Investigation of the luminescent properties of SiLiZn glass-ceramic phosphor-doped Cr^{3+}/Cr^{4+}

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Abstract—This study presents the development of Cr_2O_3 – doped glass-ceramic phosphors with the possibility of obtaining Cr^{3+}/Cr^{4+} for broadband near–infrared (NIR) emission, targeting potential applications in NIR phosphor–converted LEDs (pc–LEDs). Optimization of Cr_2O_3 doping and annealing conditions of glass-ceramic, we achieved emission in the range of NIR–I (700–950 nm) and NIR–II (1000–1700 nm) biological windows. Based on the luminescence measurements performed, in the glass sample, emission bands attributed to Cr^{3+} in an octahedral environment were observed with strong emission at 955 nm (corresponding to the transition $^4T_2 \rightarrow {}^4A_2$). In contrast, the emission of annealed glass–ceramics suggested the appearance of Cr^{4+} with a peak at 1250 nm ($^3T_2 \rightarrow {}^3A_2$).

Commercial near–infrared light sources, such as commercially available light–emitting diodes (LEDs) operating in the infrared range, are characterized by low output power, low thermic stability, narrow emission bands, and high production cost. Whereas NIR light sources based on the conversion of near–infrared phosphors (NIR pc–LED) can be promising strategies for replacing commercial LEDs due to the low cost associated with production, high thermal stability, and long materials life [1]. To obtain high–performance NIR pc–LEDs, phosphors operating in the NIR range are being sought, mainly doped with rare earth ions and transition metal ions, which can be successfully applied to commercially available LED chips. High-intensity luminescence spectra in the first (700–950 nm) and second biological windows (1000–1700 nm) are especially being sought for biosensor applications. Only a few of the rare earth ions are characterized by emission in the biological window range. In addition, the emission bands of rare earth ions (RE) have narrow-band luminescence spectra. Luminescence in the NIR-II range is mainly exhibited by trivalent ions of ytterbium, neodymium, and erbium. Despite emission transitions between 1000 nm and 1700 nm, there are still areas in the second biological window where RE ions do not exhibit radiative transitions. An alternative to fabricating phosphors from rare–earth could be phosphors from transition metals (TM) [2–3]. In recent years, scientific research has focused on Cr^{3+} ions doped phosphors characterized by broadband emission in the 700–1000 nm (NIR–I) range. The photoluminescence (PL) of Cr^{3+} is crystal–field dependent – in a strong crystal field, it exhibits narrowband emission spectra, while in a weak crystal field, it exhibits broadband emission spectra. Cr^{3+} ions show broadband absorption in the spectral range of visible light, making them suitable candidates for phosphors that can be used on commercially available LEDs [4]. The electron configuration of Cr^{4+} ions $[Ar]3d^2$ affects the luminescence properties, which depend on the crystal field environment [5].

This work presents the glass–ceramic phosphor-doped Cr_2O_3 as a matrix to obtain wide emission in the first (700–950 nm) and the second (1000–1700 nm) therapeutic windows. In the experimental part, we fabricated glass and glass-ceramic. The glass sample with the chemical composition: $(38 - x)\ SiO_2 - 24Li_2O_3 - 16ZnO - 8Al_2O_3 - 13K_2CO_3 - 1P_2O_5$ (SiLiZn), where x=0.05, 0.1 and 0.2 Cr_2O_3 (in mol%) was prepared by standard melting and quenching methods. All reagents were characterized by high purity (Sigma-Aldrich, 99.99%). A synthesized powder was placed in the platinum crucible and melted at 1500 °C. Next, the molten glass was poured into a stainless form and kept in the furnace at 500 °C to reduce thermal stress. Based on DSC measurements, the crystallization temperature was indicated at 700 °C and 800 °C. The parent glass was initially annealed at 700 °C for 2 and 4 hours. Subsequently, the annealing time was optimized, and the parameters for obtaining glass – ceramics were changed to annealing the sample at 800 °C for 30 minutes and 1 hour.

All samples were grounded, and the powders were placed in the holder for luminescence measurements. Absorption properties were measured using a Stellarnet Green-Wave spectrometer ranging from 400 nm to 1000 nm. Measurements of optical properties of SiLiZn glass were realized in the range of 700–1700 nm by using an Acton 2300i monochromator (Acton Research Corporation, Acton, MA, USA) equipped with an InGaAs detector with excitation at a wavelength of 671 nm.

