Volume 65, Issue 8, 2021
Journal of Scientific Research
of
The Banaras Hindu University

The synthesis and properties of oxyfluoride borate glasses incorporated with neodymium ion

Susheela K. Lenkennavar*[1]

*[1]Department of physics, Bangalore University, Bangalore -56, Karnataka, India
*sushhh10@gmail.com

Abstract: **The present work illustrates optical properties of potassium strontium lead boro oxyfluoride glasses doped with Nd3+ ions were prepared by using melt quenching technique. The prepared glasses were characterized with optical properties by using CIE diagram, absorption and photoluminescence (PL) spectral measurements and structural properties by X-ray diffraction (XRD) and Fourier Transform Infrared spectroscopy (FTIR). The objective of the paper is to report detailed studies of glass matrix. The Nd3+ ion has been use as an excellent optical activator. Using proper optimization method we can make use of these lasers for photonic applications. From the luminescence spectrums it's clear that synthesized glass offers red colour and can be an auspicious laser candidate. Glasses have high refractive index which shows that prepared glasses are desirable candidate.**

Index Terms: **UV-Vis Spectroscopy, CIE diagram, Photoluminescence, X-ray diffraction, FTIR**

I. INTRODUCTION

Oxyfluoride glass systems exhibit huge potential as these glass combine the advantages of both oxide and fluoride glasses. In general, the oxide glasses have good stability and chemical durability and on the other hand, fluoride glasses have very low phonon energy. In these glasses, the replacement of fluorine by oxygen affects the glass formation and the structure of glass networks, namely, their connectivity. Further, they turned out to be suitable for operating in the UV spectral range and as laser materials [1-9].

The present investigation is an attempt to study the optical and structural properties of neodymium ion-doped with potassium strontium lead boro oxyfluoride glasses. The neodymium ion is an excellent optical activator as it plays an essential role because it has multiple emission property moreover neodymium ion gives the least variation in spectroscopic properties with various glass compositions [10-17].

II. II. SYNTHESIS AND CHARACTERIZATION

A. Synthesis

Oxide glasses with composition $20Ka_2O$ -10SrO-$10PbF_2$ -$60B_2O_3$ -XNd_2O_3 with X= 1 mol% -were synthesized utilizing electric furnace by the conventional melt quenching technique and indicated as NSFB and NSFBN. The chemical composition of the 10g batch was weighted very precisely. In an agate mortar, the 10g batches chemical were grinded and mixed thoroughly. Later in a porcelain crucible, chemical compositions were taken and melted in the temperature range of 1030-1080 ^{0}C in an electric furnace for 45 minutes and then immediately poured on a brass mould which was preheated to get pellet form samples. Therefore by employing conventional melt-quench technique glasses were obtained. It includes or involves batch preparation, grinding or mixing, calcinations, melting, quenching and annealing. The aforementioned process is summarized and presented in the flow chart, Fig 1.

B. Characterizations

X-ray diffraction patterns of the present prepared glass samples, potassium- strontium-lead-boro-oxyfluoride glasses doped with Nd^{3+} ions were recorded to investigate the non-crystallinity utilizing advance XRD diffractometer RIGUKA ULTIMA IV.

The IR absorption spectra of potassium strontium lead boro oxyfluoride glasses doped with Nd^{3+} ions glasses were obtained and recorded at room temperature by a Bruker, single beam spectrometer using the KBr disk technique in the wavenumber range of 400–4000 cm−1 with a resolution of 2 cm−1. The infrared spectra were normalized to exclude the concentration influence of the powder sample in the KBr disk and also the IR absorption spectra obtained were corrected for the dark current noises.

The refractive index and density were experimentally measured and using suitable expression few physical properties has been calculated as discussed in literature [30-38].

The absorption spectra recorded at room temperature using Perkin Elmer Lambda-950 UV-Vis spectrometer. The luminescence spectrum has been recorded by Spectroflourometer, Horiba Jobin Yvon Fluorolog-3. Few physical parameters were calculated. The density is measured using Archimede's principle. Refractive indices of samples were measured at 589.3 nm using an Abbe's refractometer.

