International Journal of Engineering

Journal Homepage: www.ije.ir

UV-Vis Absorption and Luminescence Spectrum of LAS: Tb^{3+}/Gd^3 as a Laser Material

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A B S T R A C T

This article discusses detailed study on crystallization, optical properties of Li-Al-Si-La glass containing nanocrystalline LaF_3 and their optical energy gaps. The Urbach energy of glass samples was evaluated. By using (2% mole) Tb the green–blue range emission occurred, while by accumulation 1% mole Gd beside Tb, the indigo emission intensity (418 to 441 nm) increased.

1. INTRODUCTION

Multiple technological applications of glass-ceramics composites with nanometer size structures dispersed in amorphous host matriceshas attracted the attention of many researchers [1, 2]. Because of their potential as promising media for optical devices, optical properties of transparent glass–ceramics with nanosized crystals or quantum dots embedded in amorphous host matrix are investigated [2, 3]. The Oxyfluoride glass-ceramics doped with rare earths has widely been investigated in the past decades. Such materials provide a desirable low phonon energy fluoride environment for active rare earth ions while maintaining the advantages of oxide glasses such as high mechanical strength, chemical durability and thermal stability.

Silicate oxyfluoride glass-ceramics containing $Pb(Cd)F_2$ or LaF_3 nanocrystals have been reported since 1990s [3, 4]. Special attention has been made to glass-ceramics containing LaF_3 nanocrystals since Dejneka reported a new alumino silicate glass-ceramic containing LaF_3 in 1998 [5]. LaF_3 is an excellent host material for rare-earth ions because it has a high solubility for rare-earth ions, low phonon energy (300–400 cm^{-1}), and desirable thermal and environmental stability [5]. There are reports on Tb-Gd interactions in $SiO_2–Al_2O_3–CaO$ systems [6, 7], but these dopants in

LAS lithium –aluminum –silicate glass system have not been studied yet.

Determination of the UV-absorption profiles and band gap energy of these glasses is a fundamental topic and has technological importance. Applications in laser optics, microelectronic and spectroscopy require glassy materials with high transmissivity in UV and VU-Vis parts of spectrum. A spectrophotometer- based technique is frequently used to perform spectral measurements having a wide spectrum range [8].

In the present article, The optical properties of Li_2O-SiO_2 Al_2O_3 (wt%) optical glasses in form of plane–parallel slabs are determined in a very wide range of energy (0.41–6.2eV) using a spectrophotometer based technique.

Analysis of absorption edges provides both direct and indirect allowed transitions with their optical energy gaps and the Urbach energy.

X-ray diffraction (XRD), differential scanning calorimetry (DSC), the optical absorption of specimens was determined by a UV–Vis single beam spectrometer, (UV-2501), and the photoluminescence properties were studied by Emission Spectrometry (Perkin Elmer), on as-prepared glasses and glass-ceramics.

2. EXPERIMENTAL PROCEDURE

Reagent grade anhydrous oxide powders of SiO_2, Li_2CO_3, Al_2O_3, LaF_3, Gd_2O_3 and TbF_3 were used to

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prepare glasses. The compositions of lithium–lanthanum–aluminosilicateoxyfluoride glass are presented in Table 1.

Batches of 40 g were thoroughly mixed in an agate mortar and melted in a platinum crucible at 1400ºC. The melts were held for 50 min and then cast onto a copper plate and pressed by another copper plate from the top, forming a glass plate of about 3mm in thickness. The glasses were subsequently annealed at near the glass transition temperatures (400ºC) for 20 min and then allowed to cool to room temperature in the furnace. Clear glasses were formed for all batches. These glasses appear to be of very good optical quality, with no visual evidence of devitrification. Samples of 60 mg were heated at 10°C/min up to 1000°C in platinum crucibles in air. Al_2O_3 was used as the reference material. The inflexion point of the endothermic drift on the DTA curve is reported as T_g [9].

XRD measurements were performed using a Scintag X1 advanced diffraction system with a Cu Ka radiation (1.54Å). UV–visible absorption was measured from 300 to 800 nm using a Perkin-Elmer apparatus. Photoluminescence (PL) was measured using 325-nm xenon excitation wavelength Perkin Elmer S5 at room temperature.

