Optical and Upconversion properties of Nd^{+3} doped lead borate barium glass system

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Abstract: Borate glassy system of the composition $30B_2O_3$ - $30Bi_2O_3$ -$20Li_2O$-10BaO - 10PbO - x Nd_2O_3 mole %, where x = 0, 0.5, 1, 2, 3 and 4, has been prepared by conventional melting quenching method. The non- crystalline nature of the prepared samples was confirmed by X-ray. Density and molar volume of the prepared samples had been measured. Optical parameters, optical band gap, absorption coefficient, refractive index, and upconversion, had been obtained. The prepared blank sample show high transmittance in the range (2500-450 nm), high density (6.3 g/cm^3), wide band gap (2.43 eV) and high refractive index (2.70). The spectra show seven absorption bands located at 872, 806, 750, 684, 586, 528 and 516 nm which is originates from the transition from the ground to the exited states $^4F_{3/2}$, $^4F_{5/2}$, $^7F_{7/2}$, $^4F_{9/2}$, $^2H_{11/2}$, $^4G_{7/2}$ and $^4G_{9/2}$ respectively. Using 800 nm as excitation wavelength; four upconversion bands centered at 730, 716, 700 and 540 nm were observed. The bands corresponding to the transitions $^4F_{7/2} + {}^4S_{3/2} \longrightarrow {}^4I_{9/2}$, $^4F_{7/2} + {}^4S_{3/2} \longrightarrow {}^4I_{9/2}$, $^4F_{9/2} \longrightarrow {}^4I_{9/2}$ and $^4G_{7/2} \longrightarrow {}^4I_{9/2}$, respectively. [Farag MA, Abd-Allah K, Turky G and Alokr MM. **Optical and Upconversion properties of Er^{+3} doped lead borate barium glass system**. *Nat Sci* 2015;13(5):123-129]. (ISSN: 1545-0740). http://www.sciencepub.net/nature. 17

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1. Introduction

In the last decades the humanity faces a lot of challenges; Energy is the most critical one because of the depletion of conventional energy sources such as fossil fuel. One of the most suitable solutions is the renewable energies especially solar energy conversion systems due to the availability of the solar energy, reduction of the cost over time and it will last for millions of years in the future.

Solar cell (SC) is an easy direct way to transfer solar energy into electricity. However, many applications of SC in different fields are suppressed by the low efficiency of solar cells. The considered losses in the solar cell originated from the spectra mismatch between the incident solar spectra and its bandgap. One of the ways to overcome or reduce this mismatch is by applying an upconversion layer to the rear of solar cell. This layer reduces the transmitted low energy photons converting them into absorbable high energy photons hence, increases the efficiency of the solar cell [1].

Finding the suitable host material is one of the main aspects to develop these layers to increase the upconversion efficiency. Glasses are one of the preferred host materials due to its stability, the capability of easy shaping and transparency [2].

High-phonon energies in conventional oxide glasses, corresponding to the different vibrations of the oxide glass network former, limits the upconversion phenomenon in these glasses. However, it has attractive properties such as high chemical stability and ease fabricated and shaped. Many oxide glass compositions have been studied intensively to find the suitable upconversion host glass [3-9].

Borate glass has many attractive properties such as, high transparency, low melting temperature, high thermal stability, different coordination numbers, and good solubility of rare earth ions. To overcome the high phonon in borate glass a small percentage of heavy metal oxide is added. Further, the addition of rare earth oxide to alkali borate glasses is interesting for studying effects of its ions on the glass forming network.

In the present paper, the preparation and characterization of new Nd^{3+} doped lithium lead borate glass system had been carried out.

2. Experimental details

In the present study glass system of composition $30B_2O_3$ - $30Bi_2O_3$ -$20Li_2O$-10BaO - 10PbO – x Nd_2O_3 mole % (B_{30} Bi_{30} Li_{20} Ba_{10} Pb_{10}) has been prepared by conventional melting and quenching method, where x = 0, 0.5, 1, 2, 3 and 4. The starting material is reagent purity grade BO_3H_3, $(BiO)_2CO_3$, Li_2CO_3, $BaCO_3$and Pb_2O_3.

