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Luminescence Properties of Dy^{3+} and Sm^{3+}: Potassium Lithium Borate Glass

Haydar Aboud[a,b*], H. Wagiran[b], R. Hussin[b]

[a]*Baghdad College of Economic Sciences University, Iraq*
[b]*Department of Physics, Faculty of Science, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia*

*Corresponding author: han55608@yahoo.com

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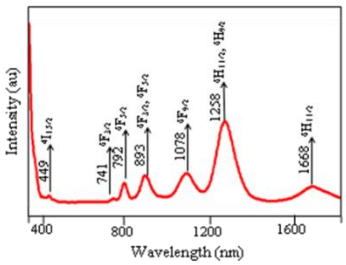
Graphical abstract



Abstract

The present paper describes the spectral properties of Sm^{3+} (0.4 mol%) and Dy^{3+} (0.4 mol%) ions-doped $20Li_2O–10K_2O–70B_2O_3$ glasses. X-ray diffraction method was use to confirm the amorphous phase of samples. The physical properties have been determined based on UV absorption spectra. The hypersensitive transition of Dy^{3+} and Sm^{3+} is found due to transition of ($^6F_{11/2}$,$^6H_{9/2}$) and ($^6F_{7/2}$), respectively. The emission bands of Dy^{3+}: glass has shown around 572 nm, 612 nm and 646 nm; these emissions are attributed to the transitions of $^4F_{9/2} \rightarrow {}^6H_{15/2}$ (yellow), $^4F_{9/2}$ - $^6H_{13/2}$ (red) and $^4F_{9/2}$ -$^6H_{11/2}$ (red). With regard to Sm^{3+}: glass has three emission bands those have been generated from $^4G_{5/2} \rightarrow {}^6H_{5/2}$ (616 nm), $^4G_{5/2} \rightarrow {}^6H_{7/2}$ (660 nm) and $^4G_{5/2} \rightarrow {}^6H_{9/2}$ (719 nm) transitions. The current results promise several applications in optical fields such as UV-sensor, developing new color light sources and tunable visible lasers.

Keywords: Glasses; rare-earth ions; physical properties; luminescence

Abstrak

Artikel ini menerangkan ciri-ciri spektra Sm^{3+} (0.4 mol%) dan Dy^{3+} (0.4 mol%) ion dop dalam kaca $20Li_2O–10K_2O–70B_2O_3$. Keadah pembelauan sinar-X telah digunakan untuk menentukan fasa amorfus dalam sampel kaca. Ciri-ciri fizikal telah ditentukan berdasarkan kepada spektra serapan lampau unggu. Peralihan hipersensitif dari Dy^{3+} dan Sm^{3+} didapati masing-masing dari peralihan ($^6F_{11/2}$, $^6H_{9/2}$) and ($^6F_{7/2}$). Jalur pancaran dari ion Dy^{3+} dalam kaca telah menunjukkan pada 572 nm, 612 nm dan 646 nm. Pancaran ini hasil dari peralihan $^4F_{9/2} \rightarrow {}^6H_{15/2}$ (kuning), $^4F_{9/2} \rightarrow {}^6H_{13/2}$ (merah) dan $^4F_{9/2} \rightarrow {}^6H_{11/2}$ (merah). Bagi ion Sm^{3+} dalam sampel kaca tersebut telah menunjukkan tiga jalur pancaran, yang dihasilkan dari peralihan $^4G_{5/2} \rightarrow {}^6H_{5/2}$ (616 nm), $^4G_{5/2} \rightarrow {}^6H_{7/2}$ (660 nm) and $^4G_{5/2} \rightarrow {}^6H_{9/2}$ (719 nm). Keputusan yang diperolehi telah menunjukkan bahawa kaca yang diperolehi berpotensi untuk beberapa kegunaan dalam bidang optik seperti penderia lampau unggu, penghasilan sumber cahaya berwarna dan laser cahaya nampak boleh laras.

