PHOTOLUMINESCENCE PROPERTIES OF Ho^{3+} - DOPED OXYFLUOROBORATE GLASSES

S. Farooq[1, 3*], Y. Munikrishna Reddy[2], R. Padmasuvarna[1].
[1]Department of Physics, JNT University, Anantapuramu - 515002, India.
[2]Department of Physics SSBN Degree & PG College, Anantapuramu-51500, India
[3]Department of Physics, RGM College of Engineering & Technology, Nandyal - 518501, India.

***Abstract:** A series of Antimony-magnesium-strontium-oxyfluoroborate glasses doped with Ho^{3+} ion at different concentration has been synthesized by conventional melt quenching method. XRD spectra recorded confirm the glassy nature of the prepared samples. Optical characteristics of the prepared glasses analyzed through absorption, excitation, photoluminescence spectra and decay measurements. The strong emission at 544 nm (green) and 664 nm (red) under 452nm excitation wavelength is observed in present Ho3+: glass systems. The decay curves are found to be single exponential at lower concentration and double exponential at higher concentration. The experimental lifetimes of Ho^{3+}: BMFSrSb glasses are found to be 0.015, 0.489, 0.446, 0.275, 0.330 and 0.01ms respectively. The resonant energy transfer among Ho^{3+} ions is responsible for decreased decay times. The CIE 1931 chromatic diagram reveals that the prepared glasses are efficient to use in green laser applications.*

***Keywords:** Holmium ions; fluoroborate glasses; optical properties; decay curves; CIE1931.*

I Introduction:

In various applications such as optical amplifiers, fiber lasers, solid state laser operating in Vis-IR spectral range, telecommunications, atmosphere transmission, Raman laser amplifier, eye-safe lidar and biomedical applications and optical oscillators [1–6] RE (rare earth) ion dope materials are still playing a vital role as active media. The 4f-4f electronic transitions of rare earth are more significant. Glasses getting much more importance as a suitable host for rare earths and are widely examined. The lasing action in visible and NIR regions makes the RE doped glasses are as a considerable materials used in laser media and single crystals have been substitute with RE doped glasses for SSL emission [7]. The optical transparency of glasses is responsible to show diversified latent laser transitions by rare earth ions. It is required to found new glass matrices having rare earth ions with greater quantum efficiency as the fluorescence properties of RE^{3+} ions influenced by host environment. The selection of host material plays an important role in increasing the quantum efficiency of RE ions. It is well established that RE^{3+}-doped borate, silicate, phosphate, and tellurite oxide glasses doped with RE ions have been recognized suitable hosts for the advancement in the field photonics.
In these prominent glass hosts, borate glasses found much attention as a host due to good RE^{3+} ion solubility, high thermal stability, chemical durability, relatively low melting temperature, mass production, cost-effective, good transparency and ability to form different structural units [8]. But, hygroscopic character of the borate glasses limits their performance as they absorb humidity and become volatile. This can be reduced by adding the modifiers such as alkali and alkaline earth metal ions which leads to enhance the optical and chemical properties [9]. Oxyfluoride glasses doped with RE^{3+} ions were found potential applications in photonics due to the combined merits of optical as well as photoluminescence properties of fluoride matrix and high chemical, thermal stability of oxides.

Glasses doped with Sb_2o_3 which is heavy metal oxide become chemically stable and more moisture resistant. Heavy metal oxides can be added to reduce the phonon energy [10]. The electronic transitions in visible, IR regions stimulate Ho^{3+} ion in spectroscopic studies. Ho^{3+} ions produce laser emission in IR region ranging from 1-4.9μm [11, 12]. Due to this an extensive investigation took place on Ho^{3+} doped glasses. Moreover the radiative transition $^5I_7 \rightarrow {}^5I_8$ at 2.0μm of Ho^{3+} ion obtained great attention owing to its significant applications for eye safe infrared lasers in medical field [13, 14]. The promising spectroscopic studies are observed due to different structural groups present in borate glasses.