About 25 g of the starting row materials were preheated at 200 – 300°C to get rid of undesired gases. Then the powder oxides were melted at 950-1000°C for 20-25 min in a porcelain crucible in electric furnace in air atmosphere. The melts were shaken during preparation to ensure homogeneity. The melt was poured into preheated molds at 250°C. The prepared samples were subjected to annealing at

250°C for several hours. Then the furnace was left to cool to room temperature.

For X-ray measurements the samples were grinded into a fine powder by ball milling then the powder was sifted with a sieve with maximum width of 160 μm.

X-ray diffraction (XRD) patterns for the prepared samples were recorded with a Philips X-ray diffractometer using monochromatized CuKα1 radiation of wavelength 1.54056Å from a fixed source operated at 45 kV and 9 mA.

The density was measured by the conventional Archimedes method using toluene as immersing liquid.

The optical absorption was recorded by Jasco V-570 spectrophotometer at wavelength ranging between 200-2500 nm with 2nm resolution. The upconversion measurements were carried out by Varian-Cary eclipse Fluorescence Spectrophotometer with excitation and emission range between 190-1100 nm.

3. Results and Discussion

Representative XRD patterns are shown in Fig. (1) no diffraction peaks are observed indicating the non- crystalline nature of the prepared sample.

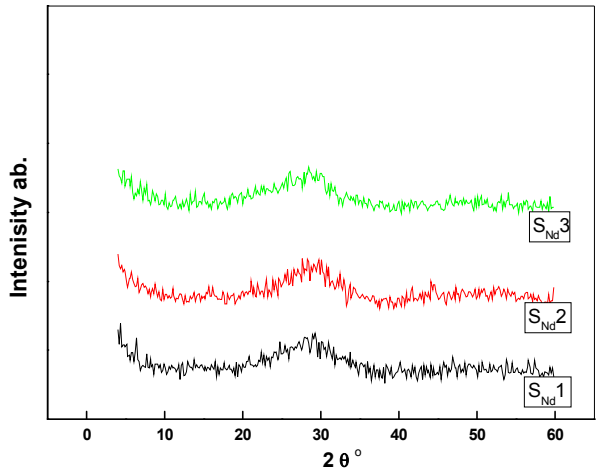

Figure 1. Representative XRD diffraction patterns of the prepared Nd glass samples

Density and Molar Volume

The density of the prepared samples was measured by conventional Archimedes with toluene as immersing liquid was calculated according to the relation: [10]

$$\rho_s = \frac{W_{air}}{W_{air} - W_l} \cdot \rho_l$$

where ρ_s is the density of the measured sample, W_{air} is the weight of the sample in the air, W_l is the weight of the sample inside the liquid and ρ_l is the liquid density.

The molar volume was calculated using the equation

$$V_M = \frac{M_W}{\rho_{glass}}$$

Figure (2) shows the dependence of density and molar volume on the Nd_2O_3 content. The dependence of both ρ and V_M exhibits no well-defined trend. However, both follow opposite trend. This behavior can be accounted for, by the addition of Nd_2O_3 the number of BO_3 and BO_4 structural units changes. The transformation of BO_3 to BO_4 structural units leads to the formation of closed structure. On the other hand the increase of BO_3 leads to the formation of open structure, which mainly the increase in number of non-bridging oxygen.