Kata kunci: Kaca; ion nadir bumi; ciri-ciri fizikal; luminesens

1.0 INTRODUCTION

The borate glass doped with rare earth (RE) ions has attracted research interests in the field of photoluminescence due to many potential optical applications such as lasers, sensors and optical amplifiers [1]. Borate glasses containing alkali or alkaline earth oxides are showing unusual properties such as high electrical resistance, excellent chemical durability, high hardness and low melting temperature compared to silicate glasses [2]. Doping of glasses with dysprosium, samarium, terbium or europium leads to emission in the visible range [3]. The emission efficiency of trivalent RE ions in oxide glasses is high by direct excitation of electrons into (parity forbidden) absorption lines of the 4*f* shell in the visible and the soft ultraviolet (UV) energy range [3].

Recently, the beneficial properties of phosphate, silicate, borate and tellurite glasses with samarium oxide and dysprosium oxide have been reported by Lakshminarayana and Qiu [4]. The advantageous of these doped are not for infrared optical devices but it is an interest to investigate in visible optical devices. Moreover, the Dy^{3+} is a good activator because the two dominated band in the emission spectra, and its position depends strongly on the crystal field of the lattice used [5]. In addition, the luminescence materials doped with Dy^{3+} could provide yield of white emission by adjusting the value of yellow

to blue intensity ratio, which can be utilized as potential white phosphors. On the other hand, Sm^{3+} ion, it gives a red color emission. Furthermore, it has had high-density optical storage and high quantum efficiency.

The increasing demand on the different types of visible lasers and light sources, more investigations were proceed in order to determine efficiency rear earth as doped and to enhance the optical properties of glass; for instance, Eu^{3+} [6-8], Dy^{3+} [9,10], Sm^{3+} [11,12] and Tb^{3+} [13] has been explored. Optimization of optical quality glasses doped with rare earth ions have been characterized through absorption and emission transition probabilities which are influenced by the ligand field of the surrounding rare earth ions [4,5]. In addition, the structure of borate glasses are interesting due to many superstructural units such as boroxol and triborate groups as seen in the corresponding crystalline polymorphs [1]. Upon the introduction of alkali or alkaline earth oxides, boron changes from threefold to fourfold coordination and BO_4 tetrahedra link the layers of boroxol rings into a three-dimensional framework. Therefore, the glass sample in the composition of $20Li_2O–10K_2O–70B_2O_3$ doped with samarium and dysprosium is interested to study. The aim of the present work is to investigate the influence of divalent oxides such as Li_2O and K_2O on the absorption and luminescent properties of the potassium lithium borate glass by means of UV and photoluminescence spectroscopy.

■2.0 EXPERIMENTAL METHODS

2.1 Glass Preparation

The potassium lithium borate glasses used in this work were prepared with the following composition in mol%, $20Li_2O–10K_2O–70B_2O_3$:$0.4Dy^{3+}$ and $20Li_2O–10K_2O–70B_2O_3$:$0.4Sm^{3+}$ by employing the melt-quenching technique, using high purity boric acid (H_3BO_3), lithium carbonate (Li_2CO_3), magnesium oxide (MgO), samarium(III) oxide (Sm_2O_5) as raw materials. All chemical mixtures were selected as a fine powdered with 99.99% purity. Before the process of melting, the powders were mixed and homogenized by milling the powders for 40 minutes. The homogenous mixture transferred to a platinum crucible and heated at 1200°C for one hour. After ensuring of homogeneity, the melt sample was poured onto a stainless steel plate for the produce glass sample. In addition, the glass was transferred to furnace for annealing at 400°C where it was kept for 3 hours to release any residual stress, which could cause loss of ductility of a material making it brittle.

2.2 Characterization

The optical absorption spectra in the visible and near ultraviolet region were measured at room temperature utilizing bulk form of the samples, using a Shimadzu 3101 UV-Vis-NIR spectrophotometer in the range of 200 –2000 nm. The absorbance signal was determine by double monochromatic diffraction grating system and photomultiplier R-928 detector with resolution about 0.1 nm. The absorption peaks and band assignments of each peak are obtain from the absorption spectra. A Perkin Elmer LS55 Luminescence Spectrophotometer is use to investigate emission spectra of samples. The luminescent properties of glass was studied rely on the emission and excitation. The glass bulk was place in the sample holder; it was scan from 200 to 2000 cm^{-1} at room temperature. The luminescence signal was analyze using a Monk-Gillieson type monochromator equipped with a photodiode detector at particular excitation wavelength.

