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Article

Glass Ceramic Materials with Luminescent Properties in the System $\text{ZnO-B}_2\text{O}_3\text{-Nb}_2\text{O}_5\text{-Eu}_2\text{O}_3$

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Abstract: In this paper glass crystallization behavior of $50\text{ZnO}:47\text{B}_2\text{O}_3:3\text{Nb}_2\text{O}_5:0.5\text{Eu}_2\text{O}_3$ (G-0h) glass has been investigated in detail by DSC, XRD and TEM analysis. The luminescent properties of resulted glass-ceramics were also investigated. By XRD and TEM analysis crystallization of several crystalline phases have been proved ($\alpha\text{-Zn}_3\text{B}_2\text{O}_6$, $\beta\text{-Zn}_3\text{B}_2\text{O}_6$ and ZnNb_2O_6). By calculating of crystal parameters it was found that europium ions are successfully incorporated in the $\beta\text{-Zn}_3\text{B}_2\text{O}_6$. Photo-luminescent spectra show an increased emission in the resulting glass-ceramic samples as compared with the parent glass sample because of the higher asymmetry of Eu^{3+} ions in the crystalline phases obtained. It was established that the optimum emission intensity is registered for glass-ceramic sample obtained after 25 hours heat treatment of the parent glass.

Keywords: glass ceramics; XRD; TEM; luminescence

1. Introduction

In recent years, a great deal of attention has been paid to rare earth doped glass-ceramic materials, which play a crucial role in many optical application as up-conversion fibers, solid-state lasers, medical sensors, optical electronic chips, luminescence labels, optical amplifiers, 3D displays etc [1,2]. Most optical applications require transparency that is due to the reduced scattering effect because of the presence of nanocrystals inside glass ceramics. In addition, nanocrystalline glass ceramics might exhibit distinct optical properties in relation to pristine glasses when the rare earth ions occupy sites in the crystalline phase. In this case, an increase of emission intensities can occur due to the presence of rare earth ions in environments with lower phonon energy [3,4]. Transparent glass-ceramics possess excellent characteristics from both glasses and crystals and lack drawbacks of these two materials. Similar to glasses, glass ceramics have a large capacity for accommodating an active rare earth dopant, are isotropic and have evenly distributes activators within their bodies. Similar to single crystals, glass ceramics contain rare earth ions within strictly ordered ligand surroundings. As a result, the presence of crystalline environment around a rare earth ion allows high absorption and emission cross section reduction in the non-radiative relaxation because of the lower phonon cut-off energy, and tailoring of the ion-ion interaction by the control of the rare earth ion partition [1,4].

The glass ceramic materials are usually obtained by subsequent thermal treatment of a glass, first melted and annealed as usual. This conventional method relies on thermally induced phase separation and in situ crystallization processes, which however, are very complex to control experimentally [4]. The choice of an appropriate glass composition is very important for luminescent glass ceramics elaboration. The search for more efficient glass compositions and guiding structures for rare earth doped glass ceramics is continuing.

More recently we have reported for the preparation, structure and luminescence properties of niobium modified zinc-borate glasses doped with Eu_2O_3 with compositions in mol% of $50\text{ZnO}:(50-x)\text{B}_2\text{O}_3:x\text{Nb}_2\text{O}_5:0.5\text{Eu}_2\text{O}_3$, ($x = 0, 1, 3$ and 5 mol.%) [5]. Through differential thermal analysis and density measurements, various physical properties such as molar volume, oxygen packing density and glass transition temperature were determined. IR and Raman spectra revealed that niobium ions enter into the base zinc borate glass structure as NbO_4 tetrahedra and NbO_6 octahedra. It was found that the incorporation of Nb_2O_5 into Eu^{3+} : $\text{ZnO}:\text{B}_2\text{O}_3$ glass creates more disordered and reticulated glass networks, which are favorable for doping with Eu^{3+} active ions. The luminescent properties of the obtained Eu^{3+} - doped glasses revealed that they could be excited by 392 nm and exhibit pure red emission centered at 612 nm ($^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition). The introduction of niobium oxide into the $\text{ZnO}:\text{B}_2\text{O}_3$ glass enhances the luminescent intensity. 3 mol% was the optimal Nb_2O_5 concentration at which the most intensive red luminescence was obtained.

In this work, we report on the preparation and luminescent properties of glass ceramic materials, obtained by controlled crystallization of glass with the composition in mol% of $50\text{ZnO}:47\text{B}_2\text{O}_3:3\text{Nb}_2\text{O}_5:0.5\text{Eu}_2\text{O}_3$. The crystallization behavior of glass–ceramics were characterized by X-ray diffraction and transmission electron microscopy. Emission spectra were measured, and color coordinates of the materials were determined

2. Results

2.1. Thermal Analysis and XRD Data

As it was mentioned at the Introduction section, in our previous study glasses with nominal composition $50\text{ZnO}:(50-x)\text{B}_2\text{O}_3:x\text{Nb}_2\text{O}_5:0.5\text{Eu}_2\text{O}_3$, ($x = 0, 1, 3$ and 5 mol.%) were obtained and their luminescent properties were examined [5]. It was established that the optimum Nb_2O_5 concentration to obtain the most intensive red luminescence is 3 mol.% ($x=3$). This was the reason to choose the glass $50\text{ZnO}:47\text{B}_2\text{O}_3:3\text{Nb}_2\text{O}_5:0.5\text{Eu}_2\text{O}_3$ (G-0h) and to investigate its crystallization ability in order to increase the luminescent properties of the resulted glass-ceramic materials comparing with the initial glass. The glass ceramics obtained after heat treatment of the parent glass for different time (5h, 10h, 15h, 20h, 25h, 30h) were labeled as GC-5h, GC-10h, GC-15h, GC-20h, GC-25h, GC-30h, respectively.

