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تهیه و مطالعه شیشه های سدیم تترابورات دوپه شده با اکسید تربیوم

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چکیده: شیشه‌های تترابورات دوپه شده با اکسید تربیوم از واکنش Tb_2O_3 و $Na_2B_4O_7.10 H_2O$ سنتز شدند. ابتدا شیشه بوراته $Na_2B_4O_7$ با ذوب بوراکس آبزدایی شده در۱۰۰۰ درجه سانتیگراد به مدت ۳۰ دقیقه تهیه بعد از سرد شدن شیشه حاصل را به صورت پودر کاملا نرم در آورده آن را با مقادیری از (۵-۲۰ مول در صد) از اکسید تربیوم مخلوط و در دمای ۱۲۰۰ درجه سانتیگراد به مدت ۱۵ دقیقه حرارت داده ضمن انتقال مذاب شیشه‌ای به قالب استیلی پرس شدند. برای جلوگیری از خرد شدن خودبخودی در دمای ۳۰۰ درجه سانتیگراد به مدت ۱ ساعت تنش زدایی و مورد مطالعه قرار گرفتند. دانسیته نمونه‌های شیشه‌ای با استفاده از قانون ارشمیدس اندازه‌گیری شده و مشخص شد که دوپه کردن Tb_2O_3 در $Na_2B_4O_7$ منجر به افزایش دانسیته می‌شود. طیف مادون قرمز شیشه‌ها در ناحیهcm^{-1} ۴۰۰۰-۴۰۰ نشان می‌دهد که با افزایش Tb_2O_3 هیچ باند جذبی جدیدی نسبت به شیشه $Na_2B_4O_7$ خالص ظاهر نمی‌شود. مقایسه طیف مادون قرمز شیشه‌های دوپه شده با تربیوم با شیشه بدون دوپه نشان می‌دهد که تغییر تدریجی باندهای IR به تغییرات ساختاری ایجاد شده با تغییر مقدار تربیوم مربوط می شود. طیف ماورای بنفش شیشه‌ها نشان می‌دهد که افزایش اکسید تربیوم لبه جذب نوری را به سمت انرژی‌های پایین تر جابجا می‌کند. خواص فلورسانس شیشه‌های $(1-x)Na_2B_4O_7.xTb_2O_3$ از طریق تحریک آنها توسط نوری با طول موج ۳۷۷ نانومتر مورد بررسی قرار گرفت و مشاهده شد که لومینسانس سبز شدیدی در طول موج تقریبا ۵۵۰ نانومتر ظاهر می شود.

واژه‌های کلیدی: *شیشه تترا بورات، اکسید تربیوم، اسپکتروسکوپی مادون قرمز.*

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Preparation and characterization of terbium oxide doped sodium tetraborate glasses

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Abstract: Terbium oxide doped tetraborate glasses were prepared from the reaction of Tb_2O_3 and $Na_2B_4O_7 .10\,H_2O$ on reagent grade. At first, the base borate glass of $Na_2B_4O_7$ was prepared by melting dehydrated borax at 1000 ˚C for 30 min and then the obtained base glass was crushed and powdered. Appropriate amounts of Tb_2O_3 (5-20 mol %) and $Na_2B_4O_7$ powdered glass were mixed and melted at 1200 ˚C for 15 min. By transferring the melt in a cold steel sample holder and pressing, the final glasses were obtained. To avoid self crushing of the obtained glass samples, they were annealed at 300˚C for 1h. The density of the samples, measured by using Archimedes´s principle, showed that the doping of Tb_2O_3 in $Na_2B_4O_7$ increases the density of the glass. The infrared spectra of the glasses in the range of 4000 - 400 cm^{-1} shows that the addition of Tb_2O_3 did not introduce any new absorption band in the infrared spectrum of pure sodium tetraborate glass. Comparing of the IR spectral features of the Tb^{+3} doped glasses with undoped glass show that the evolution of the IR spectral bands is related to the structural changes produced by varying of Tb^{+3}. UV Spectroscopic study of such glasses shows that the addition of terbium oxide shifts the optical absorption edges towards lower energies. The fluorescence properties of (1-x) $Na_2B_4O_7 .xTb_2O_3$ glass system were investigated by means of the emission Spectroscopy with excitation by 377 nm light. The glass presented intense ~ 550 nm green luminescence.