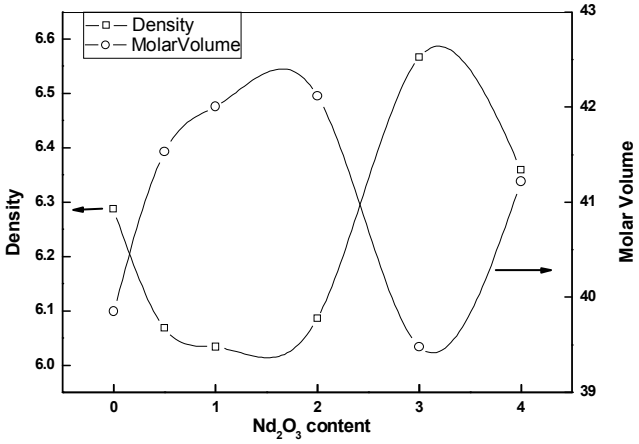

Figure 2. The dependence of glass density and molar volume on Nd_2O_3 content

Oxygen Packing Density

Using the molecular weight (Mw) and glass density ρ through [11]

$$O = \frac{\rho}{M_W} n$$

Where n is the number of atom per unit formula. The measured glass density and the calculated oxygen packing density is plotted against the Nd_2O_3 content in figure (3).

Inspection of figure (3) revels that the addition of Nd_2O_3 to the blank samples decreases the oxygen packing density up to 2 mole % then the oxygen packing density increases with the increase of Nd_2O_3 content. In addition the figure shows that the density and oxygen packing density follow the same trend which is the normal behavior for glasses. It

could be concluded that the Nd_2O_3 acts as a glass modifier in the low concentration up to 2 mole %. Beyond that, Nd_2O_3 > 2 mole %, it starts to linkup to glass network resulting increase in both density and oxygen packing density. The calculated parameters for the glass are summarized in Table (1).

Table 1. Physical parameters of the Nd_2O_3 doped (B_{30} Bi_{30} Li_{20} $Ba_{10}Pb_{10}$) glass

Nd content	Density (ρ) g/cm^{-3}	MV(V_M) cm^3/mole	Mw (g/mole)	Ion conc. (N) *10^{22} ion/cm^3	Ion radius (r_p)*10^{-8} A^0	field strength (F)*10^{16} cm^{-2}	Oxy. Pac density (O) (g atom/l)
0	6.28	39.85	250.55	0	0	0	55.20
0.5	6.06	41.52	251.99	0.72	2.08	0.691	53.33
1	6.03	42.00	253.44	1.43	1.65	1.08	53.08
2	6.08	42.11	256.32	2.85	1.31	1.72	53.66
3	6.56	39.47	259.21	4.57	1.12	2.36	58.00
4	6.35	41.21	262.09	5.84	1.03	2.78	56.28

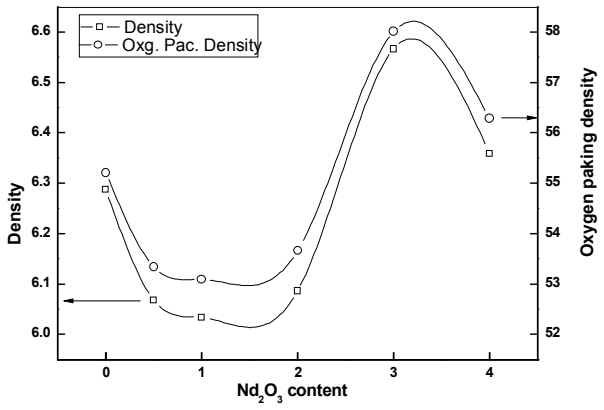

Figure 3. The density and oxygen packing density for Nd_2O_3 doped samples

Optical Properties

Figure (4) shows the optical absorption spectra of the prepared glass samples in the range 400 - 1000 nm. All Nd doped samples follow one common pattern where the line spectra due to f-f transition in rare earth. The spectra show seven absorption bands located at 872, 806, 750, 684, 586, 528 and 516 nm these bands Originate from the transition from the ground to the exited states $^4F_{3/2}$, $^4F_{5/2}$, $^7F_{7/2}$, $^4F_{9/2}$, $^2H_{11/2}$, $^4G_{7/2}$ and $^4G_{9/2}$ respectively.

