ISSN Online: 2756-3898, ISSN Print: 2714-500X https://doi.org/10.47514/phyaccess.2023.3.2.002

Influence of Rare Earth Ions (REIs) on the Visible Emission of Magnesium Sodium Borate Glasses

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Received 22-05-2023
Accepted for publication 28-07-2023
Published 28-07-2023

Abstract

Borate glass systems have been extensively studied for practical applications in optical display devices by virtue of their peculiar luminescence efficiency. However, the attainment of high emission from borate glass materials via apposite control of rare earth ions (REIs) contents remains a topical issue in Material Physics. In this paper, we report the influence of REIs (Dy^{3+}, Eu^{3+}, and Sm^{3+}) on multiple-colour emission of magnesium sodium borate (MSB) glasses fabricated by using the conventional melt-quenching method. These glasses were optically characterized via X-ray Diffraction (XRD), UV-VIS-NIR and Photoluminescence techniques. The XRD pattern confirms the amorphous nature of the as-prepared glasses. The absorption spectra disclosed several absorption bands at 347 nm ($^6H_{15/2} \rightarrow {}^6P_{7/2}$) for Dy^{3+}, 393 nm ($^7F_0 \rightarrow {}^5L_6$) for Eu^{3+} and 403 nm ($^6H_{5/2} \rightarrow {}^6P_{5/2}$) assigned for Sm^{3+} respectively. Also, the emission spectra radiate at 463 nm ($^4F_{9/2} \rightarrow {}^6F_{11/2} + {}^6H_{9/2}$), 612 nm ($^5D_0 \rightarrow {}^7F_J$) and 599 nm ($^4G_{5/2} \rightarrow {}^6H_{7/2}$) for Dy^{3+}, Eu^{3+}, and Sm^{3+} correspondingly, wherein Dy^{3+} emits blue, yellow, and red light, Eu^{3+} emits red light and Sm^{3+} emits reddish-orange light. Finally, 1.0 mol% content of Dy^{3+}, Eu^{3+}, and Sm^{3+} in MSB glasses was found to be optimal and hence considered the best optical host for colour display devices.

Keywords: Visible emission; Borate glass; Rare earth ions (REIs); Melt-quenching method.

I. Introduction

Glass is a non-crystalline solid with a short-range order of solids which can melt below the glass transition temperature [1, 2]. Among the distinct class of glasses, borate (B_2O_3) glass matrices are spotted as the most suitable host for rare earth ion doping [3-6]. However, sodium oxide (NaO) incorporation in borate glass disclosed a unique superstructure intermediate range order (IRO) that makes them fundamentally interesting through composition variation or thermal and pressure history control [7, 8]. The addition of other network modifiers such as Magnesium oxide (MgO), to the sodium borate glass network can bring appealing changes in optical and physical properties. MgO being a very good network modifier can change the local symmetry around the borate network by changing BO_3 units into BO_4 and makes the glass stronger and more closely packed [9, 10]. Moreover, the existence of MgO may also reduce the hygroscopic nature allied with the borate host which is very crucial for many glasses to get stability against devitrification [11]. Despite immeasurable studies on the impact of various dopants (rare earth ions, REIs), only a few authors have simultaneously reported the effect of three different REIs on a single glass host (12, 13). Driven by this basis, herein we present the synthesis and characterization of magnesium sodium borate glasses to ascertain the impact of three divergent rare earth ions (REIs) like dysprosium (Dy^{3+}), europium (Eu^{3+}), and samarium (Sm^{3+}) on their visible light emission performance.

II. EXPERIMENTAL PROCEDURES

A. Sample Preparation

The magnesium sodium borate (MSB) glass series with nominal composition of 20nao- *x*mgo-(80-*x*)b_2o_3 (with x =10, 20 and 30 mol%) for undoped and 20nao-30mgo-(50-*x*)b_2o_3-*x*re_2o_3 (with x = 0.1, 0.9 and 1.0 mol%) for doped samples were prepared by standard melts quench technique and the glass compositions designations alongside the digital image of the as-prepared glass samples are well-presented in Table I. 20 g of each sample was weighed using the analytical balance and thoroughly mixed in alumina crucible. The mixture was melted at 1100°c for 45 minutes and subsequently transferred to a low-temperature furnace and annealed at 350°c for 3 hours.