Keywords: *Tetraborate glass; Terbium oxide; Iinfrared spectroscopy.*

1. Introduction

Glasses are useful materials with potential applications in fabrication of switching and memory devices, transducers, superiors insulators, dielectrics and ordinary electronic material [1-2]. In recent years investigation of the properties of glasses have been the object of materials researchers in electronic terms rather than simply from the chemical point of view [3]. Boron oxide form the basis for many low melting glasses and are characterized by a covalently linked boron-oxygen network. Their network structures have the form of macro-anion with boron-oxygen chains, segments of such chains (including highly branched ones), two – dimensional layers, three – dimensional networks, and their fragments. Structural studies show that sodium borate glasses contain boroxol, tetraborate, and metaborate groups. Borate glasses have been known to be an excellent host matrices for the rare – earth oxides because of their good glass forming nature compared to other conventional systems [4]. They have attracted much attention because of their electrochemical and optical applications, namely as solid–state batteries, optical waveguides and luminescent materials [5]. Such glasses are suitable as optical materials with high transparency, low melting point, easily – shaped, high thermal stability and good rare – earth ions solubility [6, 7]. The rare – earth ion in glass occupies the centre of a distorted cube which is made of four tetrahedr of borate and each tetrahedron contributes two oxygen's to the coordination of rare earth ions. The overall coordination number is 8 as a common coordination of rare – earth oxides [8]. The optical properties of RE ions in glasses depend on the chemical composition which determines the structure and nature of the bonds in glass matrix [9]. Traditional spectroscopic studies of lanthanide salts have been reported and traditional glasses doped with small amounts of such elements have been investigated. The difference in the spectral behavior shown by ions of d- block transition elements, is due to the fact that electrons responsible for the spectral properties of rare – earth ions are 4f electrons, and the 4f orbital are very effectively shielded from the effect of external forces by the overlying $5s^2$ and $5p^6$ shells. The states arising from the 4f orbital configurations are only slightly affected by the surroundings of the ions and remain particularly invariant for a given ion various compounds [10]. Sodium tetraborate is a type of sodium borate glasses that consists of one – third of sodium oxide and two – third of boron oxide. This type of borate glasses drawn great attention due to their enhanced electrical and optical properties when modified by phthalocyanine or by rare - earth cations [11]. In order to extend the available information on borate glasses containing terbium ions, we prepared the xTb_2O_3. (1-x) $Na_2B_4O_7$ glass system with $0 \leq x \leq 0.2$. We studied the products by UV-V is, Infrared and fluorescence spectroscopy and density measurements.

2. Experimental

2.1. Sample preparation

Samples of the x Tb_2O_3. (1-x) $Na_2B_4O_7$ glass system with x =0.00, 0.05, 0.1, 0.15, 0.2 were prepared from the reaction of Tb_2O_3 and $Na_2B_4O_7$ .10 H_2O on reagent grade. At first, the base borate glass of $Na_2B_4O_7$ composition was prepared by melting dehydrated borax at 1000 ˚C for 30 min. Then it was quenched on a refractory steel block. The obtained base glass was crushed and powdered by agate ball mill. Then appropriate amounts of Tb_2O_3 and $Na_2B_4O_7$ glass were mixed and melted at 1200 ˚C for 15 min. The glass samples were obtained by pouring the melts on stainless steel. For avoid self crushing of obtained glass sample they were annealed at 300˚C for 1h.

2.2. X-Ray diffraction

The glassy nature of the samples, were confirmed by XRD studies using D5000 Siemens diffractometer with Cu – K_α line of wavelength λ = 1.5406 A˚ at the scanning rate of 1 ˚/min. and 2θ was varied from low angle to 70˚.

2.3. Infrared Spectra

Infrared spectroscopic studies were used to get essential information about the arrangement of the structural units of glass samples. The FT-IR transmission spectra in the region 4000 – 400 cm^{-1} were recorded for all samples using Shimadzu Tensor 27 by KBr pellet technique.

2.4. Density measurement

The density of glass samples were measured using Archimedes´s Law. The measurements were carried out using Shimadzu Aw 200 balance and xylene as an inert immersion liquid. The density was obtained from the relation d (g/cm^3) = [a/a-b]x (density of xylene), where a is the weight of the glass sample in air, b is the weight of the glass sample when immersed in xylene. The density of xylene is 0.865(g/cm^3) [12].