II. Synthesis of glasses

Antimony-magnesium-strontium-oxyfluoroborate glasses doped with trivalent holmium ions were synthesized by traditional melt-quenching method with a glass composition of (70-x) B_2O_3 +10 MgF_2 +15 SrO +5 Sb_2O_3+x Ho_2O_3, where x =0.1, 0.5, 1.0, 1.5, 2.0 and 2.5 mol%, and labeled as BMFSrSbS01, BMFSrSbH05, BMFSrSbH10, BMFSrSbH15, BMFSrSbH20 and BMFSrSbH25 respectively. Raw materials of H_3BO_3, MgF_2, SrO, Sb_2O_3 and Ho_2O_3 from Alfa Aesar were used for the preparation of the glasses. About 15g of the batch composition was collected and mixed carefully in an agate mortar to attain a uniform mixture. This mixture was shifted to porcelain crucible and melted in an electric furnace at 1200 ºC for 1.30 hrs. Then the liquid molten liquid was casted on the brass mold and subsequently strengthened at 350 ºC about 10-15 hrs to remove internal strain and to enhance the mechanical strength of the glass. The glass samples were cooled to room temperature and polished for various optical characterizations. Transparent and light yellow color glass systems were obtained.

III. Characterization techniques

Optical absorption spectrum of 1.0 mol% Ho^{3+}-doped powder glass was recorded by using VARIAN carry-5000 double beam absorption spectrometer in the range of ultraviolet (UV)-near infrared (NIR) through diffuse reflectance mode. Photoluminescence spectra (excitation and emission) of samples were measured using Perkin Elmer SpectroFluorometer-950. Decay curves were obtained using the same instrument. Above all characterizations have been accomplished at room temperature.

IV. Results and discussions

4.1. XRD analysis

X-ray diffraction (XRD) profile of undoped powder glass sample is presented in Fig. 1. Broad humps are observed instead of sharp peaks in the XRD profile which was measured between 6° to 80°. These broad humps in XRD pattern are distinctive property of unstructured nature of the glass sample. Therefore, the XRD profile is confirmed that the structure of the present glass matrix was amorphous.

4.2. Absorption Spectra

Fig-2 and Fig-3 exhibits absorption spectra of 1.0 mol % of BSbMgfSrH glass matrix in Vis-NIR regions which consists of 8 absorption bands at 417, 451, 485, 539, 641, 889, 1150, 1942 nm wavelengths and these were assigned to transitions (^5G, ^3G)$_5$, $^5G_6$, $^5F_3$, $^5F_4$, $^5F_6$ $^5I_5$, $^5I_6$ and $^5I_7$ respectively from the ground state $^5I_8$ of the Ho^{3+}.The method outlined by Carnall et al. [15] was used to identify and assign the energy levels. The bonding parameters ($\bar{\beta}$, δ) of the glass BSbMgfSrH10 have been calculated by using the expressions in literature [16] and given in Table-1. Negative value of bonding parameter shows that the prepared glasses possess ionic nature.

4.3. Emission spectra

The photoluminescence spectra of 1.0 mol% Ho^{3+} ion doped BSbMgfSr glass matrix excited at 539 nm has been recorded in the spectral region 450-800 nm and is displayed in Fig-4. Two emission bands at 556 and 664 nm are observed and attributed to transitions such as, $^5S_2 \rightarrow {}^5I_8$, and $^5F_5 \rightarrow {}^5I_8$ respectively. From the spectra it has been observed that the emission intensity increases with an increase in concentration of Ho^{3+} ion up to 1.0 mol% and then decrease in intensity was observed at 1.5 to 2.5 mol%. The concentration quenching took place beyond 1.0 mol% of Ho^{3+} ion for the glasses. The decrease in intensity can be attributed to the energy transfer between Ho^{3+} -Ho^{3+} ions among resonant energy levels.