3. RESULTS AND DISCUSSION

3. 1. Heat Treating and XRD   According to the XRD results shown in Figure 1, the obtained base glass was amorphous. DTA traces of GTb2, and base glass is shown in Figure 2.

The T_g (glass transition) of glasses were obtained from the point that curve starts to deviate from base glass. The Tg of base glass was approximately 414ºC and two other exothermic crystallization temperatures (T_c) were found at 653 and 671ºC, whereas the T_c of GTb$_2$ glass was at 691ºC.

3. 2. The Spectral Distribution of the Absorption Coefficient   Study of the optical absorption edge in UV-region has proved to be very useful method for elucidation of optical transitions and electronic band structure of the materials [8, 10]. It allows investigating at least three mechanisms such as: (1) quenching color centers absorbing in the edge region; (2) reducing the structure disorder; and (3) controlling the band gap. It is possible to determine indirect and direct transition occurring in band gap by optical absorption spectra at the fundamental absorption edge of the material. In both cases, electromagnetic waves interact with the electrons in the valance band, which are raised across the fundamental gap to the conduction band. A typical absorption edge can be broadly ascribed to any of the three expected processes [10]: (i) residual below-gap

absorption; (ii) Urbach tails; and (iii) inter band absorption. In amorphous materials a different type of optical absorption edge is observed. In these materials, the absorption coefficient (a) increases with the photon energy near the energy gap [11]. Figure 3 plots the absorption coefficient, a(o), curves versus wavelength for the different glass samples in the UV–Vis optical absorption region.

TABLE 1. The chemical composition of the studied glass

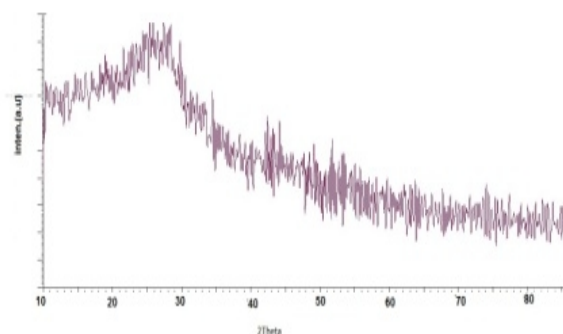| Sample Name	SiO$_2$	Al$_2$O$_3$	Li$_2$O	LaF$_3$	TbF$_3$	Gd$_2$O$_3$
base	48	8.7	12.3	31	-	-
GTb1	48	8.7	12.3	31	1	-
GTb2	48	8.7	12.3	31	2	-
GTbGd	48	8.7	12.3	31	2	1

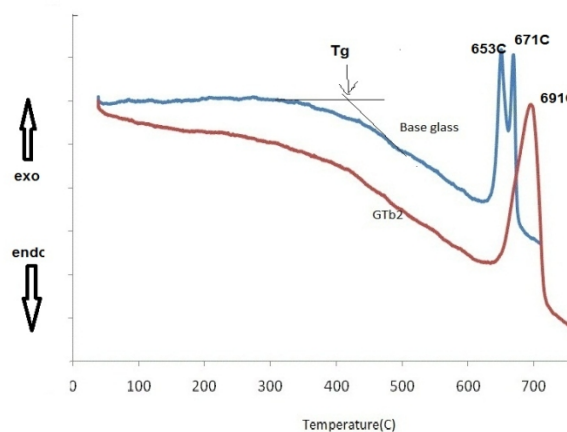**Figure 1.** XRD pattern of amorphous base glass

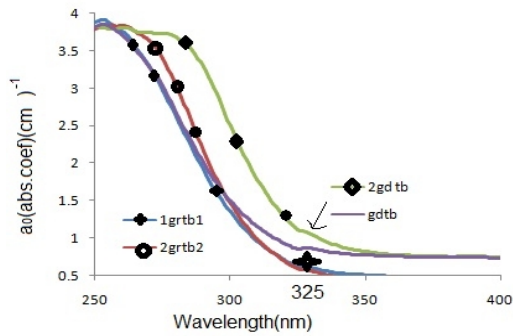**Figure 2.** DTA curves of base glass and GTb$_2$