2.5. Optical spectram

The optical spectra were recorded using Shimadzu UV-1650 PC spectrometer in the wavelength range of 200 – 1000 nm at room temperature.

2.6. Flurescence measurements

The flurescence spectra was measured using Shimadzu Rf-5301PC spectrophotometer at room temperature.

3. Results and discussion

3.1. X-ray diffraction studies

The X – ray diffraction patterns of the samples confirm the amorphous nature of the glasses. Fig.1. shows the x- ray diffraction pattern of the glass sample prepared with x = 0.05 as an example.

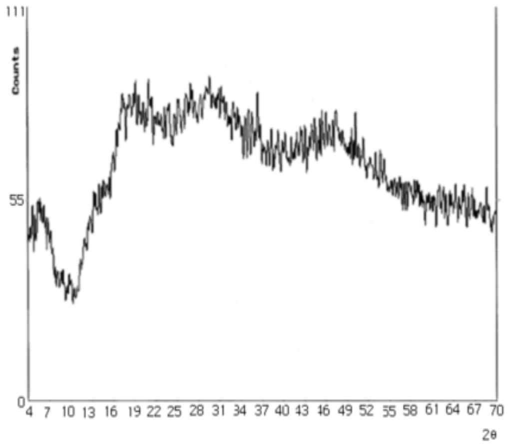

Fig 1: X –ray diffraction pattern of the sample with x = 0.05.

3.2. FT –IR analysis

The FT – IR spectra of Tb^{+3} doped sodium tetraborate glasses were obtained using KBr pellet technique in the range of 4000 – 400 cm^{-1}. Fig.2. shows the IR spectra recorded for the Tb^{+3} doped tetraborate glasses. The IR spectral features of the Tb^{+3}doped glasses are very broad due to the vitreous nature of the samples [13]. The main spectroscopic features evidentiated by these spectra are characteristic of the base $Na_2B_4O_7$ glass and were previously reported and assigned [14-15]. The weak bond around 3400 cm^{-1} is assigned to the O-H stretching which may be associated with water trapped in glasses during experiment [8].

The IR spectroscopy of borate containing compounds showed that the vibrational modes of the present network are mainly active in three infrared spectral regions [16]:

(i) The first group of bands which accour at 1200–1600 cm^{-1} is due to the asymmetric stretching relaxation of the B-O bond of trigonal BO_3 units.

(ii) The second group lies between 800 and 1200 cm^{-1} is due to the B-O bond stretching of the tetrahedral BO_4 units.

(iii) The third group is observed around 700 cm^{-1} is due to bending of B-O-B linkages in the borate networks.

In the present glass system, it appears that all Tb^{+3} doped glasses show great similarity to the sodium tetraborate glass in their general shape of absorption spectra without the appearance of any new peaks. The vibrational absorption peaks at ~450, 720, 850 to 1050 cm^{-1} in glasses could be due to bridging and non bridging oxygen ions which are doubly or singly bonded to high - state BO_4 group and low-state BO_3 groups, also to sodium ions. In the wave number region over 800 cm^{-1} two very broad absorption bands were observed at about 1000 and 1350 cm^{-1}. The absorption band around 1000 cm^{-1} results as a superposition of the absorption bands from about 850 cm^{-1} (observed at 890 cm^{-1} in the vitreous B_2O_3 and assigned to the boroxol rings) and at 1050 cm^{-1} (observed at 1070 cm^{-1} in borate glasses and assigned to the B-O stretching of the BO_4 structural units). The broad absorption bands at about 1350 cm^{-1} results as the envelope of two important bands, the first one at ~ 1260cm^{-1}(typical of BO_3 units[14]), the second one at~1370cm^{-1} (characteristic of the B-O stretching mode in borate glasses, its presence confirming the vitreous nature of the Tb^{+3}doped glasses [15]). The increase of x produces a slight decrease of the absorption band from ~ 850 cm^{-1}, mainly for $x \geq 0.15$, and increase of the absorption band at 1050 cm^{-1}. Also, the increase of x determines a decrease of the absorption band at 1260 cm^{-1} which becomes a shoulder for $0.01 \leq x \leq 0.15$ and disappears for x = 0.20. The evolution of the IR spectral features of the Tb^{+3}doped glasses by modifying their Tb_2O_3 content, x, is related to the structural changes produced by varying x. These structural changes consist mainly in a decrease of the amount of boroxol structural groups and BO_3 structural units (converted in BO_4 structural units) with increasing x up to 0.20. This increase may be due to the behavior of terbium ions as glass modifier. The structural changes are studied by the IR investigation of Tb^{+3}doped glasses. We note that the mentioned structural changes lead to a more compact structure. Such behavior was previously reported for other rare – earth ions (Gd[17], Ho[18], Dy[19], Eu[13]), too, but was not reported for the terbium ions so for.