4.5. Decay curve analysis

Luminescence decay curves of the $^5S_2 \rightarrow {}^5I_8$ level of Ho^{3+} ion in BSbMgfSrH glasses were recorded under excitation wavelength of 539 nm are shown in Fig-5.

Decay curves exhibits single exponential for 0.1 mol% and 0.5 mol% Ho^{3+}-doped glass non-exponential nature for 1.0, 1.5, 2.0, 2.5 mol% of the Ho^{3+}concentrations. Lifetime of the $^5S_2$ level can be obtained by analyzing the decay profiles with mono- and double-exponential functions as given below [17].

$$I = I_0 \exp {}^{-t}/_{\tau} \text{ (Mono-exponential decay)} \quad \rightarrow (1)$$

$$I = A_1 \exp {}^{-t}/_{\tau 1} + A_2 \exp {}^{-t}/_{\tau 2} \text{(Two-exponential decay)} \quad \rightarrow (2)$$

where I_0 is the intensity at t = 0, τ is the time required for the intensity to decay to 1/e times if its initial lifetime value for mono-exponential decay I(t) is the intensity at any time t, A_1 and A_2 are fitting parameters and τ_1, τ_2 are long and short lifetimes. The mean lifetime for non-exponential curve can be calculated by using the expression [17, 18].

$$\tau = (A_1\tau_1^2 + A_2\,\tau_2^2)/(A_1\tau_1 + A_2\tau_2) \quad \rightarrow (3)$$

Where A_1 and A_2 are the amplitude components of decay and τ_1, τ_2 are fluorescence life times. The experimental lifetimes are found to be 0.015, 0.489, 0.446, 0.275, 0.330 and 0.01ms for 0.1, 0.5, 1.0, 1.5, 2.0 and 2.5 mol%, respectively. It is observed that life time decreases with increasing Ho^{3+} ions concentration. The decreasing in lifetime with increase of Ho^{3+}- ion concentration can be attributed due to RET (resonant energy transfer) at higher concentration in between Ho^{3+}- Ho^{3+} ions by diffusion [19-20]. The energy level diagram is shown in Fig- 6.

4.6. CIE diagram for chromaticity coordinates

The color coordinates have been calculated in order to know the emission color from the fabricated glass systems by the procedure reported in our previous work [21, 22]. From the CIE 1931 chromatic diagram unveil in Fig. 7. , the produced glasses of concentration 0.5, 2.0, 2.5 mol% of Ho^{3+} are observed to cover the green region with color coordinates (0.22, 0.57), (0.18, 0.57) and (0.22, 0.57) respectively. Hence the glass systems BMFSrSbH05, BMFSrSbH20, BMFSrSbH25 can be potentially use for green lasers producing devices.

V. Conclusion

Holmium (Ho^{3+})-doped antimony-magnesium-strontium-oxyfluoroborate (BMFSrSbH) glasses have been analyzed through optical absorption, photoluminescence emission and decay measurements. The $^5I_8 \rightarrow {}^5G_6$ (539 nm) transition was found to be stronger in excitation spectrum, which was used for investigating the emission properties of BMFSrSbH glasses. Photoluminescence emission spectra were acquired upon exciting the samples at a wavelength of 452 nm. The intensity of emission peaks was increased with the increase in Ho^{3+} ions concentration up to 1.0 mol% and quenched beyond 1.5 mol%. Decay curves of Ho^{3+} ions were exhibited single exponential up to 0.5 mol%

and shifted to non-exponential with the increase of Ho^{3+} ions concentration from 1.0 mol% to 2.5 mol%. The color coordinates for the present glasses are calculated from CIE 1931 diagram and BMFSrSbH05, BMFSrSbH20, BMFSrSbH25 are situated in the exact green region. The photoluminescence properties of these glasses could be utilized for the development of suitable visible green lasers.