The DSC curve for the glass G-0h is shown in Figure 1.

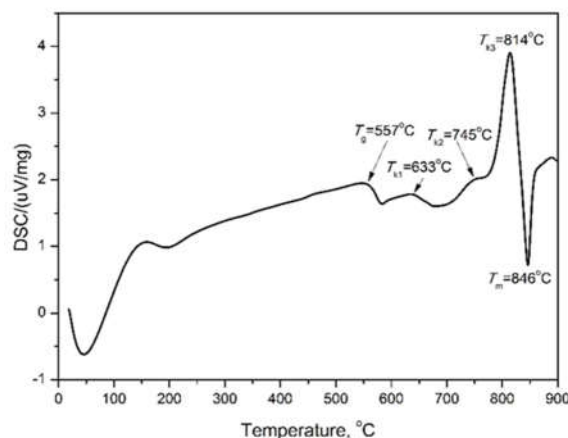


Figure 1. DSC curve of glass $50\text{ZnO}:47\text{B}_2\text{O}_3:3\text{Nb}_2\text{O}_5:0.5\text{Eu}_2\text{O}_3$ (in mol %).

The first endothermic peak corresponds to the glass transition temperature (T_g) while next three exothermic peaks are due to the crystallization of the glass (T_{kn} , where $n=1, 2$ and 3). The last endothermic effect corresponds to the melting temperature (T_m). The synthesized glass is characterizing with high glass transition temperature. The T_g value is 557 °C while the crystallization temperatures are as follows 633, 745 and 846 °C. The melting temperature is 846 °C. On the other hand, the thermal stability of the glass, i.e., $\Delta T=T_{k1}-T_g$ is 76 °C.

In the ternary system $\text{ZnO-B}_2\text{O}_3\text{-Nb}_2\text{O}_5$ it is not reported for existence of any three component crystalline phases. This means that the crystalline phases from the binary systems during the crystallization of glass G-0h would be expected. In the phase-equilibrium diagram of the system $\text{Nb}_2\text{O}_5\text{-B}_2\text{O}_3$ only one binary compound with composition $3\text{Nb}_2\text{O}_5\text{:B}_2\text{O}_3$ exists, which melts incongruently [6]. A large region of liquid phase separation exists in the range from 10 to 66 mol.% Nb_2O_5 [6]. For the binary system $\text{ZnO-Nb}_2\text{O}_5$ there are two crystalline phases $\text{Zn}_3\text{Nb}_2\text{O}_8$ and ZnNb_2O_6 (congruently melting) and Nb-rich compound labeled $\text{Zn}_2\text{Nb}_{34}\text{O}_{87}$ that melts incongruently [7,8]. The third binary system is $\text{ZnO-B}_2\text{O}_3$ that is the richest in terms of crystalline phases. In the different references the following crystalline phases have been reported: $\text{Zn}_5\text{B}_4\text{O}_{11}$, ZnB_2O_4 , $\text{Zn}_3\text{B}_2\text{O}_6$, ZnB_4O_7 and $\text{Zn}_4\text{B}_6\text{O}_{13}$ [8,9]. A large immiscibility region located above 50 mol. % B_2O_3 is also reported [8,10].

In order to avoid the full crystallization of the investigated glass we applied a glass heating temperature below first crystallization temperature ($T_{k1}\text{-}633^\circ\text{C}$). The XRD patterns at room temperature for the initial and crystallized glass for different times (5, 10, 15, 20, 25 and 30 hours) at 610°C are shown in Figure 2.

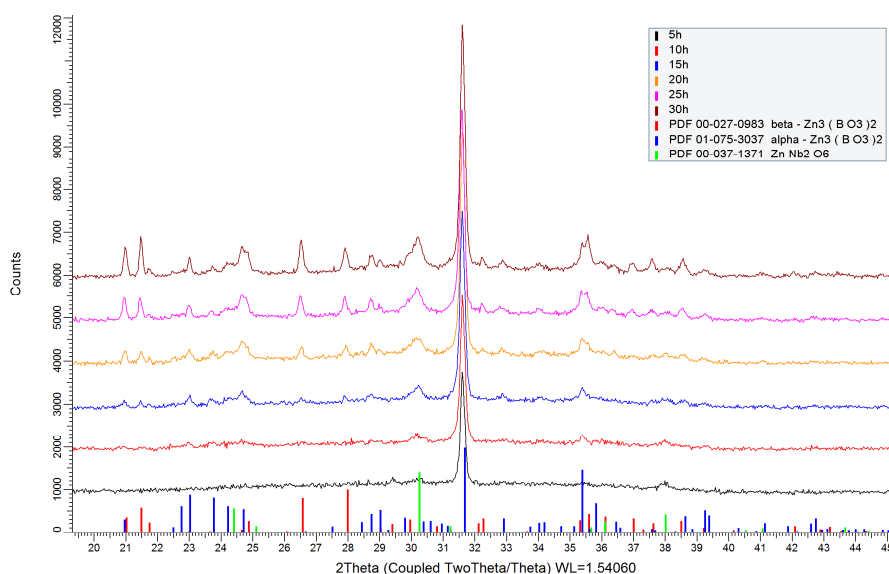


Figure 2. XRD patterns of the initial glass and of the glass ceramic samples obtained.