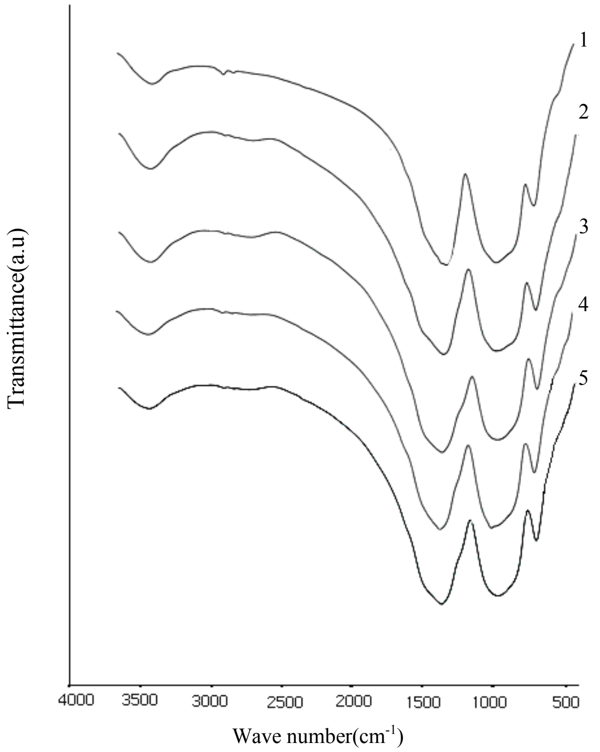

Fig 2: The infrared absorption spectra of $Na_2B_4O_7$ glasses**.** (1) pure $Na_2B_4O_7$ glass. (2)glass containing 5 mol% Tb_2O_3 (3) 10 mol% Tb_2O_3. (4) 15 mol% Tb_2O_3, (5) 20 mol% Tb_2O_3.

3. 3. Density measurement

The density of the glass and its value is important and stands on its own as intrinsic property capable of casting the light on the short range structure. Also, boron oxide in its glassy form is a laminar network consisting of boron atoms 3- fold coordinated with oxygen which can form 6-membered boroxol rings (B_3O_6), as reported earlier by Krogh – Moe [20]. When an alkali oxide modifies the pure boron oxide, the additional oxygen, obtained by the oxide dissociation, causes a conversion from the trigonal boron atoms BO_3 into 4 - fold coordinated boron atoms as BO_4. Each BO_4 structural group is negatively charged and the four oxygen's are included in the network as bridging oxygen. These units are responsible for the increase in the connectivity of the glass network. As a result , the degree of the structural compactness and modification of the geometrical configuration in the glass network can vary with a change in the composition[11]. Fig.3. and Table 1. show that the general trend of the density of Tb^{+3}doped glasses is to increase with increasing terbium ion content. This behavior is due to the higher number of terbium ions accommodated in the vitreous matrix. Note that the density vs x increase is not linear and the increase of the density is slower for the (10 = x = 15) mol% composition range. This behavior suggests that a more complicated mechanism, also implying the structural changes determined by varying x, must be considered to explain the density – composition relation. Taking into account that for (10 = x =15) mol % the IR data indicates the conversion of BO_3 into BO_4 structural units leading to a less compact structure of the glass matrix and consequently to a decrease of its density, we obtain a reasonable explanation of the density – x relation in the composition range mentioned.

3.4. Optical absorption and fluorescence measurements

Judd – ofelt theory is the most suitable theory to characterize the intensities of forced electric dipole transitions between 4f states of lanthanide ions. Since the absorption and emission probabilities for an ion matrix combination are given as a function of a set of there parameters, i. the intensity or judd – ofelt parameters [21-22].