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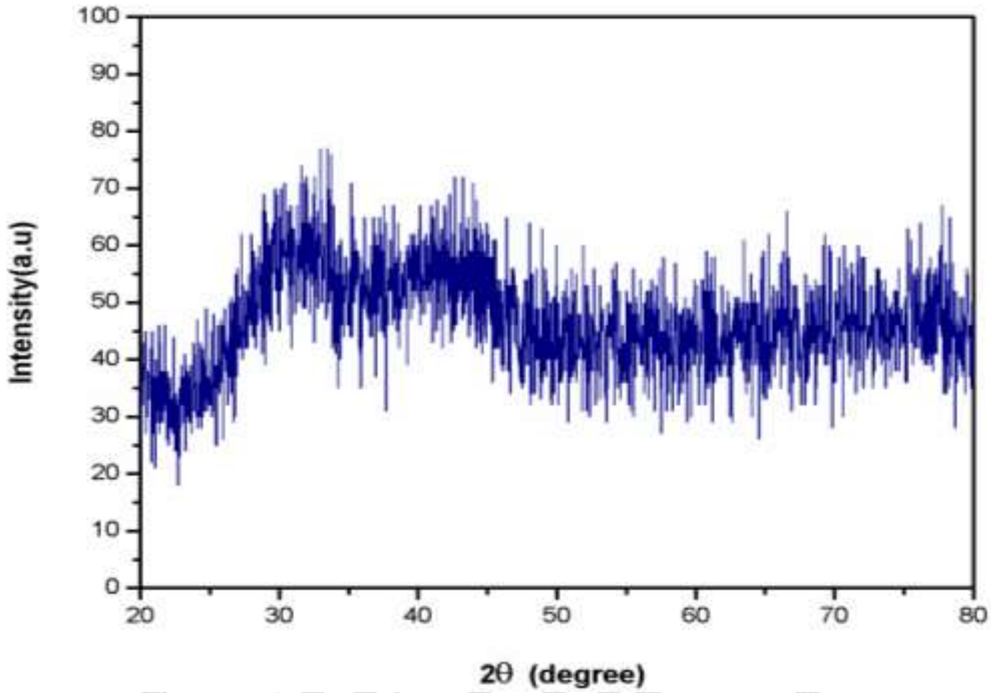

Fig.1. XRD profile of BMFSrSb glass

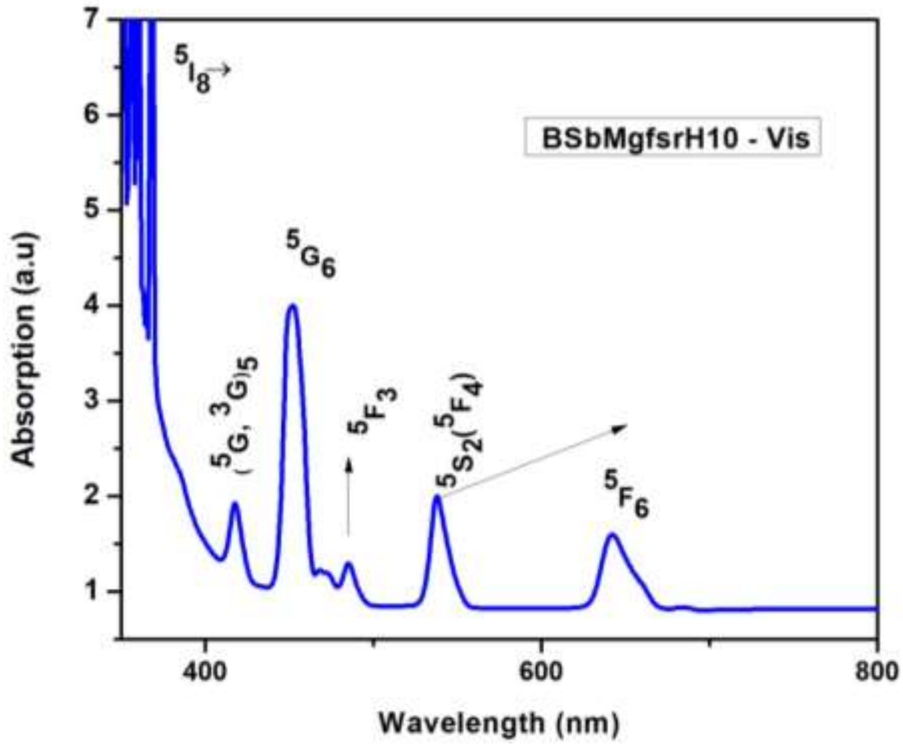

Fig - 2 absorption spectrum of the BSbMgfSrH10 glass in visible region.