■3.0 RESULTS AND DISCUSSION

The XRD pattern of the $20Li_2O–10K_2O–70B_2O_3$ doped with 0.4 mol % Dy^{3+}, 0.4 mol% Sm^{3+} glass is shown in Figure 1. It can be seen clearly that both XRD shapes did not detect the presence of any crystalline phases and confirmed the amorphous nature of glass samples.

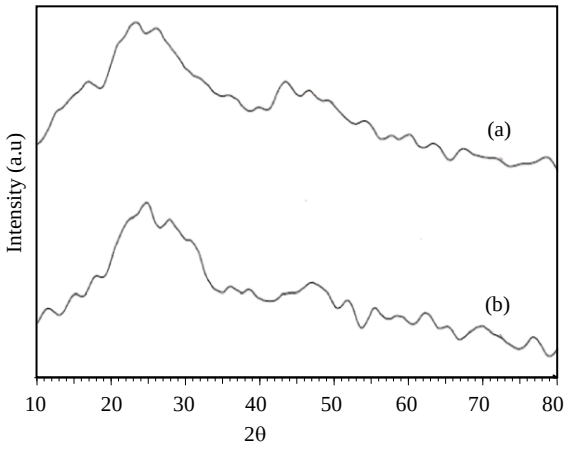


Figure 1 XRD patterns of (a) Dy^{3+} ions and (b) Sm^{3+} ions doped $20Li_2O–10K_2O–70B_2O_3$ glasses

Based on the various mathematical expressions reported earlier in the literature [14-16], we computed the physical properties and other related material characteristic parameters and to evaluate the significant effects on the glasses doped with Dy^{3+} ions and Sm^{3+} ions. The data of physical properties of study glass are shows in Table 1 for a comparison. The measurement methods of physical properties are described earlier [17]. There are no changes in refractive index and density data of the reference glasses with that of samarium and dysprosium -doped glasses. The direct and indirect optical band gaps were also calculated from the UV absorption spectrum of Dy^{3+} and Sm^{3+} ions doped glass and the results were also presented in Table 1. The optical band gaps of glasses have been computed based on their UV absorption spectra, for understanding their optically induced transitions. The principle behind this technique is that a photon with energy greater than the band gap energy will be absorbed. There are two kinds of optical transitions at the fundamental absorption edge: direct and indirect transitions, both of which involve the interaction of an electromagnetic wave with an electron in the valence band. The physical properties of the studies glasses are almost similar to each other. The rare-earth ions are characterized by partially filled 4f shell, which is provided by $5s^2$ and $5p^6$ electrons.

The VIS–NIR absorption peak of 0.4 mol% Dy^{3+} doped glass has been shown in Figure 2. The inhomogeneous broadened bands are assigned due to the transitions from the $^6H_{15/2}$ ground state to the excited states of the Dy^{3+} ion. It is clear that the absorption peaks existed around 449 nm, 741 nm, 792 nm, 893 nm, 1078 nm, 1258 nm and 1668 nm in a sample, which correspond to the transitions from ground state of $^6H_{15/2}$ to the excited state of $^4I_{15/2}$, $^6F_{3/2}$, $^6F_{5/2}$, $^6F_{7/2}$ ($^6F_{5/2}$), $^6F_{9/2}$, $^6F_{11/2}$ ($^6H_{9/2}$) and $^6H_{11/2}$, respectively. From absorption peak, it can observe that the intense peaks between 800 and 1600 which is probably due to the generation of color centers. Similar results have also been obtained by Lakshminarayana and Qiu [4].