According to the Judd-ofelt theory, the oscillator strength, P_{cal} (a J; b J′), of an electric dipole absorption transition from the initial state |aJ> to the final state|bJ′> depends on three parameters (λ =2,4,6) as given by :

$$P_{cal}(aJ;bJ') = \frac{8\pi^2 mc}{3h}\,\frac{\tilde{\nu}_p}{2J+1}\,\frac{(n^2+2)^2}{9n}\sum_{\lambda=2,4,6}\Omega_\lambda|\langle aJ\|U^{(\lambda)}\|bJ'\rangle|^2$$

Where $\tilde{\nu}_p$ is the barycenter of the transition, n is the refractive index, m is the electron mass, c is the velocity of light, h is the Plank constant and $<\|U^{(\lambda)}\|>$ are the double reduced matrix elements of the unit Tensor operators[23]. The optical absorption measurements were made at room temperature for the pure ($Na_2B_4O_7$) glasses doped with Tb_2O_3 as indicated in Table 1. Fig. 4 shows the absorption as a function of wavelength for $Na_2B_4O_7$ glass containing 10 mol% Tb_2O_3. It is clear that the region of high absorption is in the ultraviolet range and seems to move to longer wavelengths as Tb_2O_3 content increases. Furthermore, it is noted that there is a single absorption peak due to Tb^{+3} around 300 nm for all glass samples doped with Tb_2O_3 due to the transition $4f^8$ to $4f^7 5d$ and the f-f transitions withinTb^{3+} $4f^8$ configuration have not been seen clearly duo to their weak intensity.

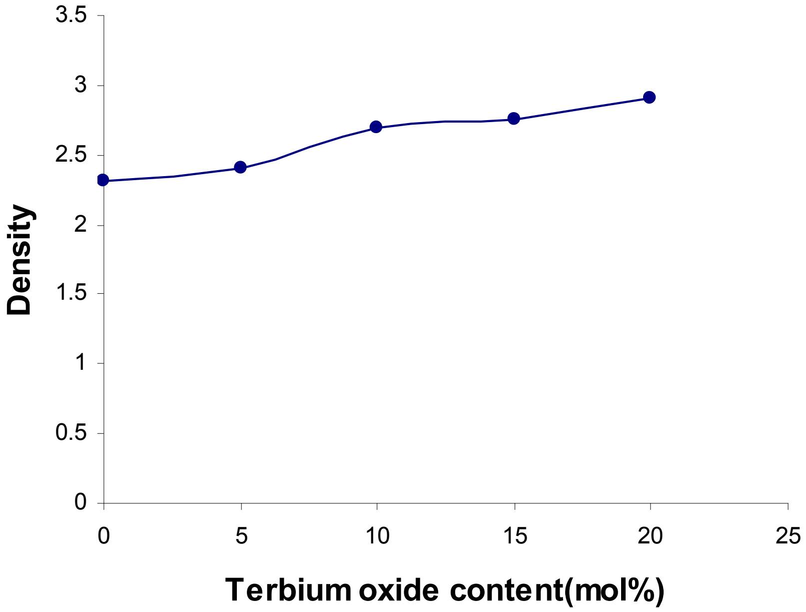

Fig.3: Variation of density with terbium oxide content.

Table1 Chemical composition and density of glasses in the system($Na_2B_4O_7$-Tb_2O_3).

Glass sample	Composition(%mol)		Density(g / cm^3)
	$Na_2B_4O_7$	Tb_2O_3	
1	100.00	0.00	2.310
2	95.00	5.00	2.40
3	90.00	10.00	2.70
4	85.00	15.00	2.76
5	80.00	20.00	2.90

