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PHOTOLUMINESCENCE PROPERITES OF Pr^{3+} DOPED $SrO-Li_2O-ZnO-B_2O_3$ GLASSES FOR SOLID STATE LIGHTING

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Abstract

Pr^{3+} doped borate glasses with chemical composition of (60-x) B_2O_3 - 15ZnO -10Li_2O - 15SrO - xPr_2O_3 (x = 0, 0.25, 0.50, 0.75 mol%) had been prepared by the melt quenching technique and characterized by X-Ray Diffractometer (XRD), UV-Vis Spectrometer and Photoluminescence (PL) Spectrofluorometer. The XRD pattern confirmed the amorphous state for all the glass samples. Optical absorption spectra comprise of four transitions as the prominent absorption spectra from the ground state $^3H_4$ to the excited states within UV-Vis region. The excitation spectra of the Pr^{3+} doped glass samples were monitored at 605 nm. In the photoluminescence spectra the four peaks of down-converted emission bands are observed under excitation wavelength of blue light. The emission bands are centered at 485 nm (blue), 545 nm (green), 605 nm (orange) and 645 nm (red) at the visible region. Out of four bands, orange emission (605 nm) was the most intense. The intensity of the peaks in the emission spectra increase with increasing concentration of Pr^{3+} ions up to 0.50 mol% and then decrease. The results indicated that the glass sample with 0.50 mol% Pr^{3+} emits reddish orange color with highest intensity among the prepared glass samples.

Keywords: Pr^{3+} doped borate glasses, Photoluminescence, CIE chromaticity color co-ordinates.

Introduction

Glass signifies any amorphous solid that completely lacking in period atomic structure exhibiting a glass transition when heated towards the liquid state (J. E. Shelby *et al*, 2005). Nowadays, glass is used in numerous applications such as laser devices, optical fibers, optical waveguides, optoelectronic devices and radiation shielding materials. Rare Earth ions (RE^{3+}) doped glasses get much interesting due to their potential application in the development of various optical and optoelectronic devices, such as, solid state laser, optical amplifier, light converters, sensors, electro-chromic display devices, solid state lightning (LED's) etc. (P.P Pawar *et al*, 2016). RE^{3+} doped glasses are excellent luminescent materials due to their intense emission efficiencies corresponding to the 4f-4f and 4f-5d electronic transitions (P.P Pawar *et al*, 2016, M. Ilhan & M. K. Ekmekic, 2015). The optical properties and luminescence properties of rare earth ions in glasses depend on the chemical compositions of the glass matrix which determine the structure and nature of the bonds (A. Aiyeshah *et. al*, 2021, S. Mitru & S. Kaur, 2015). Good glass host is very important for efficient luminescence of RE^{3+} ions.

Among oxide glasses, borates glasses (B_2O_3) show remarkable properties because of the high thermal stability, lower degree of expansion in volume due to change in temperature, high transparency, low melting point and good rare-earth ion solubility owing to its network (N. Chopra *et al*, 2021, N. Chopra *et al*, 2018, Y. Zhang *et al*, 2009). Borate glasses constitute random network of either BO_3 triangles with non-bridging oxygen or BO_4 tetrahedrons with all bridging oxygen. It is used as one of glass host matrix for luminescence of rare earth ions. However, borate glass has high phonon energy, resulting in enhanced non-radioactive process that reduces luminescence

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efficiency. By doping alkali oxides or alkaline earth oxides, the luminescence properties of borate glass may vary strongly (H. Lin *et al*, 2015, L. Yuliantini *et al*, 2017). ZnO has an advantage due their network forming as well as modifying capability when enters glass network. Moreover, glasses containing metals minimize phonon energy and lead to an increase in the luminescence from excited rare-earth ion states (O. B. Aljewaw *et a*l, 2020, S. Damodaraiah *et al*, 2017). Among rare earths, most of them show visible emission while fewer such as Nd, Pr, Dy show NIR emission (M. Naftaly *et al*, 1998). Praseodymium can show both visible and NIR emission and it can also exhibit multi-photon emission under a high energy excitation, as an instance of down conversion (M. Erdem & A. Doğan, 2020, X. Zhou *et al*, 2019). The intension of the present research is to highlight the detailed photoluminescence characterization of praseodymium doped lithium strontium zinc borate glasses with the composition (60-x) B_2O_3 - 15ZnO -10Li_2O - 15SrO - xPr_2O_3 (for x = 0, 0.25, 0.50, and 0.75 mol%).