The amorphous nature of the investigated glass was presented in our previous paper [5]. In this work, the powder pattern of the initial glass is included only for comparison and to track the crystalline phases resulted due to heat treatment of G-0h. The weight percentages (wt.%) ratio of the obtained phases is summarized in Figure 3a. For GC-5h and GC-10h samples it was impossible to determine the ratio between crystalline phases due to the low intensity of the diffraction lines. For sample GC-5h the predominated crystalline phase corresponds to formation of $\alpha\text{-Zn}_3\text{B}_2\text{O}_6$ (ICDD PDF # 01-075-3037). A small amount of ZnNb_2O_6 (ICDD PDF # 00-037-1371) crystal phase was also detected. With increasing of heat treatment time (15 hours), the appearance of $\beta\text{-Zn}_3\text{B}_2\text{O}_6$ (ICDD PDF #00-027-0983) was observed at the expense of both - $\alpha\text{-Zn}_3\text{B}_2\text{O}_6$ and the amorphous phase.

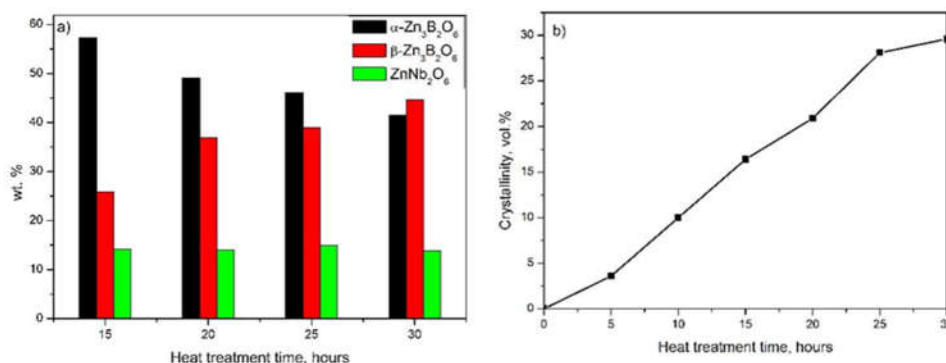


Figure 3. Comparisons of: a) the ratio between obtained crystal phases in wt.% b) degree of crystallinity of glass-ceramic materials.

After 30 hours of heating of glass (GC-30h), the X-ray analysis shows that β - $\text{Zn}_3\text{B}_2\text{O}_6$ grows and dominates compared to the other crystalline phases. Also, the amount of ZnNb_2O_6 crystalline phase does not change and remains within 14% in all glass-ceramic samples. Figure 3b traces the changes in the degree of crystallinity for all samples. It changes from 3.6 % for GC-5h and increases approximately up to 30 % for GC-30h. The crystallite sizes for all phases were calculated and the results are presented on Figure 4.

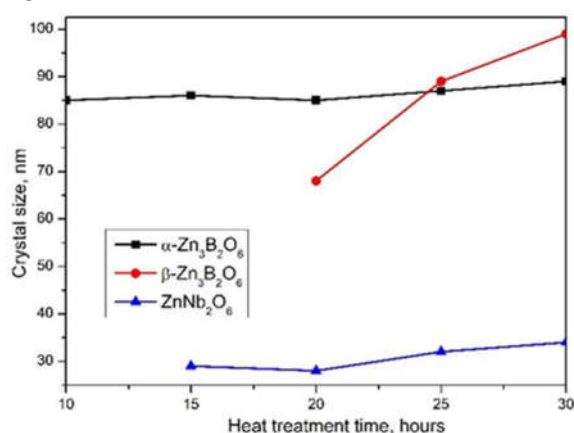


Figure 4. The crystallites size of the crystalline phases obtained in the crystallized samples.

The particle sizes of β - $\text{Zn}_3\text{B}_2\text{O}_6$ changes from 68 to 99 nm. On the other hand, for α - $\text{Zn}_3\text{B}_2\text{O}_6$ the crystal sizes do not change significantly (from 85 to 89 nm), and as well as for ZnNb_2O_6 (from 27 to 34 nm).

X-ray studies show that during the heat treatment of the glass the main crystalline phase is $\text{Zn}_3\text{B}_2\text{O}_6$ in two polymorph modifications. For the first time Chen et al. [9] reported for low-temperature α - $\text{Zn}_3\text{B}_2\text{O}_6$ crystallized in a triclinic space group $P\bar{1}$ with unit cell parameters $a = 6.302(2)\text{\AA}$, $b = 8.248(1)\text{\AA}$, $c = 10.020(1)\text{\AA}$, $\alpha = 89.85(1)^\circ$, $\beta = 89.79(1)^\circ$, $\gamma = 73.25(1)^\circ$, $V = 498.73\text{\AA}^3$ and $Z = 4$. The crystal structure of β - $\text{Zn}_3\text{B}_2\text{O}_6$ was reported for the first time by Garcia-Blanco and Fayos [11] in monoclinic space group Ic (9) with unit cell parameters $a = 23.40$, $b = 5.04$, $c = 8.38$, $\beta = 97.53^\circ$, $V = 979.78\text{\AA}^3$ and $Z = 8$. Two years later, H. Baur and Tillmanns predetermined the crystal structure in the centrosymmetric space group $I2/c$ (15) with the same unit cell parameters [12]. α - $\text{Zn}_3\text{B}_2\text{O}_6$ represents a new structural type in which ZnO_4 tetrahedra are connected to each other and also to BO_3 flat triangles by common corners giving rise to a three-dimensional framework, while β - $\text{Zn}_3\text{B}_2\text{O}_6$ is characterized by a three-dimensional network built from corner- and edge-sharing ZnO_4 tetrahedra as well as corner sharing ZnO_4 tetrahedra and BO_3 triangles [9].