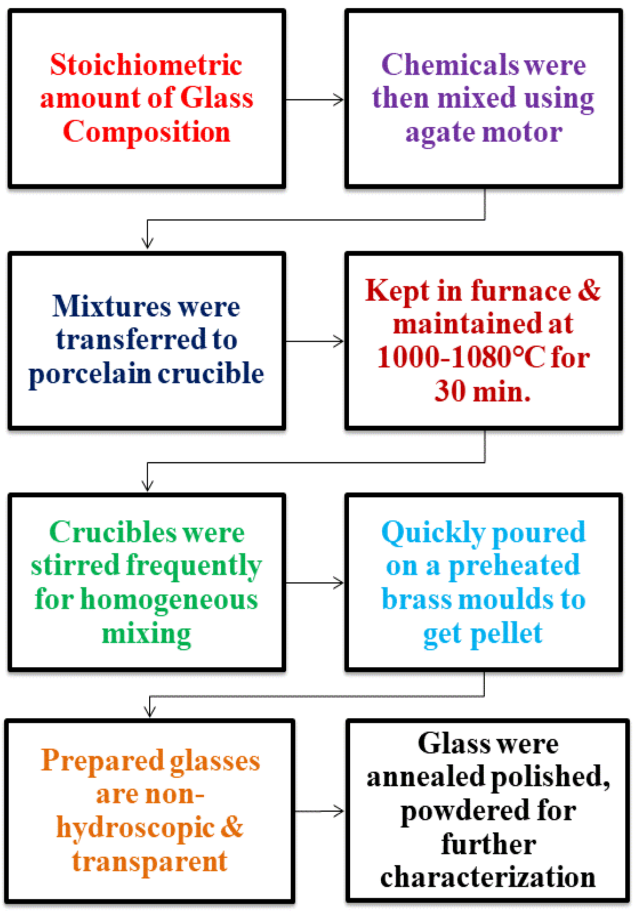

Fig. 1. Flow chart of overall process summarized for sample preparation

III. RESULTS AND DISCUSSION MANUSCRIPT

1) X-RAY DIFFRACTION

XRD pattern of potassium-strontium-lead-boro-oxyfluoride glass (undoped) and doped with neodymium ions is displayed in Fig. 2., which has no sharp peaks that is a clear indication of the absence of crystalline nature. The diffractograms exhibit just broad diffuse scattering at low angles which is characteristic of long-range structural disorder. That confirms the amorphous characteristics of the glass.

2) FOURIER TRANSFORMATION OF SPECTROSCOPY (FTIR) ANALYSIS

The IR absorption spectra of potassium strontium lead boro oxyfluoride glasses doped with Nd^{3+} ions glasses were obtained and recorded at room temperature single beam spectrometer using the KBr disk technique in the wavenumber range of 400–3500 cm−1 is displayed in Fig. 3.

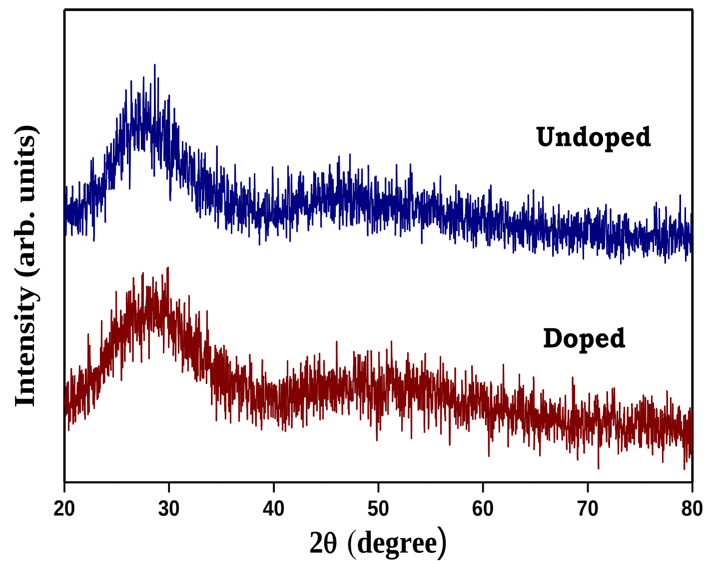

Fig 2. XRD pattern of doped and undoped glasses.

The essential information regarding the structural units arranged in glasses are studied for the present glasses using FTIR analysis. It is assumed that in the glass network, structural units vibrations are independent of other neighbouring units vibrations. Since concentration of borate is high one can expect major vibration modes are due to borate units [6, 23-27].