Table I. Composition of prepared MSB glass samples

As-prepared sample	Sample code	Composition (mol %)					
		B_2O_3	NaO	MgO	Dy_2O_3	Eu_2O_3	Sm_2O_3
	S1	70.0	20.0	10.0	-	-	-
	S2	60.0	20.0	20.0	-	-	-
	S3	50.0	20.0	30.0	-	-	-
	S4	49.9	20.0	30.0	0.1	-	-
	S5	49.5	20.0	30.0	0.5	-	-
	S6	49.0	20.0	30.0	1.0	-	-
	S7	49.9	20.0	30.0	-	0.1	-
	S8	49.5	20.0	30.0	-	0.5	-
	S9	49.0	20.0	30.0	-	1.0	-
	S10	49.9	20.0	30.0	-	-	0.1
	S11	49.5	20.0	30.0	-	-	0.5
	S12	49.0	20.0	30.0	-	-	1.0

B. Sample Characterization

The amorphous nature of the prepared glass samples is determined using the Rigaku AX-2500 Advance X-ray diffractometer that is equipped with a Cu-K-β filter having a wavelength of 1.54 Å. It was calibrated to measure in the range of 2θ from 3° to 100° whereas the absorption spectra of all MSB glasses are exposed by using Shimadzu UV-3600 UV-VIS-NIR Spectrophotometer ranging from 200 to 800 nm. The emission spectra are analyzed using Horiba Fluoromax-4 Spectrofluorometer measured from 300 to 1000 nm. The excitation wavelength of the MSB glasses was varied depending on REIs (Dy^{3+}, 347 nm, Eu^{3+}, 394 nm, and Sm^{3+}, 403 nm) to inspect their prominent visible emission.

III. RESULTS AND DISCUSSION

A. XRD Analysis

The XRD pattern of the undoped and Dy^{3+}, Eu^{3+}, and Sm^{3+} doped MSB glasses obtained in the 2θ range from 10° to 90° is epitomized in Fig. 1. Apparently, the absences of discrete peaks but the presence of broad peaks validate the amorphous nature of these glasses. A similar result was obtained in another borate host [3].

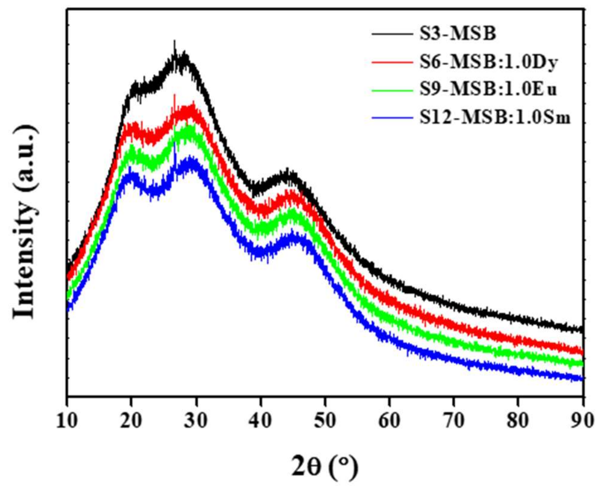

Fig. 1 The XRD pattern of selected MSB glass from each series

B. Absorption Spectra Analysis

The absorption spectra of MSB glasses with varying contents of REIs are shown in Fig. 2.