Materials and Method

Preparation of Pr^{3+} Doped Borate Glasses

Pr^{3+} doped borate glasses with different molar concentration were prepared by using melt quenching technique with the chemical compositions (60-x) B_2O_3 - 15ZnO -10Li_2O - 15SrO - xPr_2O_3 for x = 0, 0.25, 0.50, and 0.75 mol%. The details of composition of the samples used for the present work are categorized in the following list:

x = 0 : 60.00 B_2O_3 -15ZnO - 10Li_2O - 10SrO

x = 0.25 : 59.75 B_2O_3 -15ZnO - 10Li_2O - 10SrO - 0.25Pr_2O_3

x = 0.50 : 59.50 B_2O_3 -15ZnO - 10Li_2O - 10SrO - 0.50 Pr_2O_3

x = 0.75 : 59.75 B_2O_3 -15ZnO - 10Li_2O - 10SrO - 0.75Pr_2O_3

Analytical grade H_3BO_3, ZnO, $LiCO_3$, SrO and Pr_2O_3 with high purity up to 99.99% were used as starting batch materials. After batch calculations, these raw materials were weighed by using digital balance with an accuracy of ± 0.001 g, these chemicals were mixed thoroughly in an agate mortar. The total mix for each batch is 30 g. Then each batch was thoroughly grinded in an agate mortar to obtain fine and homogeneous powder. The resulting homogeneous mixture for each batch was put in an alumina crucible and melted at a temperature of 1100˚C for 1.5 hours in a temperature- controlled lifting furnace (Xiamen Tmax: SJF1600-1). The resulting molten sample was poured into a preheated steel mold. To remove sudden breaks due to thermal strains and to avoid the mechanical strains developed during the quenching process, it was annealed at 300˚C for 2 hours. The obtained undoped glass was almost transparent and colorless and all Pr^{3+} doped glasses were greenish yellow without bubble. The prepared glass samples were followed by a cooling down to room temperature. Part of prepared glass samples were ground into powder form for XRD measurement. Figure 1 and Figure 2 show the photograph for the steps in preparation of Pr^{3+} doped (60-x) B_2O_3 - 15ZnO -10Li_2O - 15SrO - xPr_2O_3 glasses and the photograph of the obtained glass samples respectively.