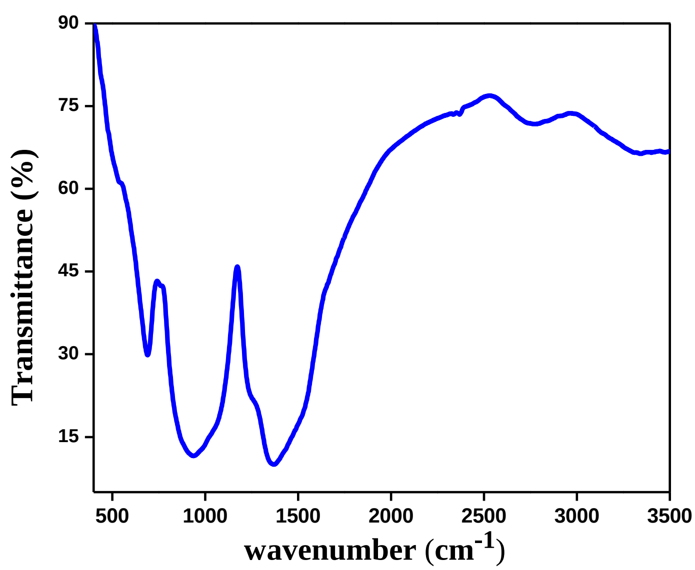

Fig 3. FTIR spectra of neodymium ions doped glass.

3) PHYSICAL PROPERTIES

Density (ρ) was estimated using (W_a) sample weight in air, (W_b) sample weight in liquid (toluene) (ρ_x=0.8669gcm^{-3} , toluene of density) using

$$\rho = \frac{W_a}{(W_a - W_b)\rho_x} \quad .....(1).$$

Molar volume (V_m) was calculated by using glass molecular weight (M.W),

$$V_m = \frac{M.W}{\rho} \quad .....(2).$$

Molar refractivity (R_m) is calculated using molar volume V_m and refractive index,

$$R_m = \frac{n^2-1}{n^2+2}(V_m) \quad ....(3).$$

The polarizabilities (α_m) is calculated using Avogadro's number (N_A) and molar refractivity (R_m) by using relation,

$$\alpha_m = \frac{3}{4\pi N_A} R_m \quad ....(4).$$

Rare earth(RE) ion concentration is calculated using relation,

$$N_i = \frac{x\,\rho NA}{y\,b} \quad ...... (5).$$

Where, x is the weight of RE ion and y is molecular weight of rare earth ion.

The inter ionic distance (r_i) and polaron radius (r_p) is calculated using the concentration of RE ion (N_i),

$$r_i = \left[\left(\frac{1}{N_i}\right)^{1/3}\right] \quad .....(6a)$$

$$r_p = \left[\frac{1}{2}\left(\frac{\pi}{6N_i}\right)^{1/3}\right] \quad .....(6b) \text{ respectively.}$$

Field strength (F) can be calculated by using charge of rare earth ion (Z) and polaron radius,

$$F = \left(\frac{Z}{r_p^2}\right) \quad ....(7)$$

Dielectric constant (ε) is calculated form,

$$\epsilon = n^2 \quad ....(8).$$

Reflection loss (R_L%) was calculated by using Refractive index,

$$R_L = \left(\frac{n-1}{n+1}\right)^2 \quad ....(9).$$

For the better understanding purpose the preliminary physical properties of potassium strontium lead boro oxyfluoride glass doped with neodymium ions are estimated and reported as follows [30-38].

Table I. Variables used in algorithm and their description

Sl.No	Physical properties	
1.	Refractive index (RI)	1.653
2.	Density (ρ) gm/cm^3	3.384
3.	Molar refractivity (R_m)cm^{-3}	9.74
4.	Molar volume (V_m)g/cm^3	26.60
5.	Molar polarizability (α_m)$\times10^{-24}$cm^3	3.86
6.	Reflection loss(R_L)%,	6.079
7.	Dielectric constant(ε),	2.734
8.	Concentration (N_i)$\times10^{20}$ ions/cc.	2.22
9.	Polaron radius (r_p)nm	0.45
10.	Inter ionic distance (r_i) nm	1.46
11.	Field strength(F) $\times10^{14}$cm^2	8.50