The second in quantity is the crystalline phase of ZnNb_2O_6 . This compound crystallizes in orthorhombic space group $Pbcn$ (60) with unit cell parameters: $a = 14.208\text{\AA}$, $b = 5.726\text{\AA}$, $c = 5.04\text{\AA}$, $V = 410.03\text{\AA}^3$, $Z = 4$. The zinc niobate has a columbite-type structure in which Zn^{2+} and Nb^{5+} are in an octahedral environment. Each of the cations forms zigzag chains made up of octahedra connected by common edges and vertices along the $[001]$ direction.

In this regard, the unit cell parameters and volume of the resulting crystalline phases during the thermal treatment of the glass were calculated and their values are presented in Table 1.

Table 1. Calculated lattice parameter and unit cell volume for crystals resulted due to heat treatment of glass. The unit cell angles are intentionally omitted.

Time	α -Zn ₃ B ₂ O ₆ ,	β -Zn ₃ B ₂ O ₆	ZnNb ₂ O ₆
	a/b/c [Å], volume [Å ³]	a/b/c [Å], volume [Å ³]	a/b/c [Å], volume [Å ³]
30h	6.311/8.267/10.035 500.9(2)	23.885/5.047/8.385 985.0(3)	14.219/5.706/5.066 411.0(4)
25h	6.312/8.265/10.035 500.8(2)	23.885/5.048/8.383 985.1(4)	14.212/5.708/5.067 411.0(4)
20h	6.310/8.264/10.031 500.5(3)	23.873/5.048/8.379 984.1(7)	14.216/5.701/5.067 410.7(6)
15h	6.302/8.255/10.023 499.0(4)	23.833/5.039/8.365 978.7(7)	14.189/5.692/5.063 408.9(6)
10h	n.a.	n.a.	n.a.
5h	n.a.	n.a.	n.a.

As can be seen, a significant difference for the a-cell parameter of β -Zn₃B₂O₆ was observed. For instance, the calculated a-parameter for β -Zn₃B₂O₆ varies from 23.833 to 23.885 Å with increasing heat treatment time. Compared to the literature data this parameter is 23.40 Å. Moreover, the volume of the unit cell increases from 979.78 Å³ for the referent β -Zn₃B₂O₆ phase up to 985.1 Å³ for the resulting β -Zn₃B₂O₆. For the other crystalline phases, no such changes are observed. This gives us reason to assume that the doped europium ions predominantly are accommodated in the β -Zn₃B₂O₆ crystal structure.

2.2. Luminescent Properties

In order to study the luminescent behavior of the synthesized glass and glass ceramics, the emission ($\lambda_{\text{ex}} = 392 \text{ nm}$) and excitation ($\lambda_{\text{em}} = 612 \text{ nm}$) spectra of the obtained samples were measured. Figure 5 displays the room temperature PLE spectra of 0.5 mol% Eu³⁺ doped 50ZnO:47B₂O₃:3Nb₂O₅ glass and glass ceramics, recorded at 612 nm emission, corresponding to ⁵D₀→⁷F₂ transition of Eu³⁺ ions.

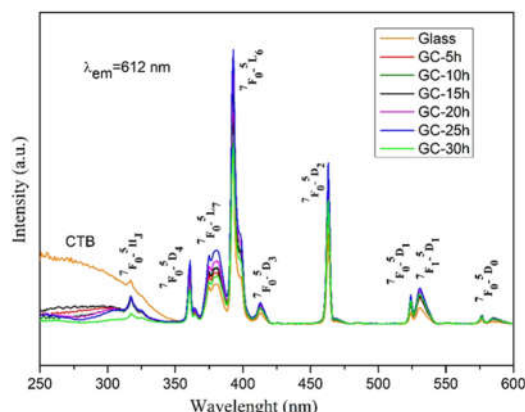


Figure 5. Excitation spectra of 50ZnO:47B₂O₃:3Nb₂O₅:0.5Eu₂O₃ glass and the corresponding glass ceramics heat treated at different time durations.

The narrow peaks located in the spectral range 350–580 nm, are assigned to the characteristic 4f - 4f transitions of Eu³⁺ ion, in particular from ${}^7F_0 \rightarrow {}^5H_1$, ${}^7F_0 \rightarrow {}^5D_4$, ${}^7F_0 \rightarrow {}^5L_7$, ${}^7F_0 \rightarrow {}^5L_6$, ${}^7F_0 \rightarrow {}^5D_3$, ${}^7F_0 \rightarrow {}^5D_2$, ${}^7F_0 \rightarrow {}^5D_1$, ${}^7F_1 \rightarrow {}^5D_1$, ${}^7F_0 \rightarrow {}^5D_0$ at 317 nm, 361 nm, 380 nm, 392 nm, 413 nm, 463 nm, 523 nm, 531 nm and 576 nm, respectively [13]. The part of the spectra in the lower wavelength region, below 350 nm, is represented by a broad band due to the charge transfer transitions of the host absorbing groups, in particular Nb₂O_n ($O^{2-} \rightarrow Nb^{5+}$) [14] and ZnO_n ($O^{2-} \rightarrow Zn^{2+}$) [15] and from oxygen 2p orbital to the empty 4f orbital of europium ($O^{2-} \rightarrow Eu^{3+}$) [16–19]. The appearance of this absorption in the excitation spectra when monitoring the Eu³⁺ emission at 612 nm, is an indication of the occurrence of a charge transfer from the matrix, in this case from NbO_n and ZnO_n structural polyhedra to the rare earth Eu³⁺ ion and previously has been shown to play an important role in the enhancement of the rare earth emission intensity. [20–24]. This process is known as “host sensitized” energy transfer.