The assignments of absorption bands are based on W.T. Carnall et al [12]. The blank samples show no peaks however, the intensities of the absorption bands are increased by increasing the Nd ion content; this indicates that the absorption is originated from the f-f transitions in Nd ions. f electrons are shielded by outer 5s and 5p bonding electrons, which leads to sharp absorption and emission bands. [13-14]. The obtained absorption spectra demonstrate an absorption edge at the short wave length side.

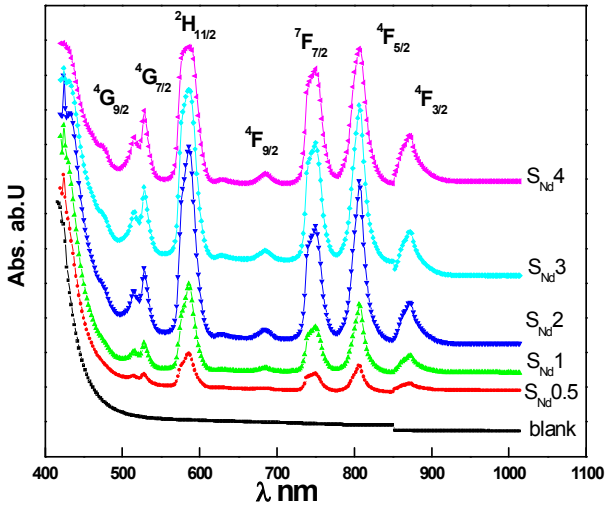

Figure 4. The absorption spectrum of the prepared (B_{30} Bi_{30} Li_{20} $Ba_{10}Pb_{10}$) glass doped with Nd_2O_3 content.

It is well known that the indirect transition is the most probable mechanism in the amorphous systems. This is due to the absence of transition symmetry in the non-crystalline solids. Hence, the value of the constant n = 2 in Mott-Davis relation: [15]

$$\alpha h\upsilon = B (h\upsilon - E_{opt})^n$$

Figure (5) show the relation between $(\alpha h\upsilon)^{1/2}$ and hν (Tauc diagram).

The dependence of Ln α on hυ, Urbach plots, is shown in Figure (6).

The band tail width (ΔE_U) can be calculated from the liner part of the relation.

$$\alpha(w) = \alpha_o \exp[h\nu/\Delta E_U]$$

Where α_0 is constant and ΔE_U is usually interpreted as the width of the tail of the localized states in the band gap and hν is the incident photon energy. ΔE_U = the inverse of the slope of lnα & hυ relation.

Energy gap values and Urbach energies are listed in Table (2). The band tail width was obtained using the relation:

The calculated energy gap for the prepared samples was decreased by adding Nd_2O_3 to the blank sample however, no well define trend was observed. The dependence of energy gap and Urbach energy on the rare earth concentration is shown in figure (7).

It is can be notice from Fig. (7) Urbach energy is follow opposite trend with respect to the band gap of the produced glass. The sample S_{Nd} 3 shows the lowest energy gap and the highest Urbach energy this may be due to the high degree of disorder in this sample. From previous results it could be concluded that the Nd_2O_3 acts as a modifier for the blank glass which changes the optical and physical properties by increasing the content of rare earth in the produced samples.