Fig. 2 (a) shows the second series which consists of different concentrations of Dy_2O_3 doped MSB glasses analysed and a total of eight peaks were observed centred at 347 nm, 363 nm, 386 nm, 424 nm, 452 nm, 471 nm, 645 nm, and 746 nm defined as the absorption bands. These absorption bands are attributed from the ground state $^6H_{15/2}$ to the excited states $^6P_{7/2}$, $^4P_{5/2}$, $^4I_{13/2}$, $^4G_{11/2}$, $^4I_{15/2}$, $^4F_{9/2}$, $^6F_{1/2}$, $^6F_{3/2}$ respectively [13]. Fig. 2 (b) demonstrates the third series having Eu_2O_3 as the dopant. Five absorption bands were observed at 378 nm, 393 nm, 414 nm, 464 nm, and 532 nm and associated respectively to the transition from the ground state $^7F_0$ to the excited states $^5G_2$, $^5L_6$, $^5D_3$, $^5D_2$, and $^5D_1$ [14, 15]. The last series of Sm_2O_3 doped MSB glass are analysed and the absorption spectra are illustrated in Fig. 2 (c). Six bands are observed and located at 344 nm, 361 nm, 374 nm, 403 nm, 440 nm, and 473 nm. These bands are associated with the transitions from the ground state $^6H_{5/2}$ to the excited states $^4D_{7/2}$, $^4D_{3/2}$, $^6P_{7/2}$, $^6P_{5/2}$, $^4G_{9/2}$ and $^4I_{3/2}$ [16]. We can conclude that the increase in dopant rare earth concentration affect the increases of absorbance to the MSB glasses.

