



Glass-ceramic materials: influence of fluoride nanocrystals on emission properties of lanthanide ions

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Abstract

In this work, the oxyfluoride glass-ceramic materials containing LaF_3 nanocrystals, prepared by using the sol-gel method, were described. The influence of fluoride nanocrystals on the photoluminescence properties of selected lanthanide ions was determined. The experimental results obtained for nano-glass-ceramics were compared to the precursor xerogels. Those Ln^{3+} -doped sol-gel materials with dispersed LaF_3 nanocrystals exhibit several visible emission bands. It was observed that heat-treatment process caused the elongation of the lifetimes of the $^5\text{D}_0$ state from $\tau = 0.22$ ms to $\tau_1 = 0.79$ ms, $\tau_2 = 9.76$ ms (for Eu^{3+} -doped materials) and of the $^4\text{F}_{9/2}$ state from $\tau = 0.027$ ms to $\tau_1 = 0.034$ ms, $\tau_2 = 1.731$ ms (for Dy^{3+} -doped materials). The performed studies clearly revealed that luminescence behaviour also depends on an activator concentration and a distribution of energy levels of lanthanide ions.

1. Introduction

Glass-ceramics (GCs) are considered as an intriguing group of modern materials, combining the unique features of both amorphous and crystalline media. The heat-treatment process carried out at controlled time and temperature conditions results in a formation of very interesting glass-ceramic materials in terms of various properties and applications. Dr S. Donald Stookey pioneered this research field [1] and George Beall progressively continued those studies [2–4]. Since then, many papers have been published on glass-ceramic systems and concentrate on their synthesis and structure [5–7], but also on commercialization fields and various, often multifunctional applications [8, 9]. The diversity of chemical compositions, the development of innovative synthesis methods, and the unique structures obtained at the nano/microscale have contributed to a renewed perspective on the definition of glass-ceramic materials [10].

Transparent glass-ceramic materials doped with lanthanide ions, capable of emitting irradiation in the visible, as well as near- and mid-infrared range, have gained significant interest in photonics, i.e., amplifiers [11],

solid-state lasers [12–14], optical fibres [15], and up-conversion devices [16, 17]. Among GCs doped with Ln^{3+} ions, the materials doped with Eu^{3+} , Dy^{3+} and Pr^{3+} exhibit interesting optical properties.

The transformation from glass to glass-ceramic results in an enhancement of luminescence bands and prolongation of the luminescence decay times of Ln^{3+} ions [18]. Additionally, manipulating plentiful parameters, e.g., temperature and time of heat treatment of as-prepared glasses, their initial composition, or type of crystallized phase, allows for a successful tunability of Re^{3+} resultant emission. Thus, Eu^{3+} -doped GCs can be successfully used as red-emitting components for white light emitted diodes (WLEDs) [19, 20] or in luminescence thermometry [21]. Further, Dy^{3+} -doped GCs are commonly utilized as white light emitters [22–24], but also – similarly as Eu^{3+} -doped GCs – in optical thermometry [25]. Finally, the luminescence features of Pr^{3+} -doped GCs predispose them to use as wide-range colour converters with for blue LEDs [26], as white-light-emitting fibre lasers [27] or in optical-fibre temperature sensing [28], as well as in down-conversion luminescence applications [29].

Among the numerous glass-ceramic materials, the oxyfluoride systems containing lanthanide ions deserve special attention. During initial glass or xerogel heat

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treatment, the fluoride nanocrystals could successfully precipitate inside an amorphous oxide host matrix. Lanthanide ions are extensively used as optically active dopants and are typically present in both amorphous phase and crystalline fraction. As a result, the optical properties change significantly due to the partial alteration of the nearest surrounding around the lanthanide ion. In recent years, a series of oxyfluoride GCs containing LaF_3 nanocrystals (where Ln^{3+} [$\text{Ln} = \text{Ho}$ [30], Yb [31], Er [32–34], Nd [35, 36], Pr/Yb [37] ions partially replace La^{3+} ones) have gained significant importance. Some of such systems were fabricated using the sol-gel method [38–40]. This paper refers to this issue. This research aimed to investigate the effect of LaF_3 nanocrystals dispersed in sol-gel materials on the emission properties of selected lanthanide ions.