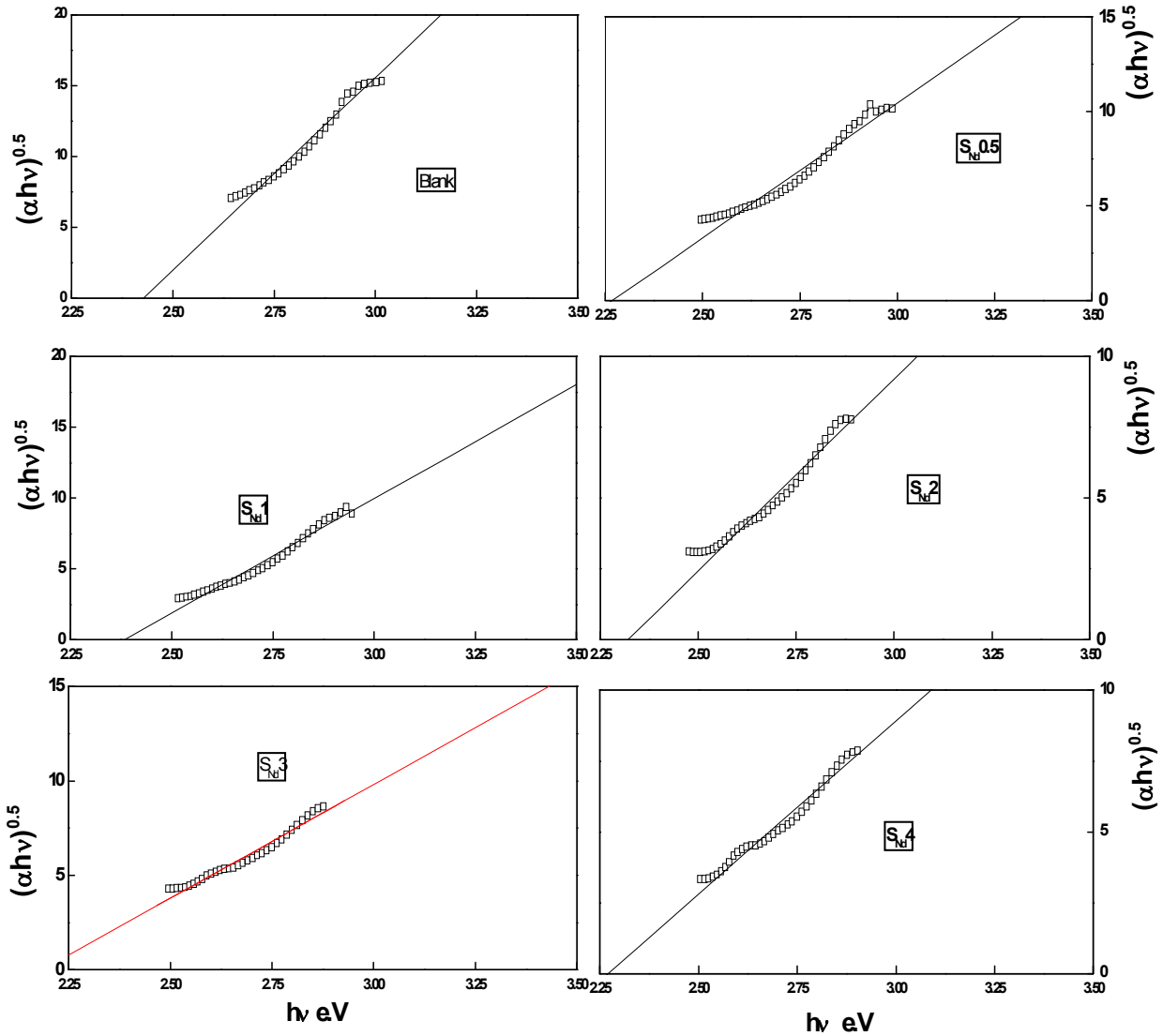

Figure 5. Tauc plot of the prepared Nd_2O_3 doped borate glass. $(\alpha h\nu)^{0.5}$ in $(cm^{-1}eV)^{0.5}$ and h is in eV