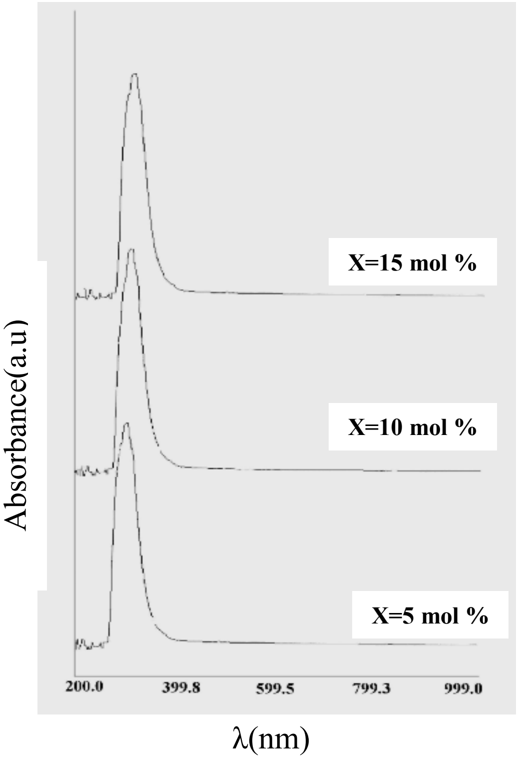

Fig. 4: UV spectram of $Na_2B_4O_7$ glass containing 5 , 10 15 mol % Tb_2O_3

When Tb^{+3} ion is excited to $^5D_3$ or a higher level, the radiative transition from $^5D_3$ to ^7F_j (j = 0 - 6) results in a series of $^5D_3$ emission in the blue region, while that from $^5D_4$ to^7F_j yields another series of $^5D_4$ emission in the green region. Since the energy difference between $^5D_3$ and $^5D_4$ matches with that between $^7F_0$ and $^7F_6$, the excited ion at $^5D_3$ (energy donor) relaxes its state to $^5D_4$, releasing the energy to resonantly excite the nearest unexcited ion (energy acceptor) from $^7F_6$ to $^7F_0$. This process is called resonant energy transfer, whose probability is proportional to $(R_0/R)^s$; where R stands for inter –ionic distance and R_0 for the critical distance. The value of R_0 for typical multipolar interaction is in the range of 10-20 A° and s = 6 for dipole – dipole and s = 8 for dipole–quadrupole interactions [24].

Terbium – activated phosphors are excellent emitters of green light. Furthermore, Tb^{+3} ion luminescence under uv excitation usually consists of four main emission lines around 490 (blue), 545 (green), 580(yellow) and 620 (red) nm. These emission lines correspond to the $^5D_4 \rightarrow {}^7F_j$ (j = 6, …, 3) transitions as shown in Fig.5 for λ_{ex} = 360 nm[25]:

In addition to these emission lines, a considerable contribution from the higher- level emission $^5D_3 \rightarrow {}^7F_j$ is often observed in the luminescence. The typical luminescence of Tb^{+3} appears to be green to the human eye, because the emission due to the $^5D_4 \rightarrow {}^7F_5$ transition (≈545 nm) usually dominates overall emissions. The fluorescence intensity is considered to be dependent on the host lattice through the crystal field [26].

The fluorescence spectra were measured by using a fluorospectrometer at room temperature. Fig.6. shows the fluorescence spectra of xTb^{+3} in $Na_2B_4O_7$ glass sample(x = 0.15). Fluorescence spectra and intensity of RE ions are dependent on the symmetry and strength of crystal field, because the optical radiation of RE ion is mainly due to forced electric dipole transition. Kuboniwa and Hoshina reported a good agreement between observed fluorescence and calculated values for Tb^{+3} in some oxides such as YPO_4, YBO_3 and $ScBO_3$. Their theoretical calculation along the Judd – ofelt [21] approximation showed that the $^5D_4 \rightarrow {}^7F_5$ transition has the largest probability in the $^5D_4 \rightarrow {}^7F_j$ (j = 3,4 5,6) transitions for all these matrices. It was also pointed out that the intensity of $^5D_4 \rightarrow {}^7F_3$ transition can become comparable to that of $^5D_4 \rightarrow {}^7F_5$ when the crystal field is very strong, where the ^7D state of the $4f^7$ (^8S) 5d configuration was assumed to be admixed into the $4f^8$ configuration [26].

