Semiconductor physics

Studying the properties of Gd_2O_3 -WO₃-CaO-SiO₂-B₂O₃ glasses doped with Tb³⁺

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Abstract. The gadolinium tungsten calcium silicon borate glasses doped with Tb^{3+} were prepared using the melt quenching technique to study physical, absorption and luminescence properties. The results show that doping with Tb_2O_3 in high concentration makes the glass density tendency to increase. The absorption spectra indicate the photon absorption of Tb^{3+} in the visible and near infrared ranges. The emission spectra of these glasses have been recorded under 275 nm (Gd³⁺) and 377 nm (Tb³⁺) excitation wavelengths, and it is has been observed that these glasses show bright green emission. From the emission spectra, Tb^{3+} doped glasses perform the strongest emission with the wavelength 544 nm. The optimum concentration of Tb^{3+} with the strongest emission in Gd₂O₃–WO₃–CaO–SiO₂–B₂O₃ is 1.50 mol.%. CIE 1931 chromaticity investigation shows that Tb^{3+} doped glasses emit the light with yellowish green color. Tb^{3+} -doped glasses have the interesting potential to further development for using as laser medium in yellowish green solid-state lasers.

Keywords: light emitting, energy transfer, optical properties, luminescence, Tb³⁺-doped glass, photon absorption.

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1. Introduction

Glasses are very attractive materials, since they can be doped with trivalent rare-earth ions (RE^{3+}), and they have highly contributed to the development of lasers, optical fibers, optical waveguides, optical amplifiers and lightemitting devices. The 4f-4f transitions observed in them are low sensitive to ion's surrounding due to the shielding effect of outer 5s and 5p shell electrons of RE ions and facilitate to obtain laser action and optical amplification in the infrared region [1-4]. In oxide-based glasses activated with Tb^{3+} ions, the latter have demonstrated to be delightful candidates for gain medium in the green region around 543 nm, since the ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$ transition of Tb³⁺-doped materials provides the four-level laser system with a lower threshold pump power to obtain strong green pulsed laser operation at 543 nm. For the first time, Bjorklund et al. [5] demonstrated green laser emission line at 547 nm, which corresponds to ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$ transition from Tb^{3+} -doped

chelate in solutions at room temperature. Moreover, the experimental branching ratios of the ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$ (543 nm) transition are usually higher than 50%, which makes Tb³⁺ a promising ion for green laser applications.

In order to design new, efficient and improved optical devices for specific application with enhanced performance, active work is being carried out to select appropriate new hosts for RE^{3+} ions. Particularly, silicoborate glasses paved the significant advantages and improvement over the silicate and borate glass systems. These silicoborate glasses are considered to be suitable host for optically active ions, because of their moderate melting point, high transparency, high thermal stability, low non-linear refractive index and good RE ion solubility, beside physical and chemical stability [6, 7]. However, there is less important property of these glasses caused by their high phonon energy [8]. It is well known that the glassy systems with low phonon energies are highly suitable for high efficiency lasers and fibers [9].

In this paper, similar host of gadolinium tungsten calcium silicon borate glasses doped with different Tb^{3+} ion concentrations was prepared, and it was investigated their luminescence properties and energy transfer from Gd^{3+} to Tb^{3+} ions as a function of the Tb^{3+} ion concentration for various green laser applications in the visible range.

2. Experimental

Tb³⁺-doped gadolinium tungsten calcium silicon borate glasses with the chemical composition $30Gd_2O_3-5WO_3-10CaO-10SiO_2-(45-x)B_2O_3-xTb_2O_3$ (x = 0.05, 0.10, 0.50, 1.00, 1.50 and 2.00 mol.%, respectively) have been prepared by the melt quenching technique. About 15 g of the batch compositions were thoroughly mixed in an agate mortar, and the homogeneous mixture was taken in an alumina crucible and kept in an electric furnace at the temperature close to 1400 °C for about 3 h. The melt was poured onto a preheated brass mold and annealed at 500 °C for 3 h to remove thermal stress and strains and then cooled to room temperature. Afterwards, these glass samples were polished to attain good transparency and flat surfaces for optical measurements. Photographic images of these glass samples are shown in Fig. 1.

The physical properties, such as density, were determined using the Archimedes method with the distilled water as an immersion liquid, and the molar volume was also determined. Absorption spectra were measured with the UV-Vis-NIR spectrophotometer (Shimadzu UV-3600) in the wavelength range 200...2500 nm. Excitation and emission spectra were recorded using a fluorescence spectrophotometer (Cary-Eclipse). All the measurements were carried out at room temperature.

