L L Hench and D R Ulrich (New York: Wiley) p. 70
11. A J Berry and T A King, 1989 *J. Phys*. **D22** 1419
12. E J A Pope and J D Mackenzie, 1993 *J. Am. Ceram. Soc*. **76** 1325
13. B J Ainslie, S P Craig and S T Davey, 1988 *J. Lightwave Tech*. **6** 287
14. T Fujiyama, M Hori and M Sasaki, 1990 *J. Non-Cryst. Solids* **121** 273
15. Y Amemiya, K Wakabayashi, H Tanaka, Y Ueno, J. Miyahara, Science 237 (1987) 164.
16. H. Burger, K. Kneipp, H. Hobert, W. Vogel, V. Kozhukharov, S. Neov, J. Non-Cryst. Solids 151 (1992) 134.
17. J Heo, Y B Shin and J N Jang, 1995 *Appl. Opt.* **34** 4284
18. Y Hu, S Jiang, G Sorbello, T Luo, Y Ding, Hwang B-C,
19. J-H Kim, H-J Seo and N Peyghambarian, 2001 *J. Opt. Soc. Am.* B **18** 1928
20. A S Oliveira, M T de Araujo, A S Gouveia-Neto, A S B Sombra, J A Medeiros Neto and N Aranha, 1998 *J. Appl. Phys*. **83** 604
21. F Vetrone, J-C Boyer, J A Capobianco, A Speghini and M Bettinelli, 2002 *Appl. Phys. Lett.* **80** 1752
22. L C Courrola, L R P Kassaba, V D D Cachoa, S H Tatumia, N U Wetter, Journal of Luminescence 102–103 (2003) 101–105
23. D E MaCumber, 1964 *Phys. Rev*. **A134** 299; **A136** 954
24. W Koechner, 1986 *Solid state laser engineering* (New York: Springer) p. 17
25. K Annapurna, R N Dwivedi, P Kundu, S Buddhudu, Materials Letters 57 (2003) 2095– 2098
26. M J A de Dood, J Knoester, A Tip and A Polman, 2005 *Phys.Rev.* B **71** 115102