The work concerned with performing a comparative analysis of photoluminescent features of silicate sol-gel materials singly-doped with Eu^{3+} , Dy^{3+} , and Pr^{3+} ions, described by us earlier [41–43]. The aim of this work was to compile the conclusions, specifying how the diversity of the energy level structure, as well as differences in the ionic radii between La^{3+} (from parent LaF_3 crystal phase) and individual active dopants determine the photoluminescent properties of the prepared sol-gel materials.

2. Experimental

The sol-gel preparation method was used to synthesize the xerogels doped with Eu^{3+} , Dy^{3+} , and Pr^{3+} ions. To obtain the nano-glass-ceramic materials, the as-prepared xerogels were annealed at selected time and temperature conditions; the details were presented elsewhere [41, 42]. The solutions of La(III) and Eu(III) , Dy(III) , and Pr(III) acetates dissolved in water and trifluoroacetic acid (TFA) were added dropwise to the pre-hydrolysis mixtures containing tetraethoxysilane (TEOS), ethanol, deionized water, and acetic acid in molar ratio equalling 1:4:10:0.5. The prepared sols were dried for several weeks, then the obtained xerogels were further transformed into glass-ceramic materials via the controlled heat treatment at appropriate temperature and time conditions.

The structural characterisation of the fabricated sol-gel materials was provided by X-ray diffraction (XRD) analysis using an X'Pert Pro diffractometer supplied by PANalytical with $\text{CuK}\alpha$ radiation with $\lambda = 1.54056 \text{ \AA}$ wavelength. The optical properties of the prepared materials were investigated using a Photon Technology International (PTI) Quanta-Master 40 (QM40) UV/VIS Steady State spectrofluorometer equipped with a tunable pulsed optical parametric oscillator (OPO) pumped by the third harmonic of a Nd:YAG laser. The laser system was supplied with a double 200 mm monochromator, a xenon lamp, as well as a multimode UV/VIS PMT detector (R928, PTI Model 914), and a Hamamatsu H10330B-75 detector.

3. Results and discussion

3.1. Structural studies

XRD studies showed that the heat treatment of the initial xerogels leads to the formation of nano-GCs. The XRD pattern confirmed the crystallization of LaF_3

phase in a $\text{P6}_3\text{cm}$ space group according to ICDD card no. 00-008-0461 [44, 45]. The average size of the precipitated fluoride nanocrystals fluctuates from 8.1 nm [41] to 13.5 nm [43]. Figure 1 presents the diffraction patterns of the sol-gel systems before and after the controlled heat-treatment process. The results from the XRD analysis were confirmed by the transmission electron microscopy (TEM) [41–43].

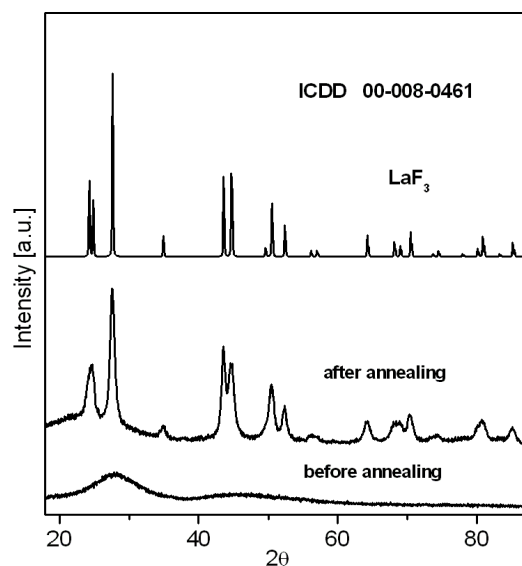


Fig. 1. XRD patterns of sol-gel materials before and after the annealing process.