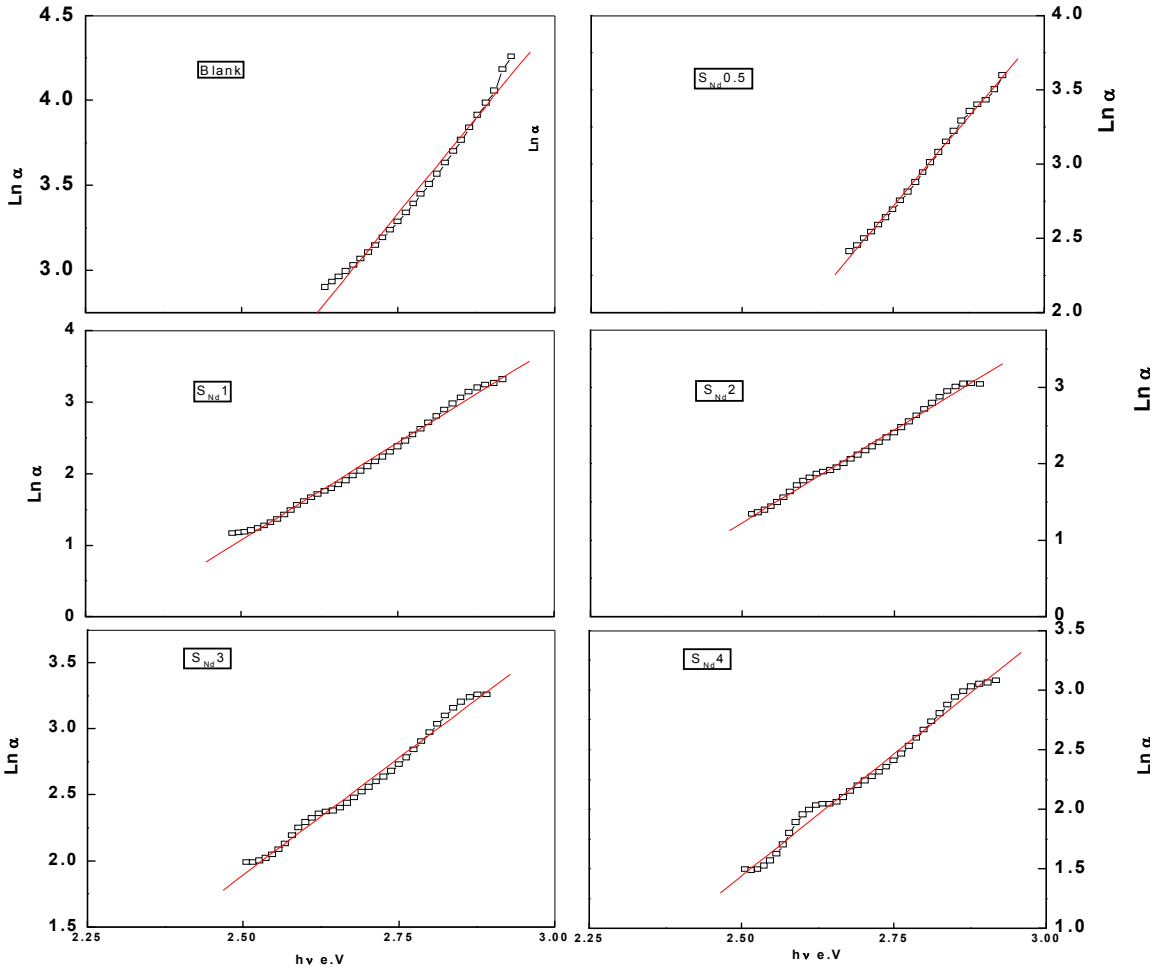

Figure 6. Urbach plots of the prepared glass samples doped Nd_2O_3

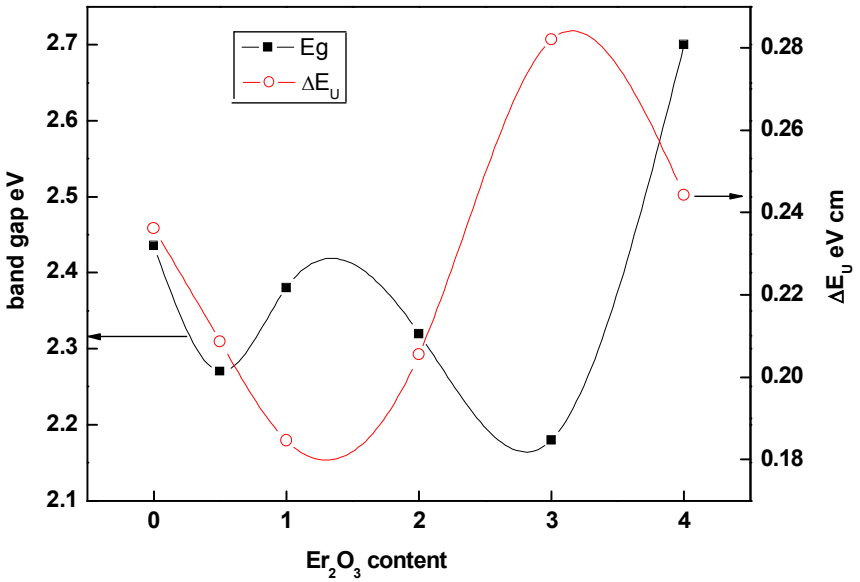

Figure 7. Band gap and Urbach energy as a function in Nd_2O_3 content in the produced samples

Using the estimated energy gap and electronegativity the refractive index was calculated. The obtained results are listed in Table (2). The refractive index for the prepared samples has no defined trend with increasing the Nd_2O_3 content. The values of refractive index are in range with the previously published values [16].

Table 2. E_g, Urbach energy, electro-negativity and refractive index for the Nd_2O_3 samples

Nd content	E_g	ΔE_U	$\Delta\chi^*$	n
0	2.436	0.2362	0.654	2.70
0.5	2.27	0.2087	0.610	2.77
1	2.38	0.1846	0.639	2.72
2	2.32	0.2056	0.623	2.75
3	2.18	0.282	0.585	2.81
4	2.7	0.2443	0.725	2.60

Upconversion

To obtain the upconversion spectra, the Nd have been obtained using a light beam of 800nm as exciting wavelength. The obtained upconversion spectra are shown in figure (8). Four