Figure 1 presents absorbance spectra of the fabricated SiLiZn glass doped 0.1 mol% Cr_2O_3 and the Tanabe –

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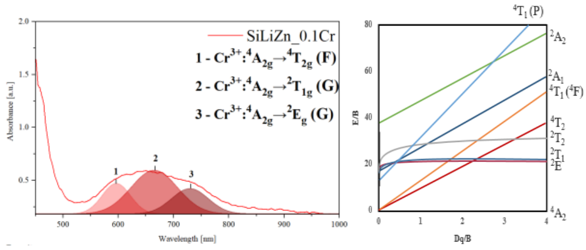
Sugano diagram. The absorbance spectrum of Cr^{3+} in glass was deconvoluted into three Gaussian components. Number 1 is the absorption band at about 590 nm, number 2 at about 670 nm, and number 3 – 730 nm identified as being due to $^4A_{2g} \rightarrow {}^4T_{2g}$ (F), $^4A_{2g} \rightarrow {}^2T_{1g}$ (G) and $^4A_{2g} \rightarrow {}^2E_g$ (G) transitions of the Cr^{3+} (d^3) ions respectively [6].



(a) (b)

Fig. 1. (a) Deconvolute absorbance spectra of the fabricated SiLiZn_0.1 Cr glass (glass sample thickness = 3 mm) (b) Tanabe-Sugano diagram of Cr^{3+}.

According to the Tanabe – Sugano diagram for d3 electronic configuration considering Cr^{3+} ions in octahedral symmetry, the crystal field parameters 10Dq, the Racah parameters B the related ligand field parameters Dq/B were calculated from spectral positions of absorption bands using the following relations (1) – (3), yielding 10Dq = 3250cm^{-1}, B = 153.9cm^{-1}, corresponding to Dq/B ratio of 2.11 [7].

$$Dq = 1/10\,[E(^4T_2) - E(^4A_2)] \tag{1}$$

$$Dq/B = [15(x - 8)]/[x^2 - 10x] \tag{2}$$

$$x = 1/Dq\,[E(^4T_1) - E(^4T_2)] \tag{3}$$

When Cr^{3+} ions are in an octahedral field, the Cr^{3+} base term is split into five energy levels, where $^4A_2$ is the ground state and the others are excited states. As the crystal field strength (Dq/B) increases, the energy levels of $^4T_1$ (^{4}F) and $^4T_2$ (^{4}F) rise, while the position of the ^2E energy level remains unchanged. The intersection of the $^4T_2$ (^{4}F) and 2E energy levels occurs at approximately Dq/B = 2.3. This value serves as the boundary between strong and weak crystal fields. When Dq/B > 2.3, the crystal field is classified as strong, causing the ^2E energy level to be positioned below $^4T_2$(^{4}F). Under these conditions, Cr^{3+} exhibits a narrow-band emission due to the spin-forbidden transition $^2E \rightarrow {}^4A_2$. Conversely, when Dq/B < 2.3, the crystal field is considered weak, with the $^4T_2$ (^{4}F) energy level lying below ^2E [3]. When the Dq/B is less than 2.3, the electron transition mode of the Cr^{3+} ion is attributed to the spin–allowed the transition of $^4T_2 \rightarrow {}^4A_2$, and the emission peak can encompass the NIR region of 700 – 1000 nm [8].

Figure 2 shows the emission spectra from 700 to 1300 nm of glasses doped with rest 0.05, 0.1, and 0.2 mol% Cr_2O_3, respectively, with excitation at 671 nm. The emission spectra of the studied samples are characterized by broadband luminescence with the highest intensity at the wavelength of 955 nm originating from the $^4T_2 \rightarrow {}^4A_2$ (Cr^{3+}) transition.

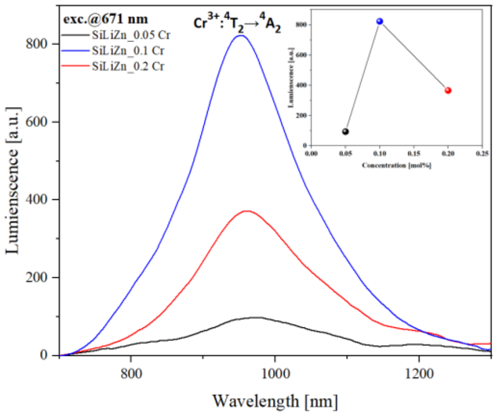


Fig. 2. Luminescence spectra of Cr^{3+} in SiLiZn glass excited at 671 nm with different chromium concentrations, and insert: intensity of selected emission bands as a function of concentration.

The appearance of an emission band corresponding to the $^4T_2 \rightarrow {}^4A_2$ spin transition identifies that Cr^{3+} ions are in an environment with octahedral symmetry and a weak crystal field. The highest level of luminescence was recorded at 0.1 mol% Cr_2O_3, so this concentration was chosen for further measurements. Measurements of the luminescence of glass and glass–ceramic samples were made at an excitation wavelength of 671 nm in the range of the first and second biological windows (Fig. 3). In the sample that was not annealed, a broad band was noticed with the highest intensity at 955 nm, corresponding to the $^4T_2 \rightarrow {}^4A_2$ transition (Cr^{3+}). As a result of annealing the glass, crystallization of the sample and a shift in the luminescence band were observed. The annealed samples were also characterized by broadband emission, occurring in the NIR-II range. The highest intensity was observed at 1250 nm. The observed changes suggest the appearance of Cr^{4+} ions, where the luminescence band corresponds to the Cr^{4+}: $^3T_2 \rightarrow {}^3A_2$ transition [3]. It is also consistent with the crystal field of Cr^{4+} in a tetrahedral environment.