3.2. Luminescent studies

Figure 2 illustrates the luminescence spectra of europium ions in xerogels and nano-glass-ceramic-materials. The series of registered luminescence bands assigned to the electronic transitions from the $^5\text{D}_0$ state to the lower-lying $^7\text{F}_J$ levels ($J=0-4$) of trivalent Eu^{3+} ions. Notably, two luminescence bands are located in the orange and red spectral ranges, respectively. Those emission bands correspond to the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ and the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transitions of Eu^{3+} ions and are also shown in the energy level diagram (Fig. 3).

The intensity ratio of the photoluminescence bands changes due to the heat-treatment process. As a result of annealing the amorphous xerogels, a decrease in a $^5\text{D}_0 \rightarrow ^7\text{F}_2$ electric-dipole band intensity was observed; subsequently, the intensity of the band, associated with a magnetic-dipole $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition significantly increased. The observed changes in the emission spectra profile clearly indicate an increase in local symmetry around Eu^{3+} ions. It also suggests a significant contribution of ionic bonds between the activator ions (Eu^{3+}) and their nearest surrounding. These differences in luminescence behavior denoted before and after controlled heat treatment of initial xerogels are strictly related to the successful migration of europium ions (with ionic radius 1.120 Å) into LaF_3 nanocrystals (ionic radius of La^{3+} : 1.216 Å) [46]. Consequently, a decrease in the luminescence intensity R/O-ratio, according to the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ and $^5\text{D}_0 \rightarrow ^7\text{F}_1$ bands, was observed [3]. Considering the results, the fabricated materials could be used as red or reddish-orange light emitters for optoelectronic applications [20, 41].

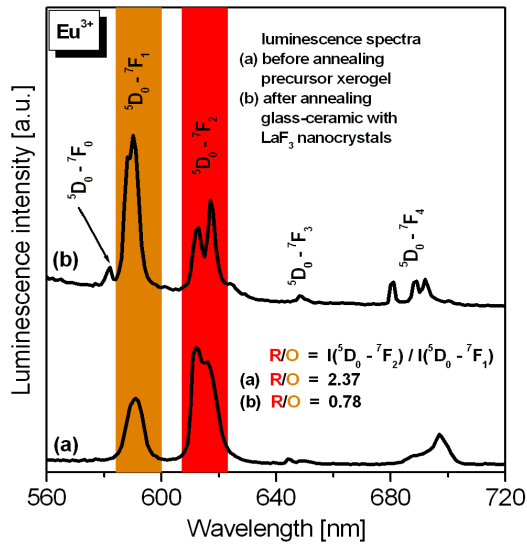


Fig. 2. Photoluminescence spectra of Eu^{3+} ions in xerogels and nano-GCs.

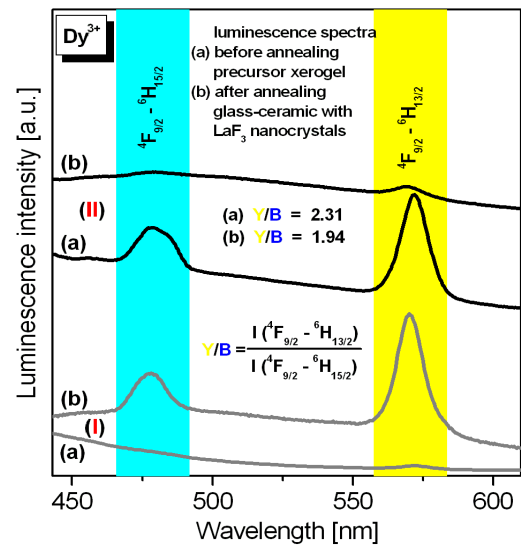


Fig. 4. Photoluminescence spectra of Dy^{3+} ions in xerogels and nano-GCs.