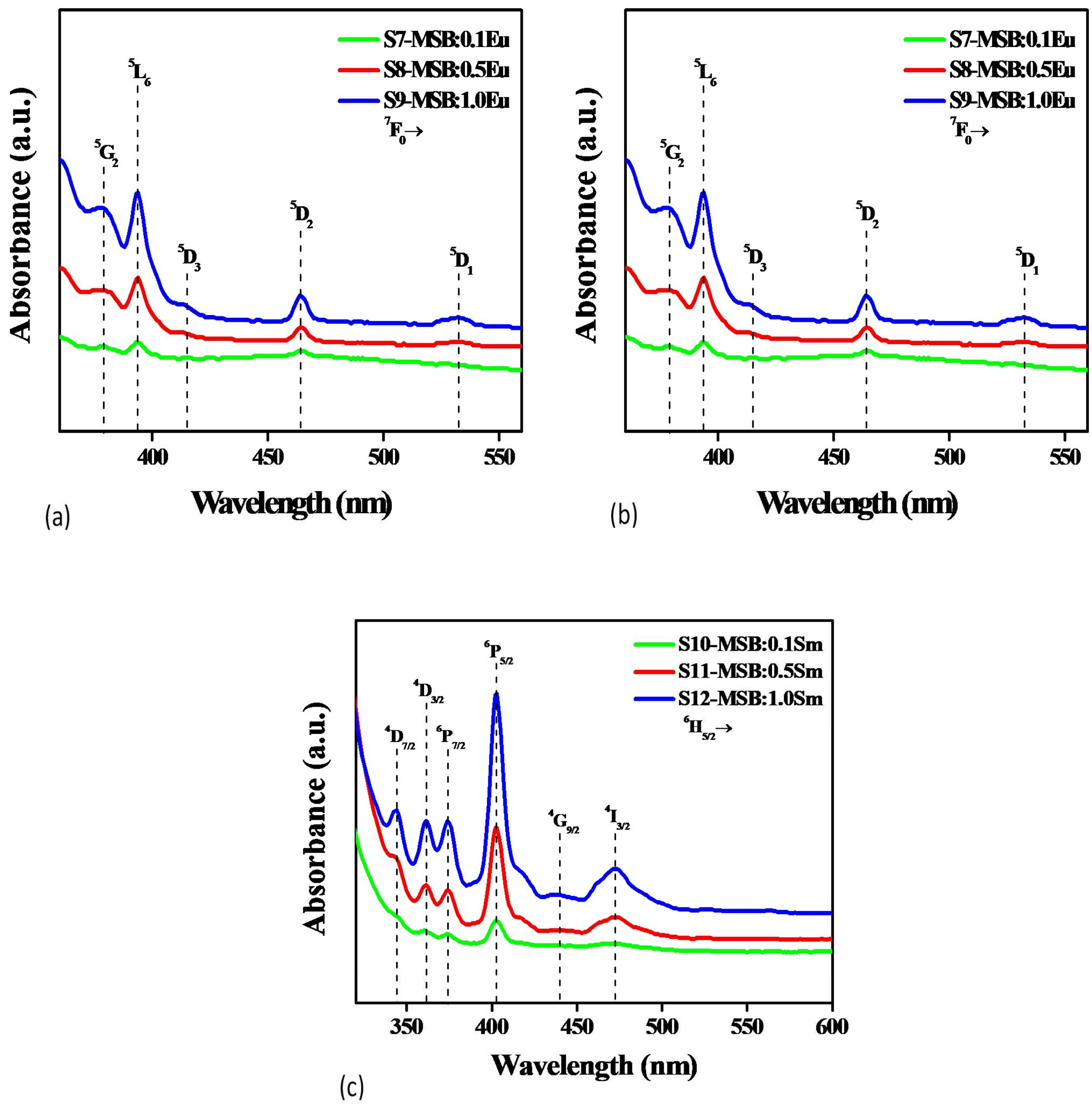

Fig. 2 The absorption spectra of MSB doped REIs (a) Dy^{3+}, (b) Eu^{3+} and (c) Sm^3

C. Emission Spectra Analysis

Fig. 3 shows the emission spectra of MSB doped with Dy^{3+}, Eu3^{+}, and Sm3^{+}. Fig. 3 (a) depicts the luminescence spectra of Dy^{3+} doped with MSB glasses excited at 347 nm. The sum of eight visible emission bands was observed at 419 nm, 443 nm, 451 nm, 463 nm, 482 nm, 573 nm, 598 nm, and 627 nm assigned to the $^4G_{11/2} \rightarrow {}^6H_{15/2}$, $^4I_{15/2} \rightarrow {}^6H_{13/2}$, $^4I_{15/2} \rightarrow {}^6H_{11/2}$, $^4F_{9/2} \rightarrow {}^6F_{11/2} + {}^6H_{9/2}$, $^4F_{9/2} \rightarrow {}^6F_{9/2} + {}^6H_{7/2}$, $^6F_{1/2} \rightarrow {}^6H_{5/2}$, $^6F_{1/2} \rightarrow {}^6F_{7/2}$, and $^6F_{1/2} \rightarrow {}^6F_{5/2}$ respectively. Among all of these transitions, the transition at 482 nm (blue) disclosed the highest intensity which is attributed to the electric dipole transition [17]. The maximum emission intensity occurs for sample S6 with 1.0 % mol Dy_2O_3.