3. Results and discussion

3.1. Physical properties

Being based on the results of studying the density and molar volume of Gd_2O_3 – WO_3 –CaO– SiO_2 – B_2O_3 – Tb_2O_3 glass, it was observed (Fig. 2) that both the density and molar volume increase with increasing the Tb³⁺ ion concentration. It is caused by higher rigidity/denser nature of these Gd_2O_3 – WO_3 –CaO– SiO_2 – B_2O_3 – Tb_2O_3 glasses. It is further confirmed by formation of non-bridging oxygen (NBO) and expansion of the structure. The high values of density are caused by the presence of heavy elements, such as Gd^{3+} and Tb^{3+} ions in the glass network [10].

3.2. Optical absorption spectra

The room temperature optical absorption spectra of Gd_2O_3 -WO_3-CaO-SiO_2-B_2O_3-Tb_2O_3 glass in UV-visible and near infrared (NIR) spectral ranges are shown in Fig. 3. It is seen that in the UV-visible range there is only one absorption peak at 485 nm that is assigned to the transition from the ground state 7F_6 to the higher



Fig. 1. Photograph of Gd_2O_3 -WO₃-CaO-SiO₂-B₂O₃ glasses doped with various mol.% of Tb³⁺ concentrations.



Fig. 2. (a) Density (g/cm³) and (b) molar volume (cm³/mol) as functions of Tb^{3+} ion concentration (mol.%) in Gd_2O_3 -WO₃-CaO-SiO₂-B₂O₃ glasses.

excited state ${}^{5}D_{4}$ of Tb³⁺ ions. In the NIR range, the detected absorption bands at the wavelengths 1888 and 2213 nm arise due to transitions from the ground state ${}^{7}F_{6}$ to the excited states ${}^{7}F_{0,1,2}$ and ${}^{7}F_{3}$, respectively. The inset to this figure shows the intensity of the ${}^{7}F_{6} \rightarrow {}^{5}D_{4}$ (485 nm) transition with respect to different Tb³⁺ ion concentrations. As can be seen from the inset in Fig. 3, the absorption intensity increases linearly with the Tb³⁺ ion concentrations, it indicates successful incorporation of Tb³⁺ ions in the used Gd_2O_3-WO_3-CaO-SiO_2-B_2O_3-Tb_2O_3 glass matrices [11-14].



Fig. 3. Optical absorption spectra of Gd_2O_3 –WO₃–CaO–SiO₂– B_2O_3 glass in UV-visible and NIR ranges. (Colour online.)



Fig. 4. Excitation spectra of Gd_2O_3 –WO₃–CaO–SiO₂–B₂O₃ glasses for different Tb³⁺ concentrations under $\lambda_{em} = 544$ nm. (Colour online.)

3.3. Analysis of excitation and emission spectra

Fig. 4 shows the excitation spectra of Gd₂O₃–WO₃–CaO– SiO₂–B₂O₃–Tb₂O₃ glasses measured by monitoring the green emission of Tb³⁺ ion at 544 nm. As can be seen from Fig. 4, excitation transition at 275 nm ($^{8}S_{7/2} \rightarrow ^{6}I_{9/2}$) is associated with the host band of Gd³⁺ ion, and other five transitions at 340 ($^{7}F_{6} \rightarrow {}^{5}L_{6}$), 352 ($^{7}F_{6} \rightarrow {}^{5}L_{9}$), 369 ($^{7}F_{6} \rightarrow {}^{5}L_{10}$), 377 ($^{7}F_{6} \rightarrow {}^{5}G_{6} + {}^{5}D_{3}$) and 485 nm ($^{7}F_{6} \rightarrow {}^{5}D_{4}$) are attributed to Tb³⁺ ion excitation. It is similar to the observation of Kesavulu *et al.* for the energy transfer from the host (Gd³⁺) to dopant (Tb³⁺) ions [15]. Among all the excitations, the intense and strong excitation peaks at 275 nm (Gd³⁺) and 377 nm (Tb³⁺) are used to investigate the emission spectra characteristics for the Gd₂O₃–WO₃–CaO–SiO₂–B₂O₃–Tb₂O₃ glasses.