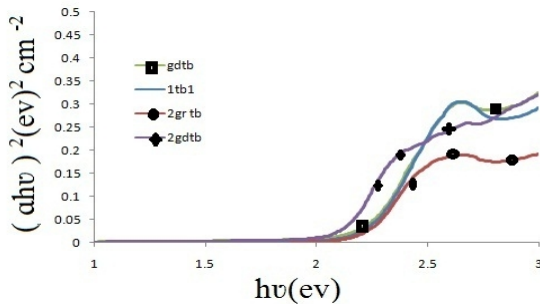**Figure 3.** The absorption coefficient, a (0), versus wavelength for the different glass samples

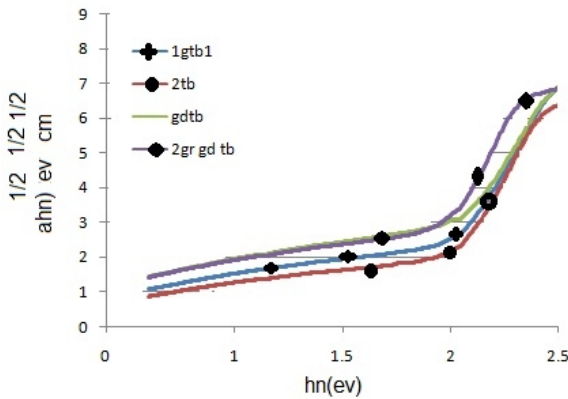**Figure 4.** $(\alpha h\upsilon)^2$ as a function of photon energy ($h\upsilon$),

Figure 5. $(\alpha h\upsilon)^{1/2}$ as a function of photon energy (hn)

It is obvious that the optical absorption edges are not sharply defined which characterizes the glassy nature of samples. The fact that the fundamental optical absorption edge for different samples shifts towards the longer wavelengths (red shift) with increased ratio of TbF_3 /SiO_2 in samples GdTb and 2GdTb. Thereafter, with sample GTb1 which has the lowest TiO_2 /SiO_2

ratio, a shift towards shorter wavelength is recognized. It may be attributed to the changes in the bonding that takes place in the glass [20]. Sample GTb1 has the highest transmissivity, followed by sample GTb2. The absorption edges of samples GdTb and 2GdTb practically coincide.

McQueen and Jonas[11] gave an express ion for the absorption coefficient, $a_{(0)}$, as a function of photon energy (hn) for direct and indirect optical transitions through the following:

$$\alpha(\upsilon) = \beta^2 \frac{(h\upsilon - E_g^{opt})^n}{h\upsilon}$$

where, the exponent n = 1/2 is for allowed direct transition, while n = 2 for allowed indirect transition, β_o is a constant related to the extent of the band tailing, and E_{gopt} is optical band gap energy. By plotting $(\alpha h\upsilon)^{1/2}$ and $(\alpha h\upsilon)^2$ as a function of photon energy (hυ), one can find the optical energy band gap for indirect E_{g2}^{opt} and direct E_{g1}^{opt} transitions, respectively. The respective values of E_g^{opt} are obtained by extrapolating to $(\alpha h\upsilon)^{1/2} = 0$ for indirect transitions, and $(\alpha h\upsilon)^2 = 0$ for direct transitions as shown in Figures 4 and 5, respectively. The goodness of the fit of the data to the formula for either n=1/2 or n=2 is determined by the square of the correlation coefficient (R^2=1 is for the perfect fit) which was 0.97in our case. From the values of R^2, it is difficult to decide whether the glass has direct or indirect band gap. The error for band gap energies is ±0.005. However, it may be noted that the indirect band gaps are larger than those of corresponding direct band gap values. In direct case, the values are systematically increasing with the increase of Gd and Tb. This observation must be attributed to the network structural differences brought by the additional presence of Tb^{3+} ion. It could be said that sample GdTb and 2GdTb (highest E_g) are corresponding to the most stable glasses. While such decrease in sample GTb1 and GTb2 may be well attributed to a decrease in the average bond energy of the system. It may lead to decrease in the energy of the conduction band edge, and thereby E_g decreases. On the other hand, E_g and the main feature of the absorption edge of amorphous materials is an exponential increase of the absorption coefficient with photon energy. When the energy of the incident photon is less than the band gap, increase in absorption coefficient followed by an exponential decay of density which is localized into the gap [12]. The absorption edge here is called Urbach edge, where values are between 10 and 10^3 cm^{-1}. The lack of crystalline long-range order in amorphous/glassy materials is associated with a tailing of density of states into normally forbidden energy [12] .Urbach energy characterizes the extent of the exponential tail of the absorption edge. The exponential absorption tails and Urbach energy is given in accordance with the empirical relation [13].