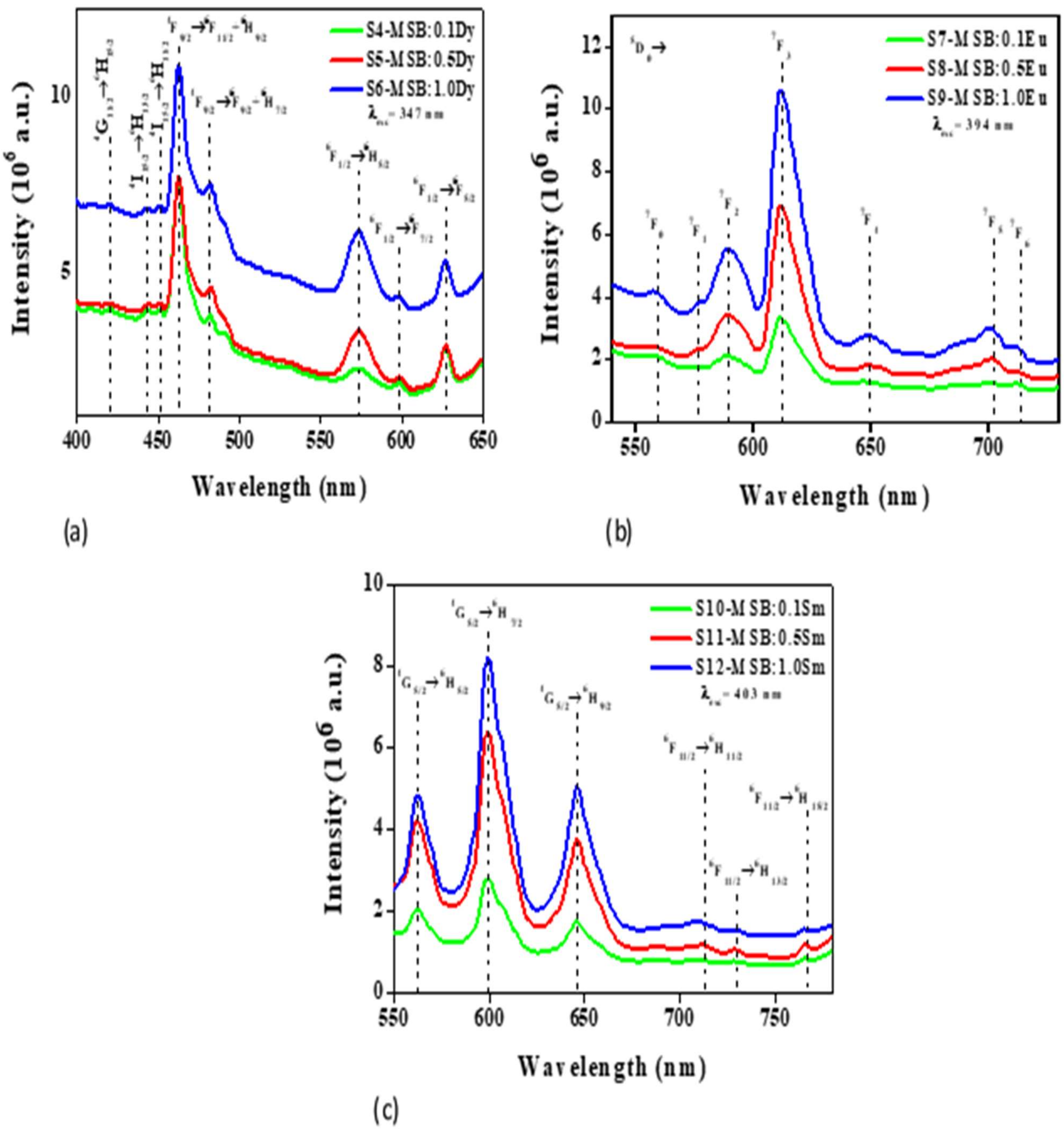

Fig. 3 Emission spectra of (a) Dy3+, (b) Eu3+, and (c) Sm3+

The Eu^{3+} doped MSB glasses series shows reasonable emission spectra (Fig. 4 (b).) ranging from 540 nm to 730 nm under 394 nm excitation light. The spectra unveiled seven emission bands situated at 558 nm, 576 nm, 589 nm, 612 nm, 649 nm, 701 nm, and 712 nm assigning to $^5D_0 \rightarrow {}^7F_J$ where J = 0,1,2,3,4,5, and 6 respectively. The most intense transition is $^5D_0 \rightarrow {}^7F_3$ centred at 612 nm (red emission) and host-dependent hypersensitive [16]. The second intense transition is $^5D_0 \rightarrow {}^7F_1$ peaking at 576 nm (yellow or bright orange region) and is ascribed to the magnetic dipole transition [16]. It is also observed from this Fig. that emission intensity is maximum for 1.0 mol % Eu_2O_3.