The emission spectra of Gd₂O₃-WO₃-CaO-SiO₂- B_2O_3 -Tb₂O₃ glasses doped from 0.05 to 2.00 mol.% Tb₂O₃ were measured by exciting at 275 nm in the wavelength range from 280 to 700 nm and were shown in Fig. 5. The emission spectrum exhibits bands at 682, 670, 647, 623, 587, 544 and 488 nm corresponding to the transitions ${}^{5}D_{4} \rightarrow {}^{7}F_{6}$, ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$, ${}^{5}D_{4} \rightarrow {}^{7}F_{4}$, ${}^{5}D_{4} \rightarrow {}^{7}F_{3}$, ${}^{5}D_{4} \rightarrow {}^{7}F_{2}$, ${}^{5}D_{4} \rightarrow {}^{7}F_{1}$ and ${}^{5}D_{4} \rightarrow {}^{7}F_{0}$, respectively. In addition, the emission spectra under 275 nm excitation contain the additional band at 310 nm that represent the transition ${}^6P_{7/2} \rightarrow {}^8S_{7/2}$ for Gd^{3+} ion. The emission intensity of Gd3+ at 310 nm decreases with increasing the Tb_2O_3 concentration. Reduction of Gd^{3+} emission simultaneously with increasing Tb³⁺ emission is quite an evidence of the energy transfer phenomena from Gd³⁺ to Tb³⁺. The emission peak at 544 nm is the intense band, while the other emission peaks are comparatively lower.



Fig. 5. Emission spectra of Gd_2O_3 -WO_3-CaO-SiO_2-B_2O_3 glasses for different Tb^{3+} concentrations under $\lambda_{ex} = 275$ nm. (Colour online.)



Fig. 6. Emission spectra of Gd_2O_3 -WO_3-CaO-SiO_2-B_2O_3 glasses for different Tb^{3+} concentrations under $\lambda_{ex} = 377$ nm. (Colour online.)



Fig. 7. Partial energy level diagram showing the emission mechanism of Tb^{3+} ions in Gd_2O_3 -WO₃-CaO-SiO₂-B₂O₃ glasses. (Colour online.)



Fig. 8. Relationship between the emitted light intensity at the wavelength 544 nm and the concentration of Tb_2O_3 .

Fig. 6 shows the emission spectra of glasses recorded at room temperature with an excitation at 377 nm. It was found that the glass sample emitted 7 lines at 488, 544, 587, 623, 647, 670 and 682 nm, with the light intensity at 544 nm being the highest. These phenomena can be explained in accordance with the energy level change diagram of Tb³⁺ in Fig. 7. The UV light with 275 nm excites the Gd^{3+} ions from ${}^{8}S_{7/2}$ ground state up to ⁶I_I excited state. After that, Gd³⁺ ions nonradiatively relax by releasing the phonon-vibration energy and decay down to the intermediate ^bP_{7/2} excited state. In this state, there are 2 optional routes for energy transformation. The first one is the ${}^6P_{7/2} \rightarrow {}^8S_{7/2}$ transition that leads to the Gd^{3+} emission line at 310 nm. The second route is the energy transfer from Gd^{3+} to Tb^{3+} . Then, the Tb³⁺ acceptor non-radiatively relaxes to its luminescence level ⁵D₄. These 7 emissions at 681, 670, 647, 623, 587, 544 and 488 nm subsequently occur under the Tb³⁺ transitions, ${}^{5}D_{4} \rightarrow {}^{7}F_{J}$ where J is 0, 1, 2, 3, 4, 5 and 6, respectively. Concerning UV excitation with the

line 377 nm, it excites Tb^{3+} ions from ${}^{7}F_{0}$ ground state to ${}^{5}D_{3}$ excited state. After that, Tb^{3+} ions non-radiatively relax to the luminescence level ${}^{5}D_{4}$. Then, the ${}^{5}D_{4} \rightarrow {}^{7}F_{J}$ transitions occur, which results in 7 emissions similar to those under 275-nm excitation.

In addition, when considering the relationship between the intensity of the emitted light and doping amount of Tb_2O_3 in the glass (for emitting the wavelength 544 nm), as shown in Fig. 8, the intensity value is maximum at 1.50 mol.% doping. When exceeding this doping level up to 2.00 mol.%, the emission intensity reduces slightly. It may be caused by the concentration quenching effect, when adding Tb_2O_3 into the glass more than 1.50 mol.%, which causes Tb^{3+} ions in the glass network to be too close one to another.



Fig. 9. 1931 CIE chromaticity diagram for Tb^{3+} -doped Gd_2O_3 -WO₃-CaO-SiO₂-B₂O₃ glasses under 377 nm excitation with photographs of bright green emission under UV lamp excitation. (Colour online.)