$$\alpha(v) = \beta \exp(\frac{hv}{E_U})$$

where β is a constant, E_U is the Urbach energy which indicates the width of the band tails of the localized states and (v) is the frequency of the radiation. The exponential absorption tails, i.e., Urbach energy depends on temperature, thermal vibrations in the lattice, induced disorder, static disorder, strong ionic bonds, and on average photon energies. The main factor contributing to edge broadening in crystalline materials is exciton-phonon coupling (dynamic disorder). In amorphous, an additional broadening due to static disordered exists. The Urbach role has been studies in detail both for crystalline [14] and glassy [9, 14] forms of silica.

Experimentally, plots [5] are drawn between the logarithm of the absorption coefficient, ln(a), against photon energy, hv, for the different glass compositions. The Urbach energy is calculated by taking the reciprocals of the slopes of the linear portion in the lower photon energy of these curves. The values of E_U for different compositions are listed in Table 1. The error for computing E_U is ±0.002.

Increase in the value of E_U is seen with increasing the ratio of TbF_3 /SiO_2 . It could be attributed to an increase in disorder related to a disorder-induced broadening. [15, 16]. The least Urbach energy is observed for the glass sample GTb1 and GTb2 , suggesting the possibility of long-range order locally arising from the minimum in the number of defects as compared to the other glass compositions (see Figure 6).The glass systems were excited by 325 nm wavelength and the PL emission spectra are shown in Figure 7. The luminescence yield of spectrum from GTb2 glass in 462,492,557nm wavelengths is higher than the PL intensity of GTbGd; this trend is opposite at 441 and 418nm wavelengths PL intensity.
In this figure we see that the ratio of emission's integrated intensity (at 471,542 nm) to blue emission (at 417,437 nm) was almost 60 in GTb2 while this ratio is 8 for GTb1. In the earlier research [12], the dependence of the intensity of the blue $^5D_3 \longrightarrow {^7F_J}$ and green$^5D_4 \longrightarrow {^7F_6}$ emissions on concentration of terbium was reported for soda glass. It was found that the intensity of the blue emission began to saturate at concentration exceeding 0.5 molar. In contrast, the intensity of the green emission increased slowly with increasing terbium concentration up to 0.5%, but thereafter increased more rapidly until saturation effects were apparent with concentration exceeding 5%. The work on the concentration dependence of the luminescence intensity in the LAS glass has been restricted to a narrow range of rare earth dopant; they have measured the variation in the integrated light intensity of the blue and green emissions. They found

that the blue emission began to saturate at concentration exceeding 0.5%, whereas there was no indication of any quenching of the green emission for concentration up to 3%".

4. DISCUSSION

It is well known that there are two groups of Tb^{3+}transitions [6]: the blue emission bands centering at 325, 415, 437, 456, 471 and 488nm attributed to $^5D_{3-7}$ F_J (J =6, 5, 4, 3, and 2), while the green-yellow ones are located at, 542, 586,and 620 nm assigned to $^5D_{4-7}$ F_J (J =6, 5, 4, and 3). In the case of terbium, all of the transitions in $^4f_8 \Longrightarrow {^4f_7}5d$ are not allowed and they are possible when the 5d electrons occupied the unparallel position denoted by $^7D_{5,4,3,2,1}$. If the electrons fill the parallel spine, the transitions will be spin-forbidden, denoted by $^9D_{6,5,4,3,2}$. So, according to Figure 7 in GTb2 glass, the Tb ions have shown $^5D_{3-7}$ F_J (J =6, 5, 4, 3, and 2) transition.