The intensity of the f-f peaks increases with the time of the heat treatment up to 25h and then decreases at 30h. The same trend is observed in the emission spectra. This behavior is most likely caused by change of the active ion surroundings after glass crystallization and hence more effective excitation of Eu³⁺ may be expected in the glass ceramic samples. [25]. The most intensive peak of the excitation spectra is located at 392 nm attributed to ${}^7F_0 \rightarrow {}^5L_6$, followed by the ${}^7F_0 \rightarrow {}^5D_2$ at 463 nm. These wavelengths can be used as excitation source to register the emission spectra and are compatible with the commercially available near ultraviolet light emitting diodes (LED) (250–400 nm) and blue LED chips (430–470 nm).

The room-temperature PL spectra are recorded in the range of 550–750 nm and are shown in Figure 6. The spectra are composed of the typical Eu³⁺ emission lines at 578nm, 591nm, 612nm, 651 and 700 nm due to the transitions from the 5D_0 excited state to the 7F_0 , 7F_1 , 7F_2 , 7F_3 , 7F_4 ground states of Eu³⁺ ion, respectively [13].

The glass spectrum is characterized by the lowest luminescence intensity. After preparing glass ceramic samples, by heat treatment and crystallization at 610°C, the emission intensity becomes stronger. The luminescent intensity of glass ceramics increases with increasing heat treatment time up to 25 hours. This behavior can be attributed to the Eu³⁺ ions incorporation into the Zn₃B₂O₆ crystal and therefore, the enhancement of the spectral intensity is due to the change of the site symmetry around the Eu³⁺ ion. This fact is consistent with the X-ray structural data. A further increase in the treatment time to 30 hours results in a sharp drop in emission intensity.

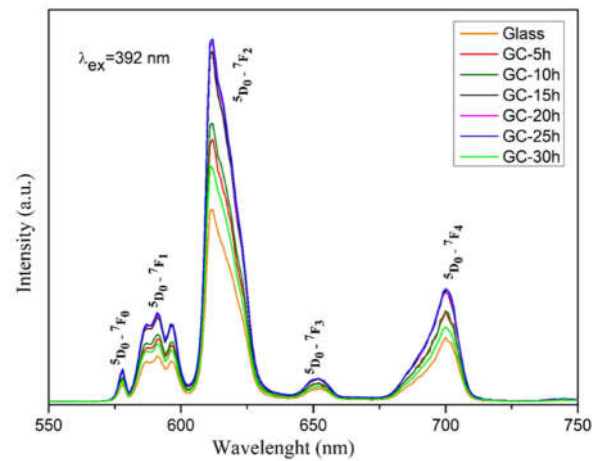


Figure 6. Emission spectra of 50ZnO:47B₂O₃:3Nb₂O₅:0.5Eu₂O₃ glass and the corresponding glass ceramics heat treated at different time durations.

As can be seen from Figure 6 the major emission line is located at 612 nm and is caused by the forced electric dipole transition (ED) $^5D_0 \rightarrow ^7F_2$. According to Judd-Ofeld theory this transition is sensitive to the chemical bonds and site symmetry in the vicinity of Eu³⁺ ions, and it is most intensive when Eu³⁺ ions are occupying non-inversion symmetry sites [26].

The magnetic dipole transition (MD) at 591nm ($^5D_0 \rightarrow ^7F_1$) is insensitive to the crystal field environment and can be used as reference, since its intensity hardly varies with the change of the site symmetry around the Eu³⁺ ions [13,16]. An indication that Eu³⁺ ions are located in lattice sites without an inversion center is the more intensive ED emission compared to MD one. Therefore, by calculating the intensity ratio of these two emissions (Table.2.), known as asymmetric ratio R, the degree of asymmetry in the local environment around the Eu³⁺ and the strength of Eu - O covalence in the different Eu³⁺ doped compounds can be studied. The lower the R value, the higher the local site symmetry around the active ion, and the lower Eu-O covalency and emission intensity [27]. Ratio values greater than 1 correspond to the location of Eu³⁺ ions into lower symmetry sites, while values below 1 indicate that the active ion occupies high symmetry sites. The higher R values (from 5.16 to 5.49), compared to ones reported for Eu³⁺ doped glasses and glass ceramics (Table) [5,20,28–32], suggest more asymmetry in the vicinity of Eu³⁺ ions, stronger Eu-O covalence, and thus enhanced emission intensity. With increasing crystallinity, the asymmetry ratio increases gradually, up to glass ceramic sample with 25 hours of thermal treatment (GC-25h). This fact is directly related to the higher emission intensity of the heat-treated samples, as the higher the asymmetry the stronger the luminescent intensity. At 30 hours heat treatment (CG-30h), a decrease in R value is observed, which is consistent with the decrease of the emission intensity of this specimen.