The emission spectra of Sm^{3+} doped MSB glasses are demonstrated in Fig. 3 (c). The emission bands centred at 563 nm, 599 nm, 646 nm, 712 nm, 728 nm, and 766 nm correspond to the$^4G_{5/2} \rightarrow {}^6H_J$ (J = 5/2, 7/2, and 9/2) and $^6F_{11/2} \rightarrow {}^6H_K$ (K =

11/2, 13/2, 15/2) transitions respectively. The transition $^4G_{5/2} \rightarrow {}^6H_{7/2}$ is the most intense followed by $^4G_{5/2} \rightarrow {}^6H_J$ (J = 9/2, and 5/2). The remaining transitions are in lower intensity thus have weak emissions. $^4G_{5/2} \rightarrow {}^6H_{7/2}$ transition has electric dipole while $^4G_{5/2} \rightarrow {}^6H_J$ (J = 9/2, and 5/2) contain magnetic dipole [18]. The trend of the emission spectra' intensity of Sm^{3+} and Eu^{3+} is almost similar which implies that more concentration (mol %) of Eu^{3+} and Sm^{3+} in MSB will increase their emission intensity. Table II shows a comparison between the excitation and the most noticeable emission wavelength attained in this study with those obtained in other related glasses.

Table II. Comparison of the observed excitation and prominent emission wavelengths with reported data on similar glass systems.

Glasses	Excitation wavelength (nm)	Prominent observed emission wavelength (nm)				Ref.
S4-MSB:1.0Dy	347	482	573	598	625	Present work
S4-MSB:1.0Eu	394	589	612	649	701	Present work
S4-MSB:1.0Sm	403	563	599	646	712	Present work
SrMB0.7Dy	347	481	572	660	–	[19]
SrMB0.5Sm	389	520	588	650	702	[19]
1Sm-CW	405	564	607	646	706	[20]
1Dy-CW	388	478	487	574	661	[20]
1Eu-CW	394	591	615	654	701	[20]

IV. CONCLUSION

In-swift, Dy^{3+}, Eu^{3+}, and Sm^{3+} singly doped MSB glasses have been successfully prepared by using a melt quenching route and optically analyze to comprehend their emission proficiency. The absorption spectra of each rare earth ion show that the most intense absorption bands for Dy^{3+}, Eu^{3+}, and Sm^{3+} were located at 347 nm, 393 nm, and 403 nm respectively depending on the concentration. Meanwhile, the emission spectra demonstrate the highest emission intensity situated at 463 nm, 612 nm, and 599 nm for Dy^{3+}, Eu^{3+}, and Sm^{3+} correspondingly where 1.0 mol% contents of Dy^{3+}, Eu^{3+}, and Sm^{3+} in MSB glasses was identified as best host with dazzling emission. This revelation reflects the potency of the present glass system in solid-state lasers and colour display device construction.

Reference

[1] W. D. Callister Jr, "Materials Science and Engineering". 7th Ed., John Wiley & Sons Inc., USA, 2007.

[2] E. Porai-Koshits, "Structure of glass: the struggle of ideas and prospects". J. of Non-Cryst. Sol., vol. 73, no. 1-3, pp. 79-89, 1985.

[3] S. A Dahaltu, R .Hussin and K. Deraman. "Structural Characterization of Sulfoborate Glasses Containing Magnesium Oxide" Jurnal Teknologi, vol. 78, no. 6-11), pp. 73-76, 2016.

[4] K. Abdellaoui, A. Ratep, A. Boumaza and I. Kashif, "The effect of the natural raw barite and the dolomite material on borate glass formation". J. of Fund. and App. Sci., vol. 10, no.1, pp. 281-300, 2018.

[5] M. Bengisu, "Borate glasses for scientific and industrial applications: a review". J. of Mat. Sci., vol. 51, no. 5, pp. 2199-2242, 2016.