band were observed located at 730, 716, 700 and 540 nm which is corresponding to the transitions $^4F_{7/2} + {}^4S_{3/2} \longrightarrow {}^4I_{9/2}$, $^4F_{7/2} + {}^4S_{3/2} \longrightarrow {}^4I_{9/2}$, $^4F_{9/2} \longrightarrow {}^4I_{9/2}$ and $^4G_{7/2} \longrightarrow {}^4I_{9/2}$, respectively. These upconversion bands for Nd were also reported [17].

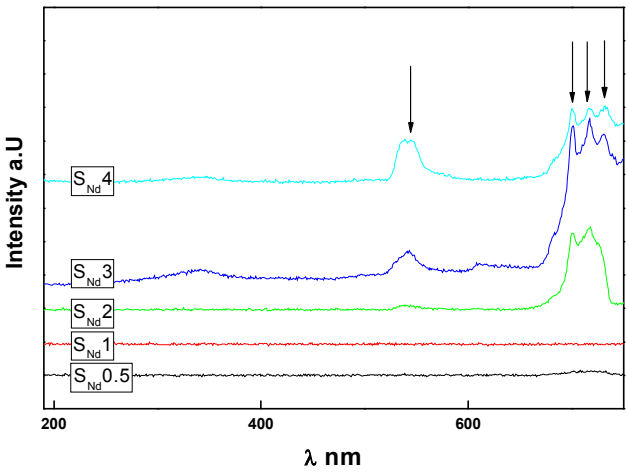

Figure 8. Upconversion spectra of the prepared glass doped with Nd_2O_3

Figure (8) also reveals that the samples $S_{Nd}0.5$ and S_{Nd} 1 show no upconversion peaks. By increasing the Nd content sample S_{Nd} 2 show only two peaks located at 730, 716nm. The appearance of the peaks at 540 and 730 nm starts with Nd concentration exceeds 3 mole %. The intensity of 730, 716,700 nm peaks in sample $S_{Nd}4$ decrease while 540 nm peak increase. This indicates that by increasing Nd content the electrons participate in the $^4G_{7/2} \longrightarrow {}^4I_{9/2}$ transition is more than the electrons participate in the other 3 transitions.