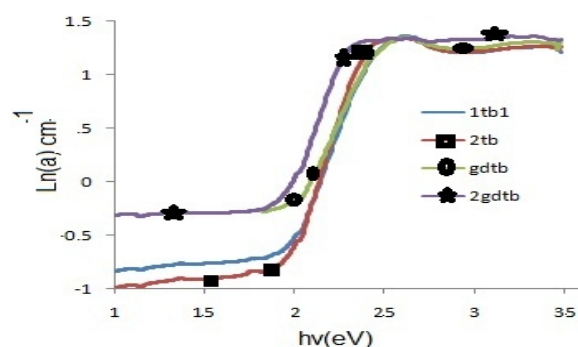**Figure 6.** The logarithm of the absorption coefficient, ln(a), against photon energy, hv, for the different glass compositions.
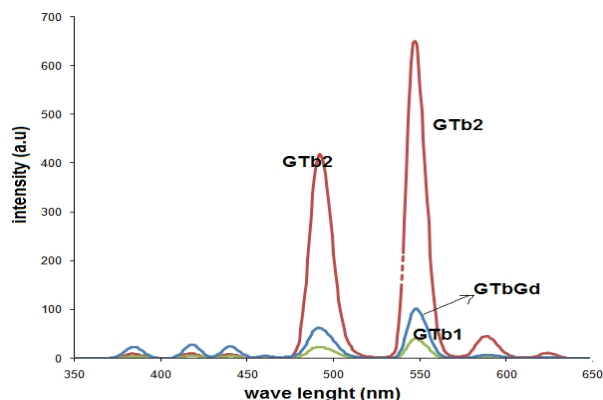
Figure 7. The PL intensity of GTb1, GTb2 and GTbGd glass excited by 325 nm

As it can be seen in Figure 7 the ratio of integrated intensity's at 418,441 nm to 462, 492, 557, 590 nm in GTbGd glass is higher than the GTb2 glass.

It sounds that, part of the energy in the $^6P_{7/2}$ level of Gd^{3+} is transferred to the $^5H_7$ level of Tb^{3+} by phonon-assistant electric dipole–dipole interaction, then relaxes rapidly to its $^5D_3$ and $^5D_4$, resulting in the enhanced Tb^{3+} (418, 441 nm) luminescence. Beside this, the energy transfer from Gd^{3+} to Tb^{3+} ions is almost known and irreversible, because the $^6P_{7/2}$ level of Gd^{3+} is about 660 cm^{-1} higher than the $^5H_7$ level of Tb^{3+}, and the probability of emitting phonons for $Gd^{3+6}P_{7/2}$ -Tb^{3+} (441 nm) process is much higher than that of capturing phonons for the inverse process. So the phonon-assisted energy transfer enhances the population of $Tb^{3+5}D_3$ and $^5D_4$ levels, resulting in the sensitization of Tb^{3+} luminescence.

5. CONCLUSION

It has been shown that in LAS glass by using Tb and Gd, the T_c of the system was increased up to 40ºC, the nano crystal phase of LaF_3 appeared at 580ºC (in GTb2) and 600ºC (in GTbGd).

The LAS glass-ceramic containing nano-crystals of LaF_3 doped by GTb2 has shown the enhanced luminescence yield and board emission band comparing to glass indicating to Tb ion diffusion in to the crystal structure.

Hence, reduction of optical band gaps and Urbach energy by increasing the Tb/Gd content of samples was attributed to the broadening of conduction band due to the generation of new bands close to the conduction band, enhancement of ionic bonds in the matrix and formation of more ordered structure due to the creation of BOs.

6. REFERENCE

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چکیده

در کار حاضر خواص اپتیکی شیشه‌های پایه لیتیوم-آلومینیوم –سیلیکات دوپه شده با ۱تا ۲درصد مولی تربیوم و گادلینیوم فلوراید بررسی شده است. طیف اسپکتروسکوپی این شیشه‌ها در محدوده طول موج ۲۲۰ تا ۷۰۰ نانومتر بررسی شد. مطالعات نشان داد که با افزایش مقدار عناصر لانتانیدی به شیشه‌ها انرژی Urbach از ۰/۰۸ تا ۰/۱٦ الکترون ولت افزایش می‌یابد نشر سبز –آبی در شیشه مورد مطالعه اتفاق افتاد و استفاده از Gd سبب افزایش نشر ٤۱۸ نانومتر شد .