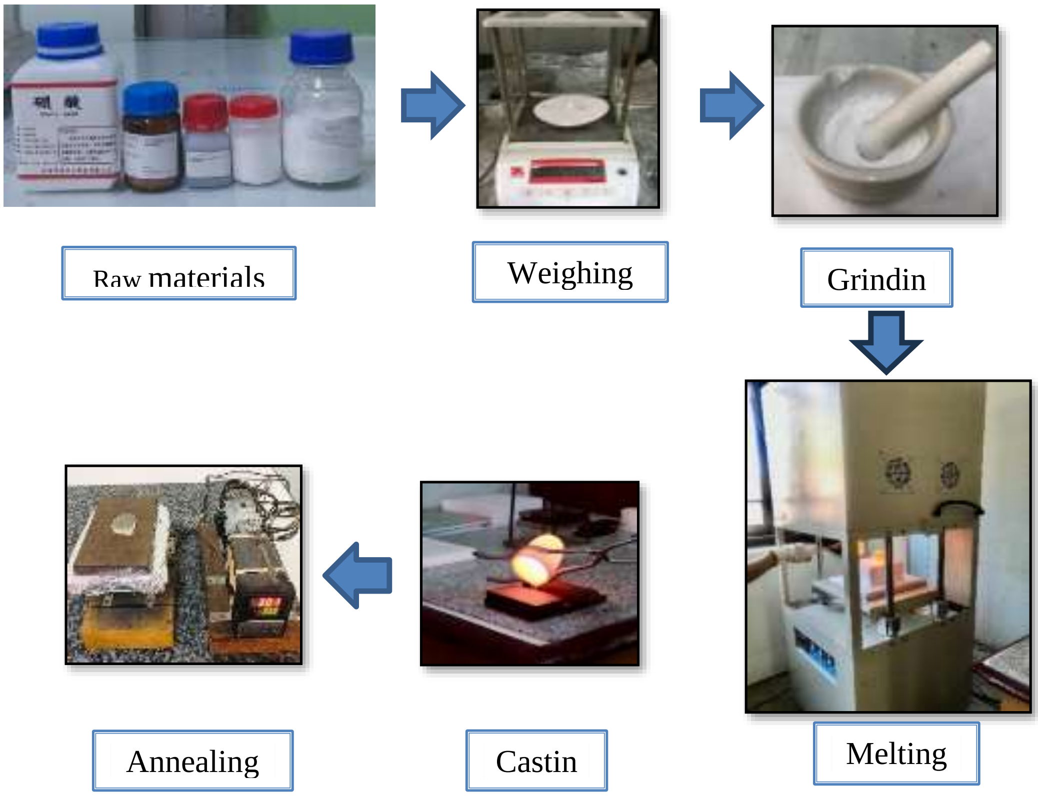

Figure 1. Photograph for the steps in preparation of Pr^{3+} doped (60-x) B_2O_3 - 15ZnO -10Li_2O - 15SrO - xPr_2O_3 glasses

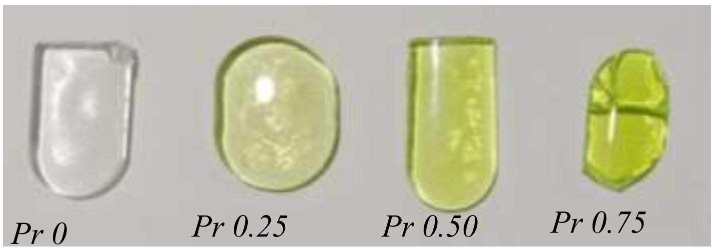

Figure 2. Photograph for the obtained glass samples

Characterization

To study the amorphous nature of the glasses, the X-ray diffraction (XRD) spectrum was recorded with X-ray diffractometer (XRD 6100 Shimadzu @ University of Magway) with copper target, operated at 40 kV and 30 mA. All data were collected at room temperature in the continuous-scan mode with a typical scanning speed of 5 degree per minute and a 2θ range of 20º to 70º. The optical absorption (UV–visible) spectrum was recorded with a Genesys 10S UV-Vis spectrophotometer (from Department of Physics, University of Mandalay) from 300 to 1000 nm, with spectral resolution of 0.1 nm. Finally, the emission and excitation were done with a FS-5 Fluorescence spectrometer (from Department of Physics, University of Mandalay) at room temperature, using a xenon flash lamp as excitation source.

Color of emission is studied via CIE (Commission International de I'Eclairage 1931) chromaticity diagram.

Results and Discussion

XRD Analysis

The XRD spectra of Pr^{3+} doped (60-x) B_2O_3 - 15ZnO -10Li_2O - 15SrO - xPr_2O_3 for x = 0, 0.25, 0.50, and 0.75 mol% are illustrated in Figure 3. It is observed that there is no definite sharp peak for all the samples. The XRD results exhibited the typical nature of the amorphous state for all the glass samples and the broad humps at lower angle indicated that there is the short -range order in glass samples.