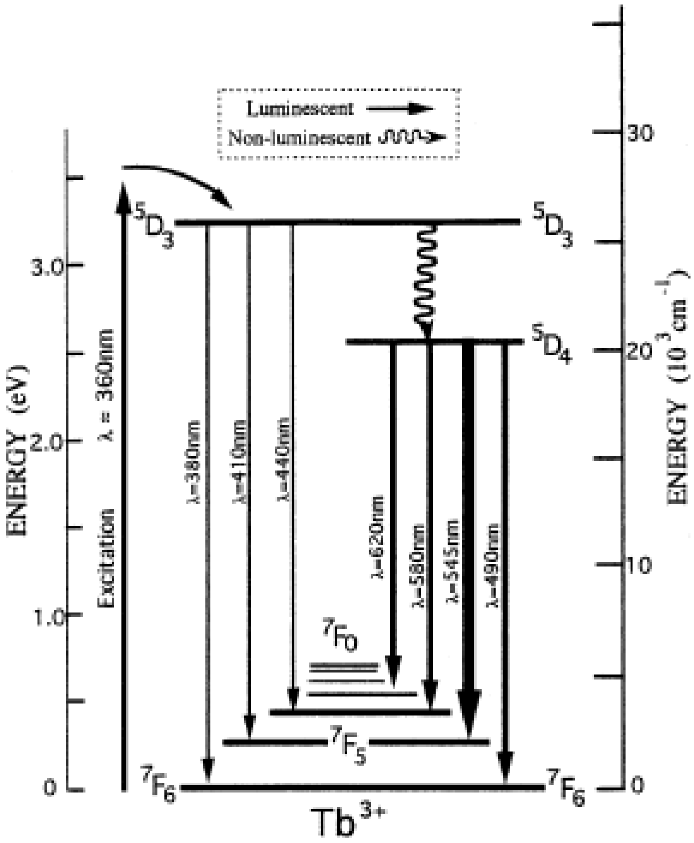

Fig.5 Energy levels and emission processes of Tb^{+3} ion at λ_{ex}= 360 nm.

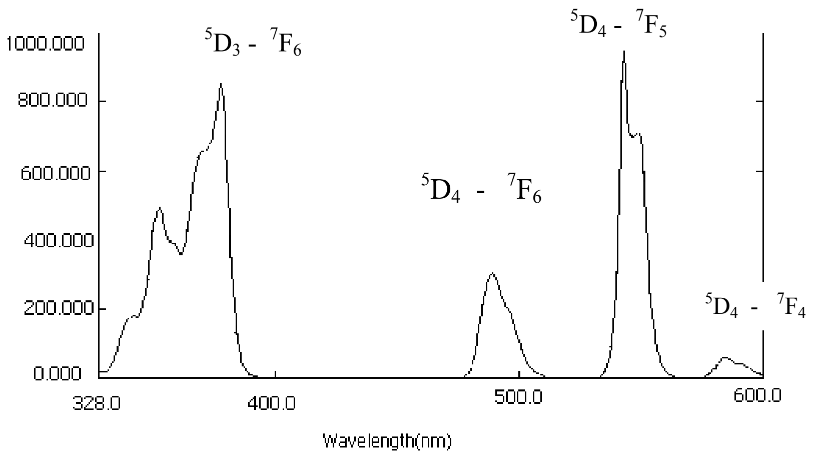

Fig. 6. Fluorescence spectra of Tb^{+3} in $Na_2B_4O_7$ glass sample(x =0.15)

4. Conclusions

Glasses in the system $(1-x)Na_2B_4O_7.xTb_2O_3$ $(0.00 \leq x \leq 0.20)$ were prepared using the press - quenching technique from the glasses melts. The FT-IR spectroscopy of the glasses were measured and evaluated to confirm the internal structure arrangements of the building units of such glasses as a result of the progressive replacement of $Na_2B_4O_7$ by Tb_2O_3. IR measurements suggests that Tb^{+3} ions play a network modifier role in Tb^{+3} doped glasses. Increase of x up to 0.15 determines important structural changes, but only slight ones for higher x values. Density measurements support this assumption. The study of the optical absorption of sodium tetraborate glasses containing Tb_2O_3 in the wavelength range from 200-1000 nm revealed an absorption peak in the ultraviolet range that seems to move to longer wavelength as Tb_2O_3 content increase. IR spectroscopic and density measurements performed on xTb_2O_3. (1 - x.)$Na_2B_4O_7$ glasses show that modifying the terbium ion content of samples leads to structural changes in the host vitreous matrix. These data show that the terbium ions play a network modifier role in the studied glasses. The fluorescence properties of (1-x) $Na_2B_4O_7$ .xTb_2O_3 glass system were investigated by means of the emission spectra with excitation by 377 nm light, the glass presented intense ~ 550 nm green luminescence.

Acknowledgements

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