Whereas, the decrease in the released intensity can be explained by the reabsorption effect responsible for large variation of the emission spectra energy due to absorption of the light emitted from Tb^{3+} . The studied materials emit yellowish green light when being pumped with UV light under optimum concentration of 1.50 mol.% Tb_2O_3 in Gd_2O_3 -WO₃-CaO-SiO₂-B₂O₃-Tb₂O₃. The effect of doping on the intensity of emission spectra is similar to that of the excitation spectra.

3.4. CIE chromaticity diagram

In general, the emission color of glass contains color pairs to analyze and is good certification for photoluminescence applications. In 1931, the Commission International de l'Eclairage (CIE) established a universal quantitative model of color spaces [16]. The researchers used the light emitting spectrum excited by the wavelengths 275 and 377 nm (from Figs 5 and 6) of the glass Gd₂O₃-WO₃-CaO-SiO₂-B₂O₃. The result can be confirmed by the CIE 1931 chromaticity standard for the emission spectra of 1.50 mol.% Tb₂O₃ doped glass, analyzing the color coordinates (x, y) plotted on the CIE 1931 chromaticity diagram as shown in Fig. 9. The coordinates (x, y) of glass are (0.30, 0.59) for both emission lines under 275 and 377 nm excitation wavelengths, which was plotted at the yellowish green region in CIE color diagram. Yellowish green emission of all the glasses was also observed by a naked eye under UV lamp excitation as shown on the right side of Fig. 9. It can be concluded that Gd₂O₃-WO₃-CaO-SiO₂- $B_2O_3{:}Tb^{^{3+}}\ glasses$ are suitable for using as the medium in yellowish green light source device.

4. Conclusions

The gadolinium tungsten calcium silicon borate glasses doped with Tb³⁺ ions have been prepared, and their physical, thermal, optical and luminescence properties have been characterized. Both the density and molar volume increase with increasing the Tb³⁺ ion concentration. The high values of density are caused by the presence of heavy elements, such as Gd^{3+} and Tb^{3+} ions, in the glass network, and hence increased compactness of glass structure with addition of Tb₂O₃ is observed. The absorption spectra indicate the photon absorption due to Tb^{3+} in the visible and near infrared ranges. The emission spectra of these glasses have been recorded under 275 nm (Gd³⁺) and 377 nm (Tb³⁺) excitation wavelengths, and it has been observed that these glasses show bright green emission. From the emission spectra, Tb³⁺-doped glasses perform the strongest emission at the wavelength 544 nm. The optimum concentration of Tb³⁺ with strongest emission in Gd_2O_3 -WO_3-CaO-SiO_2-B_2O_3 is 1.50 mol.%. CIE 1931 chromaticity investigation has shown that Tb³⁺doped glasses emit the light with yellowish green color. Hence, the present results suggest that these Gd₂O₃-WO₃-CaO-SiO₂-B₂O₃-Tb₂O₃ glasses could be a potential candidate for yellowish green color display devices and solid-state yellowish green laser applications.

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Вивчення властивостей стекол Gd₂O₃-WO₃-CaO-SiO₂-B₂O₃, легованих Tb³⁺

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Анотація. Стекла оксидів гадолінію, вольфраму, кальцію, кремнію, бору, леговані Tb^{3+} , готували за допомогою методики раптового охолодження розплаву для вивчення фізичних, абсорбційних та люмінесцентних властивостей. Результати показують, що легування Tb_2O_3 у високій концентрації зумовлює тенденцію до збільшення густини скла. Спектри поглинання вказують на фотонне поглинання Tb^{3+} у видимому та близькому інфрачервоному діапазонах спектра. Спектри випромінювання цих стекол реєстрували при хвилях збудження 275 нм (Gd³⁺) та 377 нм (Tb^{3+}), і було помічено, що ці стекла демонструють яскраву зелену емісію. Із спектрів випромінювання леговані Tb^{3+} стекла виявляють найсильнішу емісію з довжиною хвилі 544 нм. Оптимальна концентрація Tb^{3+} при найсильнішій емісії у Gd_2O_3 – WO_3 –CaO– SiO_2 – B_2O_3 становить 1,50 мол.%. Дослідження хроматичності СІЕ 1931 показує, що леговані Tb^{3+} стекла випромінюють світло жовтувато-зеленого кольору. Леговані Tb^{3+} стекла мають потенціал цікавий для подальшого розвитку та використання як лазерного середовища в жовтувато-зелених твердотільних лазерах.

Ключові слова: випромінювання світла, передача енергії, оптичні властивості, люмінесценція, леговане Tb³⁺ скло, поглинання фотонів.