Table 2. Relative luminescent intensity ratio (R) of the two transitions ($^5D_0 \rightarrow ^7F_2$)/($^5D_0 \rightarrow ^7F_1$) for 50ZnO:47B₂O₃:3Nb₂O₅:0.5Eu₂O₃ glass and ceramics heat treated at different time durations and of other reported Eu³⁺-doped oxide glasses.

Glass composition	Relative Luminescent Intensity Ratio, R	Reference
Glass 50ZnO:47B ₂ O ₃ :3Nb ₂ O ₅ :0.5Eu ₂ O ₃	5.16	Current work+ [5]
GC-5h	5.28	Current work
GC-10h	5.39	Current work

GC-15h	5.42	Current work
GC-20h	5.47	Current work
GC-25h	5.49	Current work
GC-30h	5.21	Current work
Glass 50ZnO:(50-x)B ₂ O ₃ : xNb ₂ O ₅ :0.5Eu ₂ O ₃ ; x= 0, 1, 3 and 5 mol%	4.31-5.16	[5]
Glass 50ZnO:40B ₂ O ₃ :10WO ₃ :xEu ₂ O ₃ (0≤x≤10)	4.54÷5.77	[28]
Glass 50ZnO:40B ₂ O ₃ :5WO ₃ :5Nb ₂ O ₅ :xEu ₂ O ₃ (0≤x≤10)	5.09÷5.76	[20]
Glass 66P ₂ O ₅ – 10.5Al ₂ O ₃ –3.05BaO–16.5K ₂ CO ₃ –0.7NaF–xEu ₂ O ₃ –0.5Nd ₂ O ₃ –(2.75-x) La ₂ O ₃ (mol.%), where x = 0, 0.25, 0.5, 0.75, 1.5 and 2	3.72	[29]
Glass ceramic 66P ₂ O ₅ – 10.5Al ₂ O ₃ –3.05BaO–16.5K ₂ CO ₃ –0.7NaF–xEu ₂ O ₃ –0.5Nd ₂ O ₃ –(2.75-x) La ₂ O ₃ (mol.%), where x = 0, 0.25, 0.5, 0.75, 1.5 and 2	4.72	
Glass 74.0 TeO ₂ +25.0 Li ₂ CO ₃ +1.0 Eu ₂ O ₃	3.70	[30]
Glass ceramic 74.0 TeO ₂ +25.0 Li ₂ CO ₃ +1.0 Eu ₂ O ₃	3.65	
Glass 50Li ₂ O·45B ₂ O ₃ ·5Al ₂ O ₃ ·2Eu ₂ O ₃	3.91	[31]
Glass ceramic 50Li ₂ O·45B ₂ O ₃ ·5Al ₂ O ₃ ·2Eu ₂ O ₃	4.047	
Glass 7SiO ₂ -47.4CaO-40.5Al ₂ O ₃ -4.1MgO-1Eu ₂ O ₃	4.58	[32]
Glass ceramic 7SiO ₂ -47.4CaO-40.5Al ₂ O ₃ -4.1MgO-1Eu ₂ O ₃	1.97	

Additionally, an indication of the low symmetry in the local environment around the Eu³⁺ is the appearance of the strictly forbidden ⁵D₀ → ⁷F₀ transition, which as stated by Binnemans, shows that Eu³⁺ ions are located in sites with C_{2v}, C_n or C_s symmetry [13]. Moreover, the splitting into three peaks of the ⁵D₀ → ⁷F₁ transition is also evidencing that the symmetry of the Eu³⁺ sites in the studied glass and glass ceramics are C_{2v} or lower [33].

In order to estimate the actual emitted colors, the Commission International de l’Eclairage (CIE) 1931 chromaticity diagram was used [34]. The chromaticity coordinates were calculated from the emission spectra by using color calculator software SpectraChroma (CIE coordinate calculator) [35]. The calculated values are listed at Table 3. The chromaticity coordinates of the glass and glass ceramics lie in the red region in the CIE diagram (Figure 7). Their values are almost identical and accordingly are represented in the figure as one point. The closest to the CIE coordinate of standard red light (0.670,0.330) and to the color coordinates of the commercial red phosphor Y₂O₂S:Eu³⁺ (0.658;0.340) [36] is the glass sample (0.656, 0.343).

The color-correlated temperature (CCT) of each sample were calculated by using the McCamy empirical formula [37]

$$CCT = - 449n^3 + 3525n^2 - 6823n + 5520.33;$$

$$n = \frac{(x - 0.332)}{(y - 0.186)}$$

where x and y are chromaticity coordinates, which are calculated by CIE1931 software.

Generally, color-correlated temperatures greater than 5300 K are considered as cool light, between 3300 and 5300 K are considered moderate light and less than 3300 K as warm light. As can be seen from table, the obtained values are in range 2324.60 K ÷ 2505.78 K and the Eu³⁺ doped glass and the corresponding glass ceramics can be assigned as warm light emitting materials.

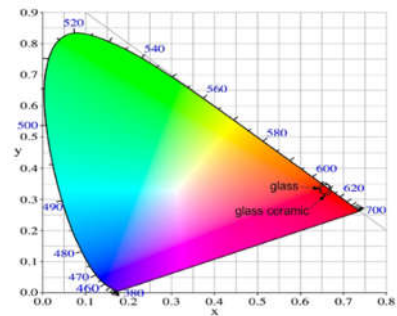


Figure 7. CIE chromaticity diagram of 50ZnO:47B₂O₃:3Nb₂O₅:0.5Eu₂O₃ glass and the corresponding glass ceramic.