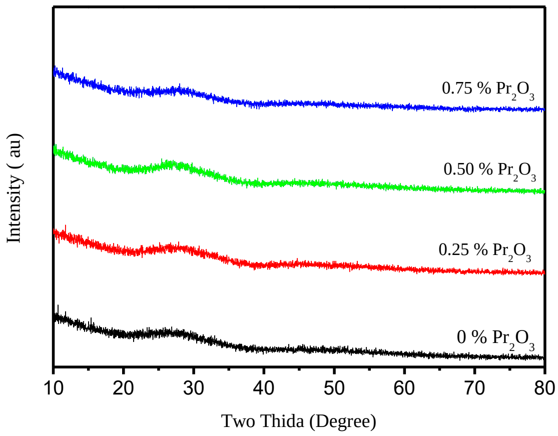

Figure 3. XRD spectra of Pr^{3+} doped (60-x) B_2O_3 - 15ZnO -10Li_2O - 15SrO - xPr_2O_3 glasses.

UV-Vis Analysis

Optical absorption spectra of (60-x) B_2O_3 - 15ZnO -10Li_2O - 15SrO - xPr_2O_3 (x = 0, 0.25, 0.50 and 0.75 mol%) glasses in the range of 300-1000 nm were measured and recorded at normal room temperature as presented in Figure 4. The spectra comprise of four prominent absorption spectra from $^3H_4$ the ground state within UV-Vis region. The absorption band are assigned the transition from the $^3H_4$ ground state to the $^3P_2$, $^3P_1$, $^3P_0$ and $^1D_2$ excited states belonging to the $4f^9$ electronic configuration of Pr^{3+} ions (M. Erdem & A. Doğan, 2020, R. Rajanavaneethakrishna *et al*, 2018, R.N.A. Prasadad *et al*, 2021). These transitions are centered at 445 nm, 470 nm, 484 nm and 660 nm respectively. All these observed transitions are in agreement with the other studied absorption data for Pr_2O_3 doped glasses. The absorption band positions of the present samples occur at almost the same wavelength. It was found that the observed absorption band intensities increase with increasing Pr_2O_3 content in the glass compositions and it signifies the good rare earth solubility of the prepared glasses. It further showed that the borate glass sample doped with 0 mol% Pr_2O_3 exhibits no detectable absorption peak in Figure 4. Different absorption transition of Pr^{3+} ions in the present glass samples were assigned with their respective wavelength and are presented in Table 1.

Table 1 The absorption peaks position and transitions of Pr^{3+} doped (60-x) B_2O_3 - 15ZnO - 10Li_2O - 15SrO - xPr_2O_3 (x = 0, 0.25, 0.50 and 0.75 mol%) glasses

Wavelength(nm)	Transition $^3H_4\rightarrow$	Refrences
444	$^3P_2$	R. Rajanavaneethakrishna *et al*, 2018
470	$^3P_1$	M. Erdem & A. Doğan ,2020
484	$^3P_0$	R.N.A Prasadad *et al*, 2021
660	$^1D_2$	Beena Bhatia1, et al, (2013)