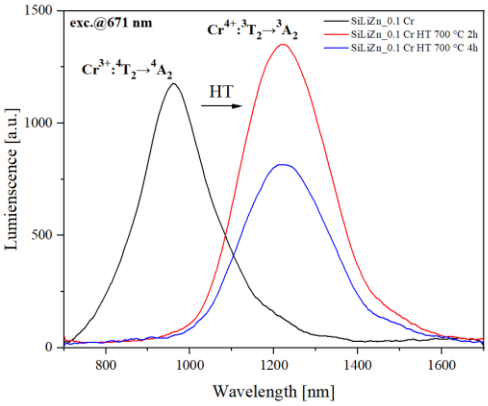


Fig. 3. Luminescence spectra of Cr^3/Cr^{4+} in SiLiZn_0.1 Cr glass and glass-ceramic (λ_{exc} = 671 nm).

Luminescence studies were performed on a sample annealed at 800 °C for 30 minutes and 1 hour (Fig. 4). The analyses were conducted in the range of the 2nd biological window with excitation at a wavelength of 671 nm. A broadband emission from 1000 to 1600 nm was obtained, suggesting the appearance of Cr^{4+} ions with a $^3T_2 \rightarrow {}^3A_2$ transition, which is characteristic of Cr^{4+} ions in tetrahedral coordination. It is noticeable that the emission intensity increases as the annealing time increases. In both cases, the maximum luminescence peak was found at 1250 nm.

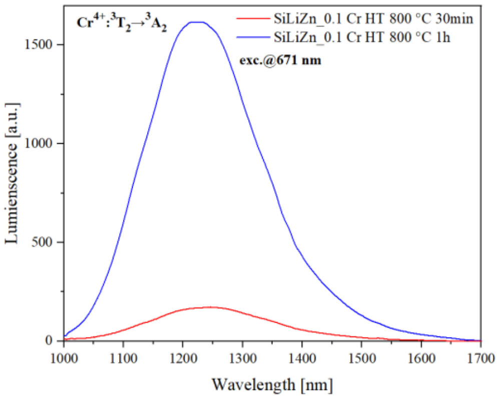


Fig. 4. Luminescence spectra of Cr^{4+} in SiLiZn_0.1 Cr glass – ceramic HT 800 °C 30 min and 1 h (λ_{exc} = 671 nm).

Comparison of the luminescence results of samples annealed at 700 °C for 2 hours and 800 °C for 1 hour, respectively, provided the opportunity to compare the emission shapes depending on the optimization of annealing time and temperature (Fig. 5).

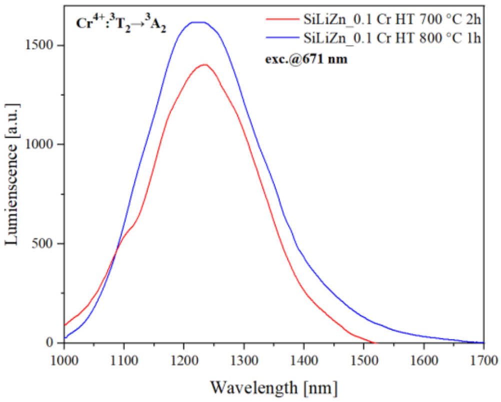


Fig. 5. Luminescence spectra of Cr^{4+} in SiLiZn_0.1 Cr glass – ceramic HT 800 °C 1 h and 700 °C 2 h (λ_{exc} = 671 nm).

In the 2nd biological window range, when excited with a wavelength of 671 nm (power = 100 mW), broadband emission was obtained in each case, with the highest intensity occurring at 1250 nm (Cr^{4+}:$^3T_2 \rightarrow {}^3A_2$). The luminescence spectrum of the sample annealed at 800 °C for 1 h is broader (FWHM = 230 nm) than that of the sample annealed at 700 °C for 2 h (FWHM = 208 nm); in addition, an increase in emission intensity is evident as the temperature increases.

The performed research gave the possibility to shape the phosphor emission spectrum depending on the temperature and annealing time. Phosphors Cr_2O_3 – doped with the possibility of obtaining Cr^{3+}/Cr^{4+} for broadband near–infrared (NIR) emission may find potential applications in NIR phosphors converted LEDs (pc – LED); they are also an alternative to materials doped with rare–earth ions.

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