IV. OPTICAL ANALYSIS

UV–Vis-NIR spectra of potassium strontium lead boro oxyfluoride glass doped with neodymium ions with possible transitions in the wavelength range 400–850 nm is displayed in Fig. 4. The neodymium ion possesses the $^4f_3$ electronic configuration with $^4I_{9/2}$ ground state. The observed transitions are $^4I_{9/2}$ to $^4G_{11/2}$, $^4G_{9/2}$, $^4G_{7/2}$, $^4G_{5/2}$, $^4H_{11/2}$, $^4F_{9/2}$, $^4F_{7/2}$, $^4F_{5/2}$, $^2D_{3/2}$, $^2P_{3/2}$. The $^4I_{9/2}$ to $^4G_{5/2}$ transitions occurring in the visible region which is hypersensitive[10-29].

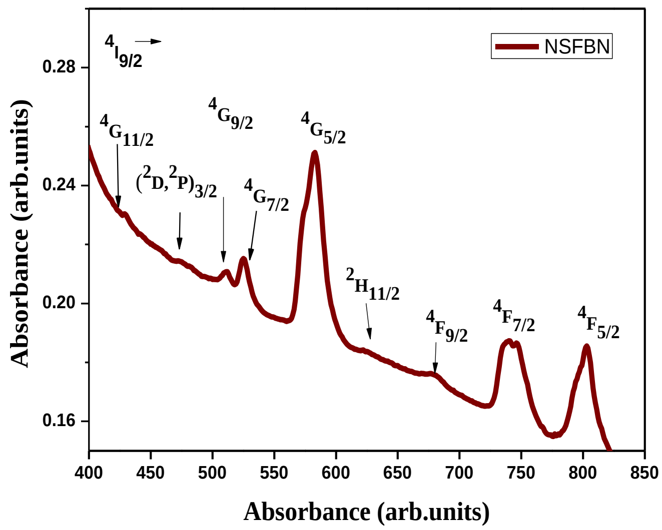

Fig 4. Absorption spectra of neodymium ions doped glass.

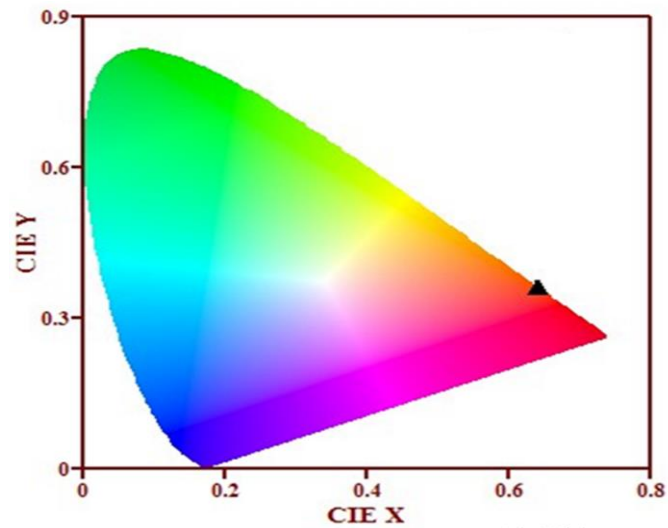

Fig. 6. CIE diagram for neodymium ions doped glass.

V. EMISSION PROPERTIES

Photoluminescence spectrum of potassium- strontium-lead-boro-oxyfluoride glass doped with neodymium ions with possible transitions in the wavelength range 620–660 nm is displayed in Fig. 5. The glass samples were excitation at 580 nm [39-40] and we can suspect red emission as the emission peak is obtained at 637 nm, with transition in the visible region $^4G_{5/2} \rightarrow {}^2H_{11/2}$.