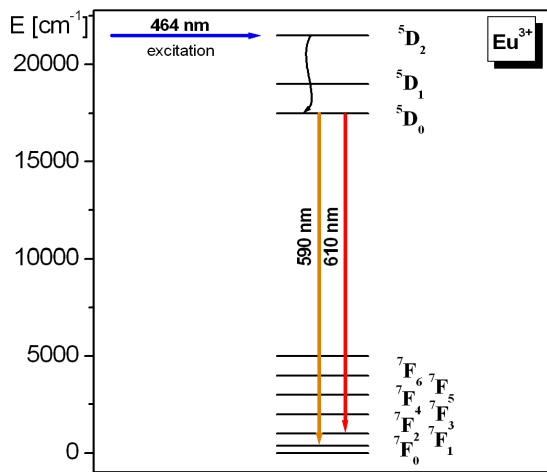


Fig. 3. The energy level scheme for Eu^{3+} ions. Orange and red arrows illustrated the major emissions.

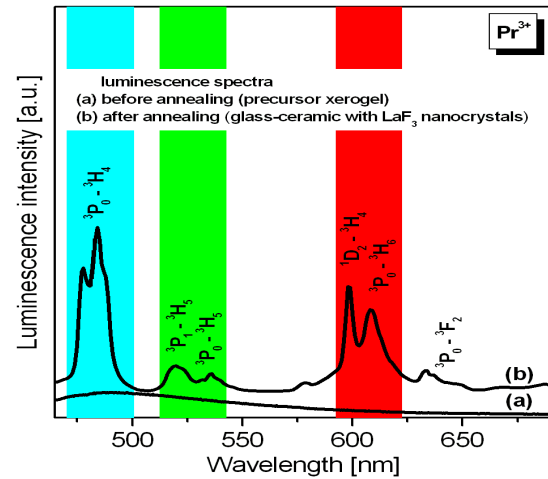


Fig. 5. The energy level scheme for Dy^{3+} ions. Blue and yellow arrows illustrated the major emissions.

Figure 4 presents the emission spectra of trivalent dysprosium ions in fabricated sol-gel materials before (xerogel) and after heat treatment (nano-glass-ceramic). The $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{15/2}$ and $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{13/2}$ transitions of Dy^{3+} ions are located within blue and yellow light spectral ranges, respectively. Those transitions are schematically presented in the energy level scheme (Fig. 5).

The emission spectra were presented for two selected systems, (I) and (II), which differ in the $\text{La}^{3+}:\text{Dy}^{3+}$ ratio, equalling 0.988:0.012 and 0.7:0.3. The results clearly showed that the luminescence properties of Dy^{3+} ions critically depend on the activator concentration [42]. For low Dy^{3+} concentrations (determined by molar ratio $\text{La}^{3+}:\text{Dy}^{3+}=0.988:0.012$), the heat-treatment process influenced an increase in the luminescence intensities. Concerning a higher activator concentration (determined by molar ratio $\text{La}^{3+}:\text{Dy}^{3+}=0.7:0.3$), the conversely luminescence behavior is observed, and the emission intensity of Dy^{3+} ions is higher for xerogels than for glass-ceramic materials. This phenomenon could be explained by the significant reduction of the inter-ionic distances (and the simultaneous unfavorable increase in interaction)

between neighboring $\text{Dy}^{3+}:\text{Dy}^{3+}$ ions inside LaF_3 nanocrystals, leading to the concentration quenching of the luminescence. Similarly as for Eu^{3+} ions, a decrease in the calculated Y/B-ratio values (associated with the $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{13/2}$ and $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{15/2}$ band intensities of Dy^{3+} ions) is noted. The values of both R/O (Eu^{3+}) and Y/B (Dy^{3+}) ratios are lower for nano-GCs compared to those denoted for the initial xerogels and other inorganic oxide glasses synthesized by the conventional melt-quenching method [47, 48], indicating incorporation of Ln^{3+} ions inside the LaF_3 nanocrystalline phase. However, it should be clarified that the denoted decrease in Y/B ratio is not as noticeable as for R/O ratio (Eu^{3+}), suggesting less efficient migration of Dy^{3+} into LaF_3 nanocrystals. Such a result could be explained by greater differences in ionic radii in Dy^{3+} (1.083 Å) - La^{3+} (1.216 Å) pair than in Eu^{3+} (1.120 Å) - La^{3+} (1.216 Å) one [46]. The results suggest that the obtained GCs could find application as visible light emitters [22, 42].