Table 1 Physical properties of Sm^{3+} (0.4 mol%) and Dy^{3+} (0.4 mol%) ion doped $20Li_2O–10K_2O–70B_2O_3$ glasses

Physics properties	Data	
	Dy^{+3}	Sm^{+3}
Density g cm^{-3}	2.45	2.49
Refractive index, n_d	1.86	1.79
Average molecular weight, M (g)	73.11	73.03
Molar Volume (cm^3/mol)	29.8	29.3
N ($\times10^{20}$ ions/cm^3)	0.8872	0.8215
Polaron radius (Å)	1.946	1.996
Cut-off wavelength (nm)	398	388
Inter-nuclear distance (Å)	4.83	4.955
Direct optical band gap, E_g (eV)	3.12	3.2
Indirect optical band gap, E_g (eV)	3.08	3.14
Field strength F (10^{16} cm^{-2})	0.792	0.753

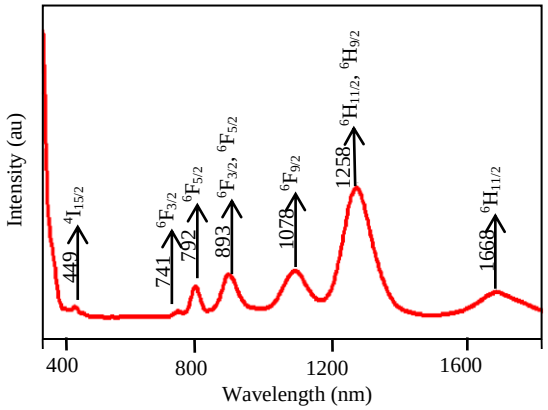


Figure 2 VIS–NIR absorption spectra of Dy^{3+} ions doped $20Li_2O$-$10K_2O$-$70B_2O_3$ glass

The VIS–NIR absorption spectrum of Sm^{3+} ion is shown in Figure 3, with strong absorption bands in the NIR region. It is that the absorption peaks of Sm^{3+} existed around 397 nm, 469 nm, 943 nm, 1078 nm, 1226 nm, 1371 nm, 1470 nm ,1470 nm, 1529 nm and 1862 nm in sample, which corresponding to the transitions from ground state $^6H_{5/2}$ to the excited state $^4F_{7/2}$, $^4I_{11/2}$, $^6F_{11/2}$, $^6F_{9/2}$, $^6F_{7/2}$, $^6F_{5/2}$, $^6F_{3/2}$, $^6H_{15/2}$ and $^6H_{13/2}$ respectively. In the case of Sm^{3+} ion, the hypersensitive transition ($^6F_{7/2}$) was noted more intense than the other transitions. Where, this behavior is found similar to those obtained in the previous research [18].

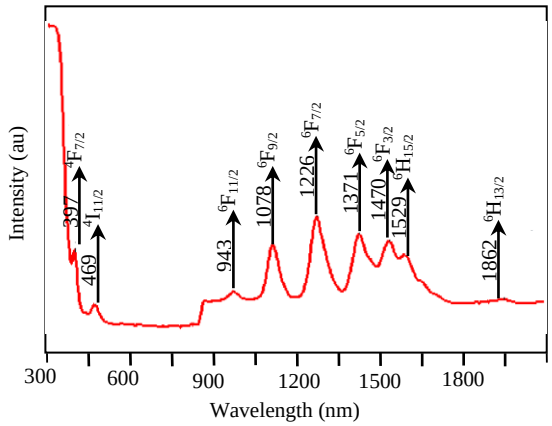


Figure 3 VIS–NIR absorption spectrum of Sm^{3+} ions doped $20Li_2O$–$10K_2O$–$70B_2O_3$ glass

Jorgensen and Judd explained that the position and intensity of certain transitions of rare-earth ions are found to be very sensitive to the environment around the ion. Such transitions are termed as hypersensitive transitions [18]. All known hypersensitive transitions obey the selection rule $|\Delta S=0|$, $|\Delta L=0|$, $|\Delta J=0|$ (18). In this work the Dy^{3+} ion and Sm^{3+} reveals that the hypersensitive transitions are found at ($^6F_{11/2}$, $^6H_{9/2}$) and ($^6F_{7/2}$) respectively. The result of this study shows that the best result of oscillator strength for $20Li_2O–10K_2O–70B_2O_3$: Dy^{3+} is obtained at $^6F_{3/2}$ (9.7345×10^{-6}) and $20Li_2O–10K_2O–70B_2O_3$: Sm^{3+} is obtained at $^6H_{13/2}$ (9.293×10^{-6}) than other bands.