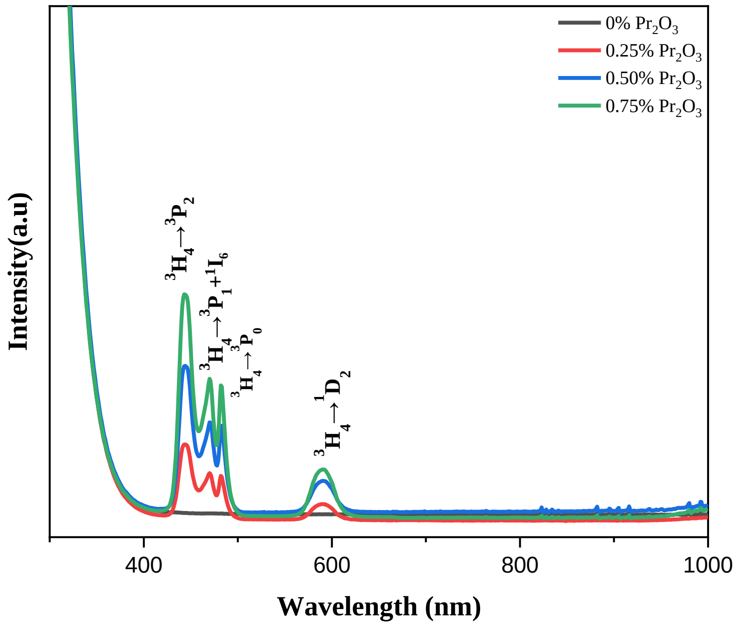

Figure 4. Optical absorption spectra of (60-x) B_2O_3 - 15ZnO -10Li_2O - 15SrO - xPr_2O_3 (x = 0, 0.25, 0.50, and 0.75 mol%)glasses for UV-Vis region.

Photoluminescence Properties

The excitation and emission spectra of (60-x) B_2O_3 - 15ZnO -10Li_2O - 15SrO - xPr_2O_3 (x = 0, 0.25, 0.50 and 0.75 mol%) glasses were carried out to study the photoluminescence properties of the present glasses. The excitation spectra, monitored at an emission wavelength of 605 nm, exhibit three excitation peaks in the blue region; namely, at 445, 470, and 483 nm, with corresponding transitions $^3H_4 \rightarrow {}^3P_2$, $^3H_4 \rightarrow {}^3P_1$ + $^3I_6$, and $^3H_4\rightarrow{}^3P_0$, respectively (R. Rajanavaneethakrishna *et al*, 2018, R.N.A. Prasadad *et al*, 2021, K.Neeraja *et al*,2013). It was obvious that the position of peaks is not affected but the intensity of peaks is affected by the changing of concentration of Pr^{3+} as shown in Figure 5. Among those three excitation transitions, the transition $^3H_4\rightarrow{}^3P_2$ (at 445 nm) exhibits the maximum intensity as compared to the other two transitions. Hence, the transition $^3H_4\rightarrow{}^3P_2$ was selected as excitation wavelength for emission. The emission spectra of the glass samples monitored at 445 nm excitation wavelength are presented in Figure 6. It was observed four the peaks of down-converted emissions of Pr^{3+} ions located at 485 nm (blue), 545 nm (green), 605 nm (orange) and 645 nm (red) at the visible region (M. Erdem &

A. Doğan, 2020, R. Rajanavaneethakrishna *et al*, 2018, R.N.A. Prasadad *et al*, 2021). These peaks correspond to the $^3P_0 \rightarrow {}^3H_4$, $^3P_0 \rightarrow {}^3H_5$, $^3P_0 \rightarrow {}^3H_6$, $^3P_0 \rightarrow {}^3F_2$ transitions at the visible region (M. Erdem & A. Doğan, 2020, R. Rajanavaneethakrishna *et al*, 2018, R.N.A. Prasadad *et al*, 2021). In the present glass system, orange luminescence dominates. It is also found that there is no change or any significant shift in the position of emission bands with the increase in concentration of Pr_2O_3 except the intensity in the emission spectra. The luminescence intensities of the emission transitions were found to increase with increasing in Pr^{3+} ion content up to 0.5 mol% due to increasing absorption intensity from the pump source at initial concentration. However, the emission intensity was obviously decreased at 0.75 mol% of Pr_2O_3 concentration. The result indicates that the absorption saturation was achieved at this stage and emission intensity began to decrease. This is known as a quenching effect between Pr^{3+} ions and that concentration quenching may occur at higher concentration due to the non-radiative energy transfer process which takes place between nearby Pr^{3+}- Pr^{3+} ions (P. Yasaka and J. Kaewkhao, 2016, M. Shwetha and B. Eraiah, 2021, M. A. Marzouk *et al*., 2012, H. A. Abd El-Ghany,2018). In the emission spectra, the highest emission peak obtained from $^3P_0$ to $^3H_6$ transition centered at 605 nm (reddish orange region). From emission spectra, it was observed that materials show the excellent luminescence properties in visible range under blue excitation wavelength due to f-f and d-f transition of Pr^{3+} ions (V. B. Pawade *et al*, 2017). It was clearly seen that the glass sample with 0.50 mol% Pr_2O_3 emits highest intensity.