Figure 6 presents the photoluminescence spectra recorded for the sol-gel materials doped with Pr^{3+} ions. For xerogel, none of the characteristic luminescence bands

were observed. The probable reason for this observation is correlated with too small energy gaps between the appropriate states of Pr^{3+} ions and the presence of high-vibrational energy hydroxyl groups. The vibrations of OH groups overlap with the gaps between Pr^{3+} states, which is responsible for effectively quenching the photoluminescence. It should be noted that for xerogel, only a broad band was registered. Based on the literature, this broad band could be originated from defects inside the sol-gel host [49]. The effect of photon recombination in the silicate sol-gel host could be reduced or disappear after the thermal treatment. Conversely, the spectrum recorded for the nano-glass-ceramic material revealed the well-visible emission bands within the blue, green, and red ranges, assigned to the characteristic transitions of Pr^{3+} ions, i.e., $^3\text{P}_0 \rightarrow ^3\text{H}_4$, $^3\text{P}_1 \rightarrow ^3\text{H}_5$, $^3\text{P}_0 \rightarrow ^3\text{H}_5$, $^3\text{P}_0 \rightarrow ^3\text{H}_6$, $^1\text{D}_2 \rightarrow ^3\text{H}_4$, and $^3\text{P}_0 \rightarrow ^3\text{F}_2$ (Fig. 7). Since the intensities of emission bands from the $^3\text{P}_{0,1}$ levels are enhanced, it could be expected that Pr^{3+} ions are well-incorporated inside precipitated LaF_3 nanocrystals. Indeed, there are differences in ionic radii between Pr^{3+} (1.179 Å) and La^{3+} (1.216 Å), compared to other Eu^{3+} - La^{3+} and Dy^{3+} - La^{3+} ionic pairs [46]. It is worth noting that in the case of the studied Pr^{3+} -doped GCs, the combination of

blue, green, and reddish-orange luminescence is appropriate for white light generation, described by chromaticity coordinates (0.400|0.337) and correlated colour temperature equal to 3124 K [43].

Furthermore, the decay analysis from the appropriate excited states of studied Ln^{3+} ions was also performed. The lifetimes of the $^5\text{D}_0$ (Eu^{3+}) and the $^4\text{F}_{9/2}$ (Dy^{3+}) levels were determined both for xerogels and glass-ceramic materials after controlled heat-treatment process. The resultant values were collected in Table 1.

Table 1.

The lifetimes of appropriate excited states of Ln^{3+} ions estimated for xerogels and nano-GCs.

Ln^{3+}	Excited state	Luminescence lifetimes (ms)	
Eu^{3+}	$^5\text{D}_0$	xerogels	0.22
		nano-GCs	0.79 9.76
Dy^{3+}	$^4\text{F}_{9/2}$	xerogels	0.027
		nano-GCs	0.034 1.731

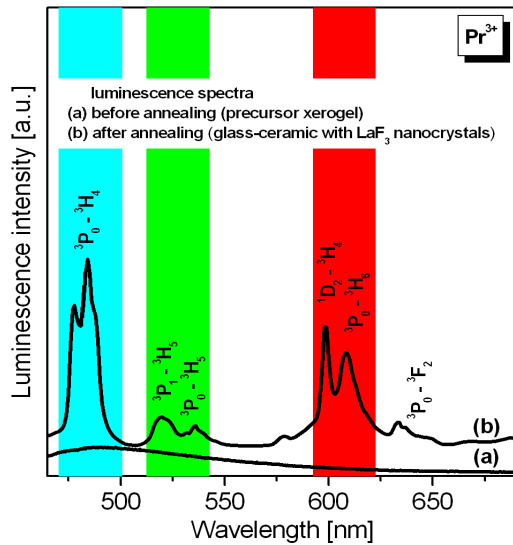


Fig. 6. Photoluminescence spectra of Pr^{3+} ions in xerogels and GCs.