Table 3. CIE chromaticity coordinates and correlated color temperature (CCT, K) of 50ZnO:47B₂O₃:3Nb₂O₅:0.5Eu₂O₃ glass and the corresponding glass – ceramics.

Glass composition	Chromaticity coordinates (x,y)	CCT(K)
Glass 50ZnO:47B ₂ O ₃ :3Nb ₂ O ₅ :0.5Eu ₂ O ₃	0.656, 0.343	2505.78 [5]
GC-5h	0.652, 0.347	2350.82
GC-10h	0.652,0.348	2333.75
GC-15h	0.652, 0.348	2333.75
GC-20h	0.652,0.348	2333.75
GC-25h	0.652,0.348	2333.75
GC-30h	0.651,0.348	2324.60
NTSC standard for red light	0.670,0.330	
Y ₂ O ₂ S:Eu ³⁺	0.658, 0.340	

The obtained results indicate that the studied glass and glass ceramics emit warm red light, which is very useful for development of red-emitting lightning solid state devices.

2.3. TEM Investigations and Density Measurment

The morphology, particle size distribution, and phase composition of the glass ceramic sample obtained after 25 hours heat treatmnnnet that is characterised with the best luminescent properties were investigated using TEM and HRTEM analytical methods. Morphology studies (Figure 8) show

that the sample contains spherical and rectangular nanosized particles, as well as larger particles with sizes of about 80-90 nm. The inset of the Figure 8 illustrates the particle size distribution.

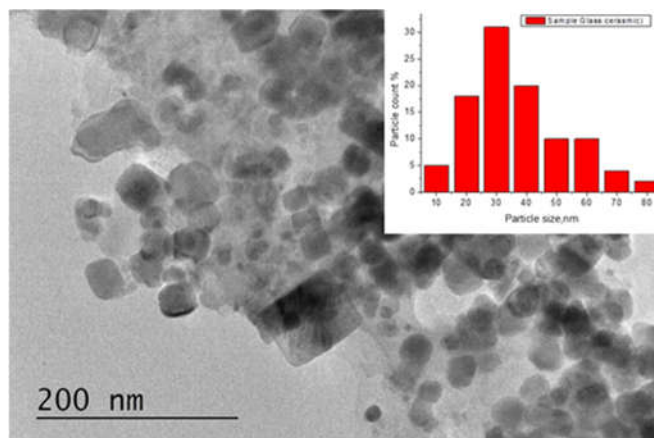


Figure 8. Bright field micrograph and particle size distribution (inset).

The average particle size of the glass ceramic sample obtained after 25 hour heat treatment of the parent glass is 33 nm. The particle sizes range between 10 and 80 nanometers, with some larger particles also present. The majority of the particles are in the range of 20-40 nm. HRTEM analysis (Figure 9) reveals the presence of both high-temperature monoclinic and low-temperature triclinic $\text{Zn}_3(\text{BO}_3)_2$ phases in the sample, with cell parameters of $a = 23.400$, $b = 5.040$, $c = 8.38$ for the monoclinic phase, and $a = 8.248$, $b = 10.020$, $c = 6.302$ for the triclinic phase. The interplanar distances are $d = 3.9$ Å and $d = 3.2$ Å, respectively.

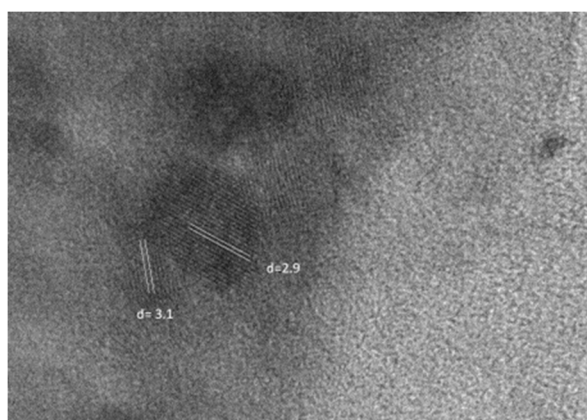


Figure 9. HRTEM picture of glass ceramic obtained after 25 hours heat treatment of the parent glass.

The luminescent properties measured showed that the glass ceramic sample obtained after 25 hours heat treatment of the parent glass (GC-25h) is characterized with the highest luminescence intensity. That is why we have measured the density of the GC-25h by applying the Archimedes method, which is found to be 5.577 ± 0.002 g/cm³. The density of GC-25h obtained is similar to the density of the parent glass with same composition (5.663 ± 0.001 g/cm³) [5], which is an evidence for the homogeneous nucleation of the glass [38].