The emission bands of Dy^{3+} were measured after the excitation of photon with 450 nm wavelength, which are centered at 572 nm, 612 nm and 646 nm attributed to the transitions of ($^4F_{9/2}\rightarrow{}^6H_{15/2}$), ($^4F_{9/2}\rightarrow{}^6H_{13/2}$) and ($^4F_{9/2}\rightarrow{}^6H_{11/2}$). Figure 4 shows the major part of the emission intensity is contained in the $^4F_{9/2}\rightarrow{}^6H_{13/2}$ transition; it has shown bright yellow emission intensity and ($^4F_{9/2}\rightarrow{}^6H_{13/2}$) ($^4F_{9/2}\rightarrow{}^6H_{11/2}$) bright red. The previous transitions are illustrated in Figure 5.

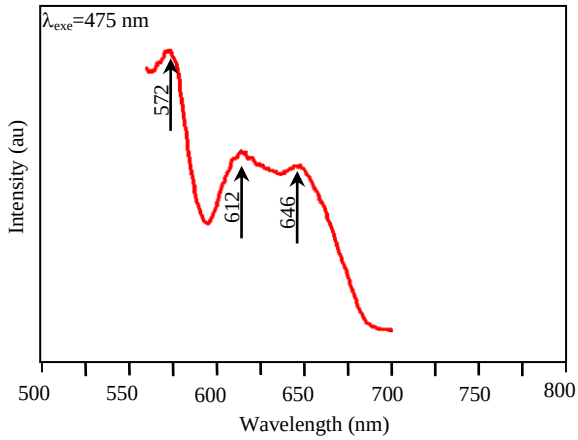


Figure 4 Emission spectra of Dy^{3+} ions doped $20Li_2O–10K_2O–70B_2O_3$ glass

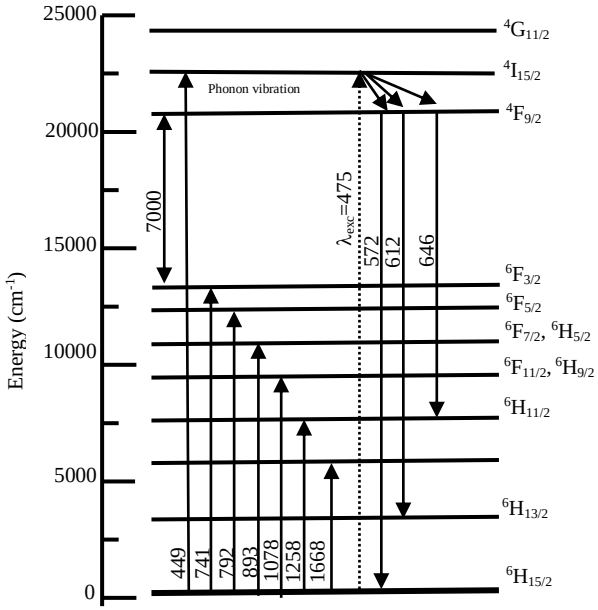


Figure 5 Absorption, excitation, emission energy levels scheme of Dy^{3+}

The emission spectra of Sm^{3+} under excitation 480 nm at room temperature are shows in Figure 6. The emission bands around 616 nm, 660 nm and 719 nm was due to the transitions $^4G_{5/2} \rightarrow {}^6H_{5/2}$, $^4G_{5/2} \rightarrow {}^6H_{7/2}$ and $^4G_{5/2} \rightarrow {}^6H_{9/2}$. Figure 7 describes the energy level scheme involved in the emission process with 480 nm as the excitation wavelength.