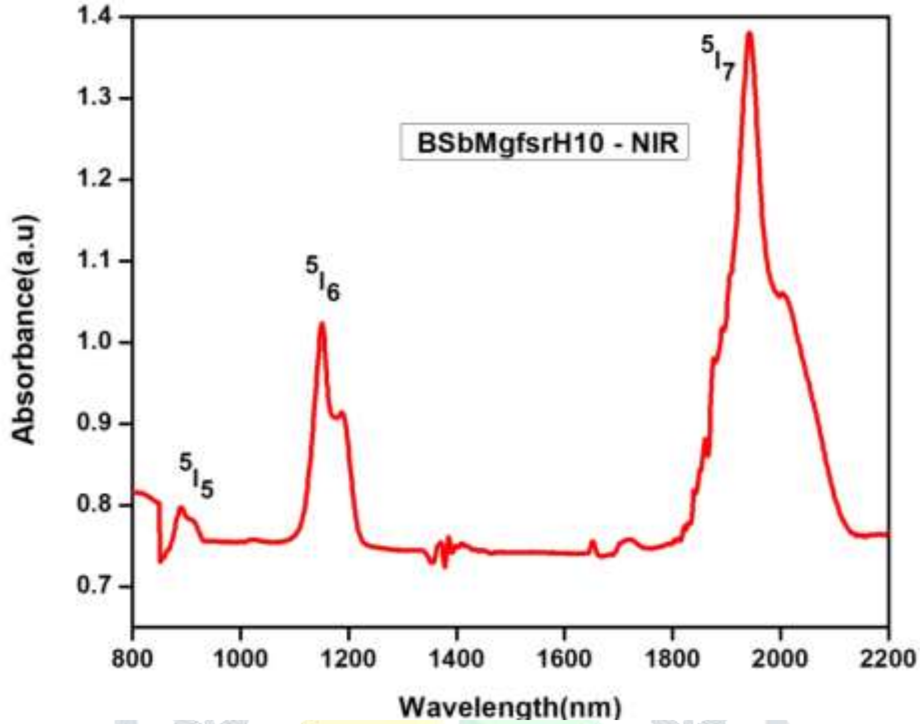

Fig - 3 absorption spectrum of the BSbMgfSrH10 glass in NIR region.

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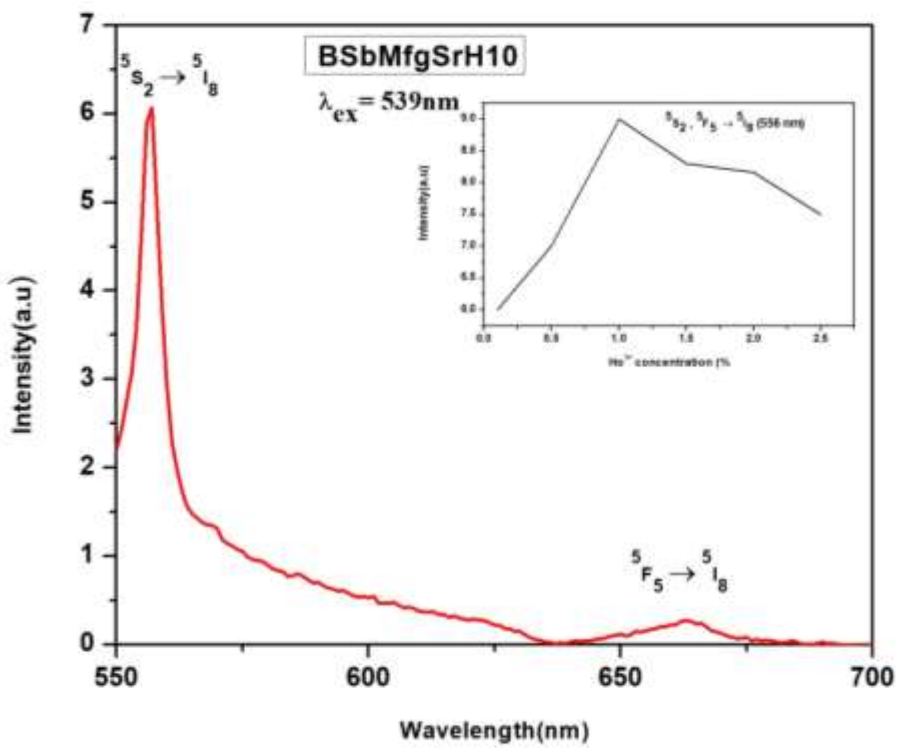