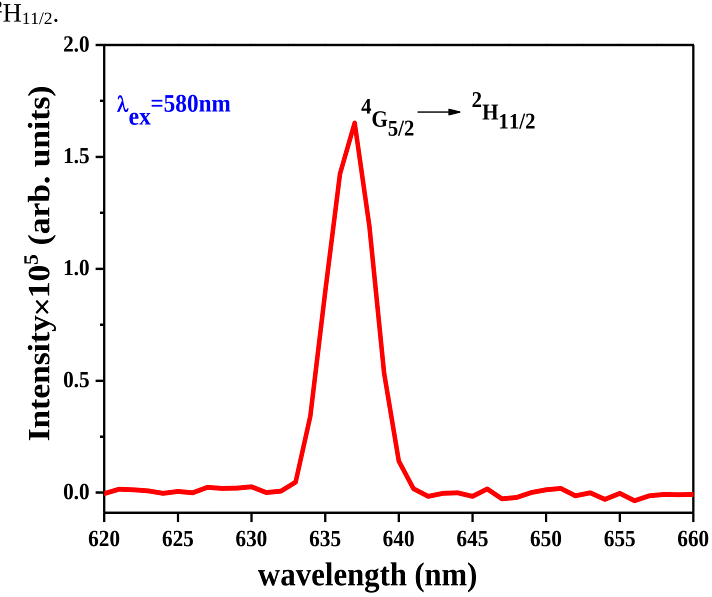

Fig 5. .Emission spectra of neodymium ions doped glass

VI. COLOUR ANALYSIS

For the estimations of the emission color, the (CIE) chromaticity coordinates were determined for the glass matrices. The luminescence colour of the potassium- strontium-lead-boro-oxyfluoride glass doped with Nd3+ ions was excited under suitable excitation was determined by CIE 1931 chromaticity diagram. The glass incorporated with neodymium oxide glass exhibits red colour as explicated in Fig. 6.

CONCLUSION

UV–Vis-NIR spectra of potassium strontium lead boro oxyfluoride glass doped with neodymium ions with possible transitions observed form $^4I_{9/2}$ ground state to $^4G_{11/2}$, $^4G_{9/2}$, $^4G_{7/2}$, $^4G_{5/2}$, $^4H_{11/2}$, $^4F_{9/2}$, $^4F_{7/2}$, $^4F_{5/2}$, $^2D_{3/2}$, $^2P_{3/2}$ excited state. The glass samples were excitation at 580 nm and we can suspect red emission as the emission peak is obtained at 637 nm, with transition in visible region $^4G_{5/2} \rightarrow {}^2H_{11/2}$. The chromaticity diagram conforms that the neodymium oxide glass exhibits red colour. For the better understanding purpose the preliminary physical properties of potassium strontium lead boro oxyfluoride glass doped with neodymium ions are estimated and reported. The influence of neodymium ions on the potassium-strontium-lead-boro-oxyfluoride glasses has been examined employing X-ray diffraction (XRD) including infrared spectrophotometer (FTIR) and even density of the sample also found. The greater role played by the neodymium oxide as a glass-modifier, since it influences the conversion of $BO_3 \leftrightarrow BO_4$. When BO_3 units are converted to BO_4 units, a similar influence is also observed in molar volume and density variation due to non-bridging oxygen's (NBO) created. The glasses have high refractive index which shows that prepared glasses are desirable candidate for optical fibre glass application.

ACKNOWLEDGEMENTS

Author (SKL) would like to thank (Late) Prof. R.V. Anvekar for his guidance and suggestions.

REFERENCES

Shantala.P, V M Jali and R V Anavekar, Bulletin of Materials Science, 31(2008) 4.