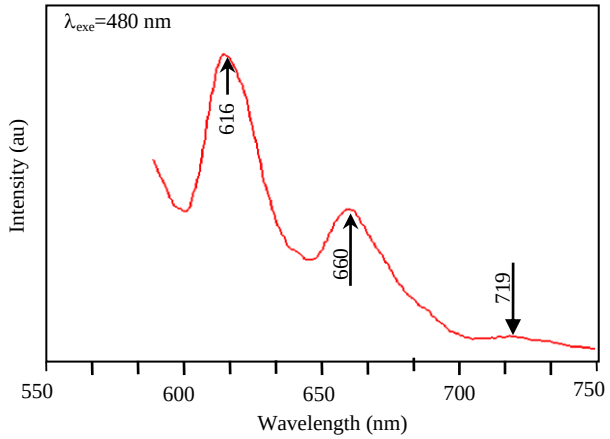


Figure 6 Emission spectra of Sm^{3+} ions doped $20Li_2O–10K_2O–70B_2O_3$ glass

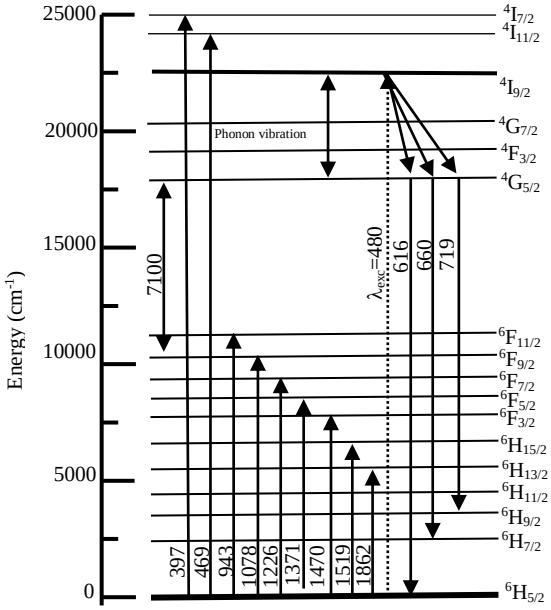


Figure 7 Absorption, excitation, emission energy levels scheme of Sm^{3+}

■4.0 CONCLUSION

The UV-VIS–NIR absorption spectra of Sm^{3+} and Dy^{3+} -doped of potassium lithium borate glasses have been determined. Emission spectrum of 0.4 mol% Dy^{3+}: glass has shown absorption peaks around 449 nm ($^6H_{15/2} \rightarrow {}^4I_{15/2}$) , 741 nm ($^6H_{15/2} \rightarrow {}^6F_{3/2}$) , 792 nm ($^6H_{15/2} \rightarrow {}^6F_{5/2}$), 893 nm ($^6H_{15/2} \rightarrow {}^6F_{7/2}$, $^6F_{5/2}$) , 1078 nm ($^6H_{15/2} \rightarrow {}^6F_{9/2}$) , 1258 nm ($^6H_{15/2} \rightarrow {}^6F_{11/2}$ - $^6H_{9/2}$) and 1668 nm ($^6H_{15/2} \rightarrow {}^6H_{11/2}$) occur in a sample. With regard to 0.4 mol% Sm^{3+} : glass absorption peaks around 397 nm, 469 nm, 943 nm, 1078 nm, 1226 nm, 1371 nm, 1470 nm, 1470 nm, 1529 nm and 1862 nm occur in sample, which corresponding to the transitions from ground state $^6H_{5/2}$ to the excited state $^4F_{7/2}$, $^4I_{11/2}$, $^6F_{11/2}$, $^6F_{9/2}$, $^6F_{7/2}$, $^6F_{5/2}$, $^6F_{3/2}$, $^6H_{15/2}$ and $^6H_{13/2}$, respectively. In addition, the significant part of the emission intensity has shown bright yellow emission (572 nm) under excitation 475 nm and a strong orange emission at (616 nm) under 480 nm for Dy^{3+} and Sm^{3+}, respectively.

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