Fig-4 Emission spectra of BSbMgfSrH10 glasses

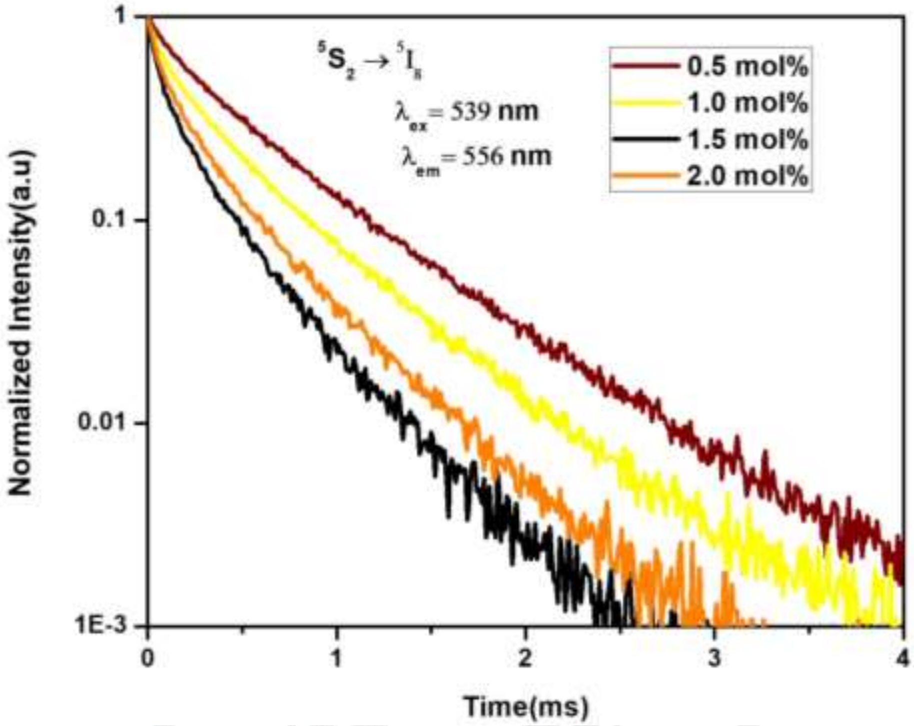

Fig-5 Decay profiles of BSbMgfSrH05, BSbMgfSrH10, BSbMgfSrH15 and BSbMgfSrH20 glasses