3. Discussion

In this paper glass crystallization behavior of $50\text{ZnO}:47\text{B}_2\text{O}_3:3\text{Nb}_2\text{O}_5:0.5\text{Eu}_2\text{O}_3$ (G-0h) glass has been investigated in details by XRD and TEM analysis. XRD data show that the crystallization started after 5 hours heat treatment at 610 °C with separation of two crystalline phases $-\alpha\text{-Zn}_3\text{B}_2\text{O}_6$ and ZnNb_2O_6 . After 15 hours of heat treatment $\beta\text{-Zn}_3\text{B}_2\text{O}_6$ appears additionally and with further heating

increases in amount at the expense of both α -Zn₃B₂O₆ and glass phase. Comparative analysis of structural data of referent zinc borate and zinc niobate crystalline phases and glass-ceramics obtained here (see Table 1) shows more significant changes in both the parameter (a) and unit cell volume for β -Zn₃B₂O₆ obtained from glass crystallization. This observation suggests that doped europium ions preferentially are accommodated in the β -Zn₃B₂O₆. This suggestion is confirmed by the luminescence measurements as a drastic increase of the emission intensity of the GC-15h was observed when β -Zn₃B₂O₆ appears. With increasing time of heat treatment (20 and 25 hours) the luminescence emission increases most probably because the amount of β -Zn₃B₂O₆ also increases. However, 30 hours heat treatment leads to decrease of luminescence intensity due to the emission quenching effect of europium ions. We assume that this quenching is a result of decreased average distance between europium ions because of increasing amount of β -Zn₃B₂O₆. The enhanced photoluminescence emission in the glass ceramic samples compared with the glass is related to the covalence and structural changes in the vicinity of RE³⁺ ions (short range effect) [39]. The higher intensity of the ⁵D₀→⁷F₂ emission band in glass ceramics spectra and as well as the higher values of luminescence intensity ratio R in comparison with that of parent glass can be related to the more asymmetrical coordination environment around Eu³⁺ ions in the glass ceramics. On other hand the increased emission efficiency of Eu³⁺ ions in the crystallized samples as compared with the glass, can be explained with the fact that in the glass ceramics the crystalline particles are embedded in the amorphous matrix and more of them are separated each other's which improve the light scattering intensity from the free interfaces of the nanocrystallites [40].

4. Materials and Methods

Glass with nominal compositions 50ZnO:47B₂O₃:3Nb₂O₅:0.5Eu₂O₃, was obtained by applying the conventional melt-quenching method, using commercial powders of reagent grade Nb₂O₅ (Merck KGaA, Darmstadt, Germany), ZnO (Merck KGaA, Amsterdam, The Netherlands), H₃BO₃ (SIGMA-ALDRICH, St. Louis, MO, USA), and Eu₂O₃ (SIGMA-ALDRICH, St. Louis, MO, USA) as starting materials. The details of glass synthesis were given in ref. 5. To prepare the glass ceramics (GC), the precursor glass 50ZnO:47B₂O₃:3Nb₂O₅:0.5Eu₂O₃ was subjected to the heat treatment at 610°C for 5h, 10h, 15h, 20h, 25h and 30h. The glass transition (T_g) temperature of the glass was determined by differential scanning calorimetry (DSC) using a Netzsch 404 Pegasus instrument, 2021 Selb, Germany at a heating rate of 10 K/min in Ar flow of 10 ml/s, using corundum crucible with lids. The XRD investigations were performed by using Bruker D8 Advance X-ray powder diffractometer equipped with X-ray tube with copper anode (CuK α = 1.542 Å, 40 kV and 40 mA) and LynxEye position sensitive detector. The powder patterns were collected in the angular k-range 5.5 - 80.0° 2 θ with a step of 0.03° 2 θ and total of 52.5 sec/step counting statistics, integrated over the whole area of the detector. The qualitative phase analysis was performed using DIFFRAC.EVA v.4 software program [41] in combination with ICDD PDF-2 (2021) reference database. The quantitative phase analysis, crystallite size, unit cell parameters and degree of crystallinity were determined using Topas v.4.2 software program [42]. The crystal structure parameters for α -Zn₃B₂O₆, β -Zn₃B₂O₆ and ZnNb₂O₆ were taken from the literature cited in "Thermal analysis and XRD data" section earlier in this text. The TEM observations were carried out using transmission electron microscope JEOL JEM 2100 with GATAN Orius 832 SC1000 CCD Camera at accelerating voltage of 200 kV. The specimen for TEM investigation was prepared by grinding the sample in an agate mortar and then disintegrating it in the form of ethanol suspension by ultrasonic treatment for 6 min. A droplet of the suspension was coated on standard carbon films on Cu grids. The size distribution of the particles was performed with the image processing program ImageJ, the measurements of the interplanar distances were performed with the specialized software Digital Micrograph. The density of the glass ceramic obtained after 25 hours heat treatment was measured at room temperature by the Archimedes principle using toluene (ρ = 0.867 g/cm³) as an immersion liquid on a Mettler Toledo electronic balance of sensitivity 10⁻⁴ g. Photoluminescence (PL) excitation and emission spectra at room temperature for all glasses were measured with a Spectrofluorometer FluoroLog3-22, 2014 (Horiba Jobin-Yvon, Longjumeau, France).

5. Conclusions

Glass ceramics materials with enhanced photoluminescence emission have been obtained by controlled crystallization of glass with nominal composition $50\text{ZnO}:47\text{B}_2\text{O}_3:3\text{Nb}_2\text{O}_5:0.5\text{Eu}_2\text{O}_3$. Photoluminescence spectra revealed that obtained glass ceramics can emit red light under excitation of 392 nm originating from the dominant dipole transition $^5\text{D}_0 \rightarrow ^7\text{F}_2$ of Eu^{3+} ions. Based on the results from the emission spectra it was established that the formation of $\beta\text{-Zn}_3\text{B}_2\text{O}_6:\text{Eu}^{3+}$ nanocrystals and an appropriate degree of crystallinity are decisive factors to improve the luminescence properties of the samples.

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