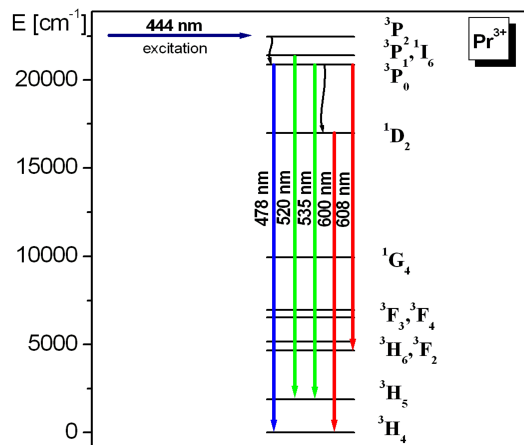


Fig. 7. The energy level scheme for Pr^{3+} ions. The major emissions were illustrated by blue, green, and red arrows.

Conversely to the initial xerogels, the photoluminescence decay curves recorded for nano-GCs exhibited a biexponential character. The curve with shorter and longer decay components is associated with the distribution of Eu^{3+} and Dy^{3+} ions between the amorphous sol-gel host and the nanocrystalline fluoride phase. The obtained results clearly showed that the overall emission and luminescence lifetimes are significantly enhanced for nano-glass-ceramic systems containing LaF_3 nanocrystals compared with initial fully amorphous xerogels.

4. Conclusions

This paper presents the selected research results for xerogels and nano-glass-ceramic materials fabricated by the sol-gel technology. The emission characterisation was conducted for samples doped with selected Ln^{3+} ions, i.e., Eu^{3+} , Dy^{3+} , and Pr^{3+} ions.

The results revealed that for prepared nano-glass-ceramic materials, the luminescence intensities are noticeably enhanced and the decay times are prolonged ($^5\text{D}_0$ (Eu^{3+}): $\tau_1 = 0.79$ ms, $\tau_2 = 9.76$ ms; $^4\text{F}_{9/2}$ (Dy^{3+}): $\tau_1 = 0.034$ ms, $\tau_2 = 1.731$ ms) compared to the initial xerogels ($^5\text{D}_0$ (Eu^{3+}): $\tau = 0.22$ ms; $^4\text{F}_{9/2}$ (Dy^{3+}): $\tau = 0.027$ ms). This phenomenon could be explained by successfully entering trivalent Ln^{3+} ions inside LaF_3 nanocrystal lattice, formed during a heat treatment of xerogels. A decrease in the values of the R/O- (xerogel: 2.37, GC: 0.78) and Y/B-ratio (xerogel: 2.31, GC: 1.94) also indicates the migration of the dopant ions into the crystalline phase. The studies demonstrated the impact of LaF_3 nanocrystals dispersed in a sol-gel host on the photoluminescence properties of Eu^{3+} , Dy^{3+} , and Pr^{3+} ions. The luminescence behaviour also depends on the activator concentration, similarity in ionic radius in individual Ln^{3+} - La^{3+} pair, and individual distribution of the energy levels.

Nano-glass-ceramic materials obtained by the sol-gel method are promising systems able to generate visible light and may find applications in photonics, like optical hosts

for multicolour displays or colour screens. Indeed, Eu^{3+} -doped GCs can generate red or reddish-orange luminescence, while Dy^{3+} -doped samples produce efficiently yellow light. Importantly, in the case of Pr^{3+} -doped GCs, the intensities of blue, green, and reddish-orange emissions are relevant for warm-white light generation.

Authors' statement

Research concept and design, W.A.P.; collection and/or assembly of data, J.Ś. and N.P.; data analysis and interpretation, J.Ś. and N.P.; writing the article, J.Ś., N.P., and W.A.P.; critical revision of the article, W.A.P., J.P., and N.P.; final approval of article, W.A.P. and J.P.

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