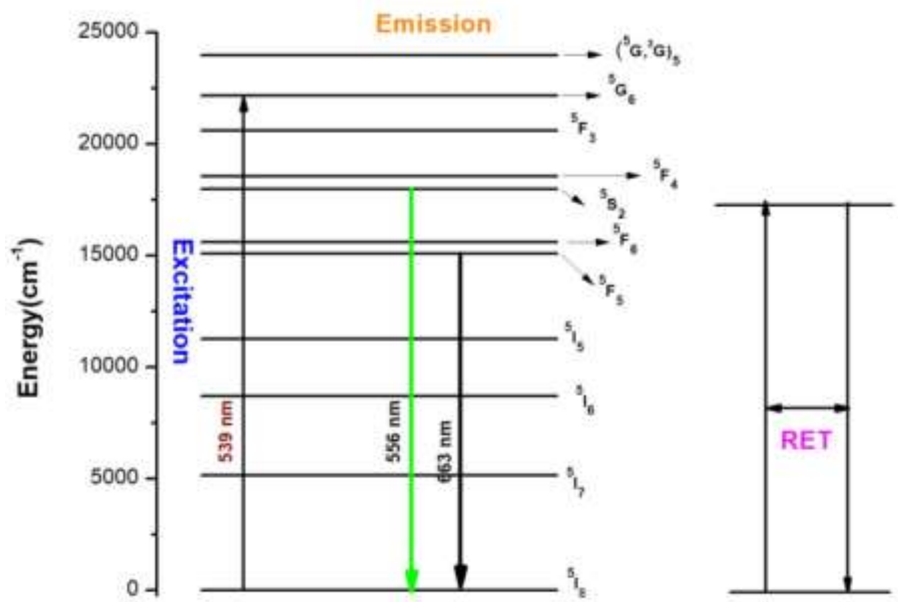

Fig-6 Energy level diagram of Ho^{3+} ion in BSbMgfSr glass systems

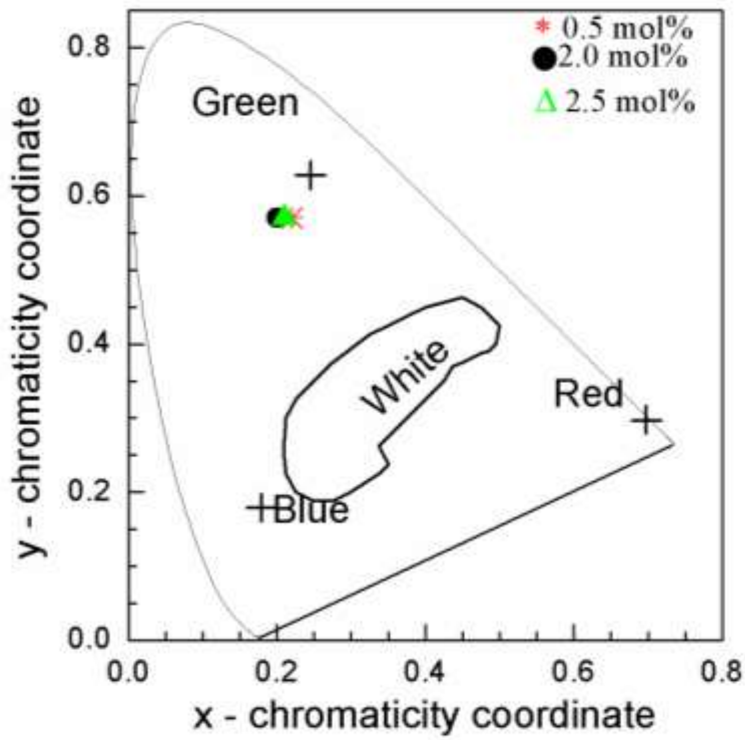

Fig.7. Representation of chromaticity coordinates of Ho^{3+}-doped glasses in CIE chromatic diagram.

Table-1 Transition, Peak wavelength (λ), absorption bands, 1.0 mol% Ho^{3+}- doped BSbMgfSr glass.

Transition $^5I_8 \rightarrow$	**Wavelength λ(nm)**	**Energy E (cm^{-1})**
$(^5G, ^3G)_5$	417	23980
$^5G_6$	451	22172
$^5F_3$	485	20618
$^5F_4$	539	18552
$^5F_6$	641	15600
$^5I_5$	889	11248
$^5I_6$	1150	8695
$^5I_7$	1942	5149
$\bar{\beta}$	1.0166	
δ	-0.0163	