[6] H. Othman, H. Elkholy and I. Hager, "FTIR of binary lead borate glass: Structural investigation". J. of Mole. Struct., vol. 1106, pp. 286-290, 2016.

[7] E. I. Kamitsos, M. A. Karakassides and G. D. Chryssikos, "Far-infrared spectra of magnesium-sodium-borate glasses". Sol. St. Comm., vol. 60, no. 11, pp. 885-888, 1986.

[8] S. Sen, "Temperature Induced Structural Changes and Transport Mechanisms in Borate, Borosilicate and Boroaluminate Liquids: High-Resolution and High-Temperature NMR Results". J. Non-Cryst. Solids, vol. 253, no. 1, pp. 84–94, 1999.

[9] J. Wu, M. Potuzak and J. F. Stebbins, "High-Temperature in Situ NMR Study of Network Dynamics in Boron-Containing Glass-Forming Liquids". J. Non-Cryst. Solids, vol. 357, no. 24, pp. 3944–3951, 2011.

[10] M. N. Svenson, et al., "Composition-Structure-Property Relations of Compressed Borosilicate Glasses". Phys. Rev. Appl., vol. 2, no. 2, pp. 24006, 2014.

[11] S. P. Jaccani and L. Huang, "Understanding Sodium Borate Glasses and Melts from Their Elastic Response to Temperature". Int. J. of App. Glass Sci., vol. 7, no. 4, pp. 452–463, 2016.

[12] J. Singh1, D. Singh, S. P. Singh, G. S. Mudahar and K.S. Thind, "Optical Characterization of Sodium Borate Glasses with Different Glass Modifiers". Mat. Phy. & Mech., vol. 19, pp. 9-15, 2014.

[13] R. S. Dawaud, S. Hashim, Y.S.M. Alajerami, M.H.A. Mhareb and N. Tamchek, "Optical and structural properties of lithium sodium borate glasses doped Dy^{3+} ions". J of Mole. Struct., vol. 1075, pp. 113- 120, 2014.

[14] V. Hegde, C. S. D. Viswanath, V. Upadhyaya, K. K. Mahato and S. D. Kamath, "Red light emission from europium doped zinc sodium bismuth borate glasses" Physica B: Condensed Matter, vol. 527, pp. 35-43, 2017.

[15] M. Sesha dri, M. Radha, D. Rajesh, L. C. Barbosa, C. M. B. Cordeiro and Y. C. Ratnakaram, "Effect of ZnO on spectroscopic properties of $Sm3^{+}$ doped zinc phosphate glasses" Physica B: Condensed Matter, vol. 459, pp. 79-87, 2015.

[16] P. P. Pawar, S. R. Munishwar, and R. S. Gedam, "Physical and optical properties of Dy^{3+}/Pr^{3+} Co-doped lithium borate glasses for W-LED" J. of Alloys and Comp., vol. 660, pp. 347-355, 2016.

[17] P. S Wong, M. H. Wan, R. Hussin, H. O. Lintang and S. E. Lintang, "Structural and luminescence studies of europium ions in lithium aluminium boro phosphate glasses". J. of Rare Earth, vol. 32, no. 7, pp. 585, 2014.

[18] S. Mohan, S. Kaur, D. P. Singh and P. Kaur, "Structural and luminescence properties of

samarium doped lead alumino borate glasses". Opt. Mat., vol. 73, pp. 223-233, 2017.

[19] A. Ichoja, S. Hashim, S. K. Ghoshal, Y. A. Yamusa, and A. M Aliyu, "Spectroscopic behaviour of Dy^{3+} and Sm^{3+} impurity-doped strontium magnesium borate glasses: A comparative evaluation". Optik, vol. 224, p.165641, 2020.

[20] P. Kaur, A. Khanna and M. Fabian, "Effects of annealing temperature on structural and photoluminescence properties of Eu, Dy and Sm doped CaWO4 nanoparticles". Ceramics Inter., vol. 46, no. 17, pp. 27262-27274, 2020.