4. Conclusion

Borate glassy system of the composition $30B_2O_3$ - $30Bi_2O_3$ -$20Li_2O$-10BaO - 10PbO - x Nd_2O_3 mole %, where x = 0, 0.5, 1, 2, 3 and 4, has been prepared by conventional melting quenching method**.** XRD confirmed the amorphous glass structure. The optical properties of the produced samples, such as optical absorption, refractive index and optical band gap had been obtained. The produced glass sample has a high transmittance in the range (2500-450 nm), high density (6.3 g/cm^3), wide band gap (2.43 eV) and high refractive index (2.70). the upconversion process had been confirmed. These result supports the usage of $30B_2O_3$ - $30Bi_2O_3$ - $20Li_2O$-10BaO - 10PbO doped with Nd_2O_3 as upconversion media for solar cell applications and other upconversion applications.

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References

1. H. Lian, Z. Hou, M. Shang, D. Geng, Y. Zhang, J.Lin, Energy 2013; 57 : 270-283.
2. Joshua P., Futures 2002; 34(7): 663 – 674.
3. S. Xu, Z. Yang, S. Dai, G. Wang, L. Hu, Z. Jiang, Materials Letters 2004;58 : 1026 – 1029.
4. A. Miguel, M. Arriandiaga, R. Morea, J. Fernandez, J. Gonzalo, R. Balda, Journal ofLuminescence 2014; 154 : 136–14.
5. R. Wang, Z. Yang, D. Zhou, Z. Song, J. Qiu, Journal of Non-Crystalline Solids 2014; 383 : 200–204.
6. Z. Zhou, L. Li, Q. Duan, L. Feng, H. Tian, Optics Communications 2012; 285 : 1854–1858.
7. C. Kesavulu, V. Sreedhar, C. Jayasankar, K. Jang, D. Shin, S. Yi, Materials Research Bulletin 2014; 51 : 336 –344.
8. M. Lluscà, J. López-Vidrier , A. Antony, S. Hernández , B. Garridob, J. Bertomeu, Thin Solid Films 2014; 562 : 456–461.
9. Q. Lu, Q. Yang, Y. Yuan, C. Jiang,Y. Wang, Ceramics International 2014; 40 : 7367–7372.
10. R. Barde, S. Waghuley, Journal of Non-Crystalline Solids 2013; 376 : 117–125.
11. D. Saritha, Y. Markandeya, M. Salagram, M. Vithal, A.K. Singh, G. Bhikshamaiah, Journal of Non-Crystalline Solids; 2008, 354 : 5573–5579.

12. W. Carnall, P. Fields, K. Rajnak, Journal of Chemical Physics 49, 1968, 10 : 4424-4442.
13. J. Sole', L. Bausa', D. Jaque, An Introduction to the Optical Spectroscopy of Inorganic Solids, Wiley (2005).
14. G. Liu, B. Jacquier, Spectroscopic Properties of Rare Earths in Optical Materials, Springer series in materials science, (2005).
15. N. Mott, E. Davis, Electronic processes in Non-Crystalline Materials, Clarendon, Oxford, (1979).
16. J. Shelby, Introduction to Glass Science and Technology, Royal Society of Chemistry, 1997.
17. Z. Piskuła, J. Czajka, K. Staninski, S. Lis, J. OF RARE EARTHS; 2014, 32 – 3 : 221.

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