V Ravi Kumar & N Veeraiah, Bulletin of Materials Science. 20, (1997) 667–675.
S. K. Lenkennavar et al., Materials Today: Proceedings, Elsevier Publication, Vol. 33(7) (2020) 2550-2554, https://doi.org/10.1016/j.matpr.2019.12.066
S. Arunkumar, K. Marimuthu, J. Alloys compd. 565 (2013) 104.
Susheela K. Lenkennavar et al., International Journal of ChemTech Research, 2019, 12 (2) 90-94.
M. Reben, M. Sroda, J. Therm. Anal. Calorim. 113 (2013) 77.
Susheela K. Lenkennavar et al., AIP Conference Proceedings 2134, 050006-3 (2019).
R.G. Fernandes, J. Ren, S. S.A. de Camargo, A. C. Hernandes, H. Eckert, J. Phys. Chem. C 116 (2012) 6434.
J. Ezequiel De Souza, A. Carlos Hernandes, Jean-Claude M'Peko , J. superconductivity and novel mag. 26 (2013) 2493.
B. Karthikeyana , S. Mohanb, M.L. Baesso, Physica B. 249–254 337(2003).
S. Liu, G. Zhao, H. Ying, J. Wang, G. Han, Opt. Mater. 31 (2008) 47.
Susheela K. Lenkennavar et al., Int. Arch. App. Sci. Technol; Vol 10 [1] March 2019 : 106-10
J.H. Campbell, T.I. Suratwala, J. Non-Cryst. Solids 263 & 264 (2000) 318.
Susheela K. Lenkennavar et al., AIP Conf. Proc. 2115, 030240-1–030240-4;
D. L. Sidebottem, M. A. Hrushka, B. G. Potter, and R. K. Brow, Appl. Phys. Lett. 71(1997) 1963.
S. K. Lenkennavar et al., Materials Today: Proceedings, (2020) https://doi.org/10.1016/j.matpr.2020.02.235.
L. Zhang, L. Wen, H. Sun, J. Zhang, L. Hu, J. Alloys Compd. 391 (2005) 156.
A. H. Verhoef and H.W. den Hartog, J. of Non-Cryst. Solids, 182 (3) (1995) 221.
V.T. Adamiv, I.M. Bolesta, V. Ya, R.V. Burak, I.D. Gamernyk, I.I. Karbovnyk, M.G. Kolych, O.O. Kovalchuk, M.V. Kushnir, I. Periv, M. Teslyuk, Phys. B Condens. Matter 449 (2014) 31.
M.R. Dousti, M.R. Sahar, S.K. Ghoshal, R.J. Amjad, A.R. Samavati, J. Mol. Struct. 1035 (2013) 6.
Chandkiram Gautam, Avadhesh Kumar Yadav, and Arbind Kumar Singh, ISRN Ceramics (2012) 428497.
Kashif I, Abd El-Maboud A, Ratep A, Physics, 4,1–5(2004).
Manisha pal A, Hirota K, Tsujigami Y, Sakata H. J Phys D: Appl Phys, 34, 459(2001).
Susheela K. Lenkennavar et al., AIP Conf. Proc. 1953, 090025-4 (2018)
Iordanova R, Dimitriev Y, Dimitrov V, Kassabov S, Klissurski D, Non-Cryst J.Solids, 231, 227(1998).
Susheela K. Lenkennavar, et al., IOP Conf. Series: Materials Science and Engineering 310 (2018) 012052
Soppe W, Alden kamp F, Den Hartog HW. J Non-CrystSolids., 10 (1985) 1.
Susheela K. Lenkennavar et al., J. Applicable Chem. 7 (4) (2018) 933–948.
Chimalawong P, Kaewkhao J, Kittiauchawal T, Kedkaew C, Limsuwan P. Am J App Sci., 7(4) (2010) 584.
E.J. Friebele, Radiation effects, in: D.R. Uhlmann, N.J. Kreidl (Eds.), American Ceramic Society, Westerville, OH, USA, 1991, pp. 205.
G. Venkateswara Rao, N. Veeraiah, P. Yadagiri Reddy, Opt. Mater. 22 (2003) 295.
R.C. Lucacel, C. Marcus, V. Timar, I. Ardelean, Solid State Sci. 9 (2007) 850.
A. Murali, R.P. Sreekanth Chukrodhar, J. Lakashmana Rao, Physica B, 364(2005) 142.
G. Sharma, K. Singh, Radiat. Phys. Chem., 75 (2006) 959.
H.A. El-Batal, F.A. Khalifa, M.A. Azooz, Ind. J. Pure Appl. Phys., 39 (2001) 565.
Kamitsos, E. I., Physics and Chemistry of Glasses, 44, (2003), 79.
Kathleen MacDonald, Margaret A. Hanson, Daniel Boyd , Journal of Non-Crystalline Solids,443,(2016),184.
Myrtille O.J.Y. Hunault, Laurence Galoisy, Gérald Lelong, Matt Newville, Georges Calas, Journal of Non-Crystalline Solids**,**451, (2016),101.
Susheela K. Lenkennavar et al., AIP Conf. Proc. 1951, 030009-5 (2018).
S. K. Lenkennavar et al., Materials Today: Proceedings, Elsevier Publication, Vol. 26(2) (2020) 1167–1174, https://doi.org/10.1016/j.matpr.2020.02.235

***