The Commission International deI'Eclairage (CIE) chromaticity coordinates are measured for all prepared glass samples by using emission spectra under the excitation of 445 nm. The CIE coordinates are used to find color of light emitted by the material. The emission spectrum shows four bands as mentioned above. From CIE chromaticity-1931, the chromaticity diagram can be plotted. Figure 7 represents the CIE plot with color coordinates for Pr^{3+} doped glass samples. The color coordinates for all glass samples are listed in Table 2. CIE color coordinates for all Pr^{3+} doped glasses were well located in reddish orange region with slight variation of co-ordinates.

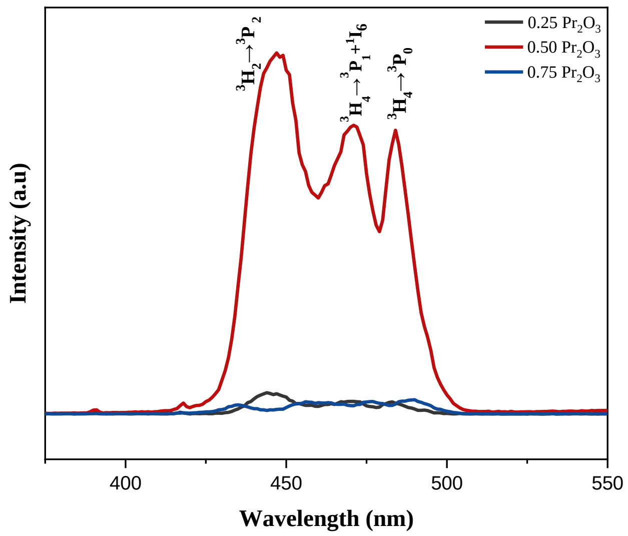

Figure 5. The excitation spectra of (60-x) B_2O_3 - 15ZnO -10Li_2O - 15SrO - xPr_2O_3 (x = 0, 0.25, 0.50, and 0.75 mol%)glasses with 603nm emission wavelength.

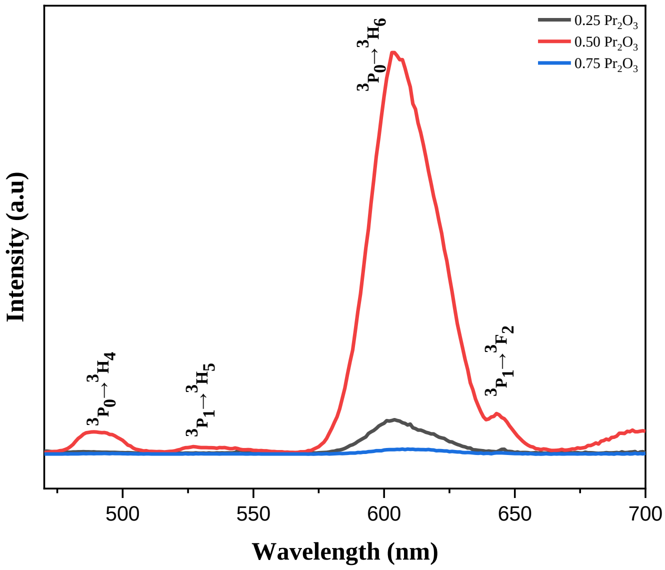

Figure 6. The emission spectra of (60-x) B_2O_3 - 15ZnO -10Li_2O - 15SrO - xPr_2O_3 (x = 0, 0.25, 0.50, and 0.75 mol%) glasses with 445 nm excitation wavelength.

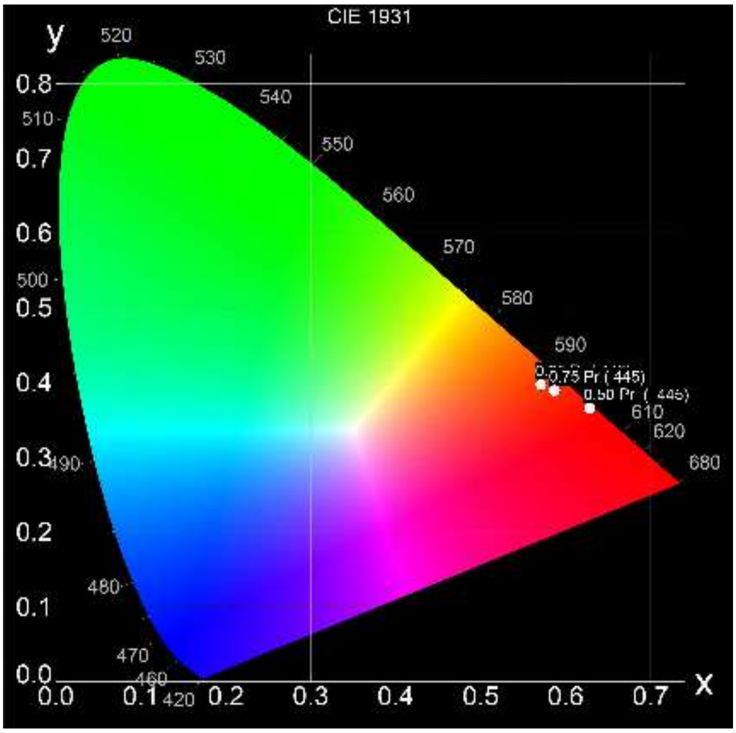

Figure 7. CIE graph of (60-x) B_2O_3 - 15ZnO -10Li_2O - 15SrO - xPr_2O_3 (x = 0, 0.25, 0.50, and 0.75 mol%) glasses

Table 2 CIE 1931 Chromaticity Color Coordinates (x, y) for Pr^{3+} doped (60-x) B_2O_3 - 15ZnO -10Li_2O - 15SrO - xPr_2O_3 glasses

Glasses	CIE coordinates	
	X coordinate	Y coordinate
0.25 Pr_2O_3	0.5710	0.3969
0.50 Pr_2O_3	0.6281	0.3652
0.75 Pr_2O_3	0.5869	0.3893

Summary and Conclusion

Pr^{3+} doped borate glasses with different molar concentration were prepared by using melt quenching technique with the chemical compositions (60-x) B_2O_3 - 15ZnO -10Li_2O - 15SrO - xPr_2O_3 (x = 0, 0.25, 0.50 and 0.75 mol%). The obtained glasses are transparent and colorless. The glasses samples were investigated by using XRD, UV- Vis and PL analysis. The measured XRD spectra confirmed the amorphous nature of the Pr^{3+} doped borate glasses. The optical absorption spectra for all glasses showed the four intense peaks due to transitions as from the $^3H_4$ ground state to the $^3P_2$, $^3P_1$, $^3P_0$, and $^1D_2$ excited states within UV-Vis region. According to PL analysis, the photoluminescence excitation spectra for the glass samples showed the strongest peak at 445 nm which has the maximum intensity and clearly indicated that the glass samples were efficiently excited by blue region. From emission spectra, it was seen that glasses show the good luminescence properties in visible range under blue light (445 nm). The results show the mechanism of down conversion by emitting the low energy photon after exciting it with high energy photon. The band at 605 nm is the highest one which is obtained from $^3P_0$ to $^3H_6$ transition (orange region). The photoluminescence intensity increases with increasing concentration of the Pr^{3+} ions up to 0.5 mol% then decrease. This decrease is due to the concentration quenching effect which is non-radiative energy transfer among excited Pr^{3+} ions. According to CIE chromaticity coordinates, the color coordinates of the present Pr^{3+} doped glasses all fall in the reddish orange region under excitation of the blue wavelength. Among three samples the sample with Pr^{3+} (0.5 mol%) showed highest emission intensity. Based on the obtained results, the studied Pr^{3+} doped glass samples may have possible application in emitting light source as the reddish orange component.

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