


Cite this: *Nanoscale*, 2024, **16**, 4249

White light and near-infrared emissions of Pr³⁺ ions in SiO₂-LaF₃ sol–gel nano-glass-ceramics

Natalia Pawlik,^a Tomasz Goryczka,^b Maciej Zubko,^{b,c} Joanna Śmiarowska^a and Wojciech A. Pisarski^a

In this work, we report the results of our investigations on the structural and luminescence properties of SiO₂-LaF₃:Pr³⁺ nano-glass-ceramics synthesized using the sol–gel method. Based on XRD, microscopic (TEM), and ATR-IR measurements, the crystallization of LaF₃ nanocrystals favorably occupied by Pr³⁺ ions and overall transformations within the silicate sol–gel hosts dependent on heat-treatment conditions of the as-prepared amorphous xerogels were characterized. The fabricated oxyfluoride nano-glass-ceramics revealed the emissions within the greenish-blue (³P_{0,1} → ³H₄, ³P_{0,1} → ³H₅), reddish-orange (³P_{0,1} → ³H₆, ¹D₂ → ³H₄, ³P₀ → ³F_{2,3}), and NIR spectral scopes (¹D₂ → ³F₄, ¹G₄, ¹G₄ → ³H₅, ³F_{3,4} → ³H₄). Based on the luminescence spectra in the VIS range, the CIE chromaticity coordinates, correlated color temperatures (CCT), and color purities (CP) were calculated. The obtained results clearly indicate that the prepared Pr³⁺-doped sol–gel nano-glass-ceramics exhibit warm or neutral white light emissions with CCT values in the range from 2567 K to 3962 K. The lowest CP value was estimated at 12.8%, indicating that the fabricated samples are able to emit bright white light. Additionally, the NIR emissions cover E, S, C, and L bands, which are important for devices applicable in telecommunication technologies. For further characterization, the τ(³P₀) and τ(¹D₂) decay times were estimated. It was established that the emissions from the ³P₀ and the ¹D₂ excited states of Pr³⁺ ions, as well as the participation of cross-relaxation (CR) processes, are dependent on the size of crystallized LaF₃ phase, distribution of optically active Pr³⁺ ions between amorphous and crystalline phase (determining the Pr³⁺–Pr³⁺ inter-ionic distances), and relative content of OH groups in the prepared sol–gel hosts.

Received 11th August 2023,
Accepted 22nd January 2024

DOI: 10.1039/d3nr04030e

rsc.li/nanoscale

Introduction

Trivalent praseodymium ion is one of the most promising rare-earth dopants, whose energy level diagrams and abundant metastable multiplets (*i.e.*, ³P_{0–2}, ¹D₂, and ¹G₄) enable the generation of luminescence across the broad spectral ranges from blue, green, and reddish-orange light up to near-infrared irradiation.^{1,2} Thus, such a tremendous spectrum of emitted wavelengths opens vast application possibilities for optical materials containing Pr³⁺ ions. For instance, the emission within the red or reddish-orange light area predisposes Pr³⁺-doped materials as essential parts of optical devices with great utility in LED technologies^{3–7} or as gain media for laser output at ~645 nm.^{8–10} Additionally, the modifications in the composition of the host materials as well as in Pr³⁺ concentration

allow for obtaining the appropriate combinations of blue, green, and reddish-orange luminescence, which could result in the generation of white-light emission, as described for LaAlO₃:Pr³⁺ and YF₃:Pr³⁺ nanocrystals or K₃La(PO₄)₂:Pr³⁺ phosphors.^{11,12} The infrared luminescence of Pr³⁺-doped materials at ~1.0 μm (¹D₂ → ³F_{3,4} transitions), ~1.35 μm (¹G₄ → ³H₅ transition), and ~1.6 μm (³F_{3,4} → ³H₄ transition), which covers NIR-II and NIR-III biological windows, make them interesting host matrices in the field of *in vivo* bioimaging.^{13–15} The above-mentioned infrared emissions cover E, S, C, and L bands belonging to the fifth optical telecommunication window; thus, Pr³⁺-doped materials are also considered as promising candidates for waveguide amplification.^{16,17} Additionally, since the de-excitation channels of the ³P₀ and the ¹D₂ excited states, such as phonon-assisted cross-relaxation (CR) and multiphonon relaxation (MPR), reveal varied temperature-dependent behavior, Pr³⁺-doped materials could also be used as optical thermometers, as was described for LiYO₂:Pr³⁺ (additionally adjusted by the phase transformation between α and β polymorphs) or La₂MgTiO₆:Pr³⁺.^{18,19} Another pathway relates to the involvement of excitations by ground-state absorption (GSA, λ_{ex} = 444 nm) and excited-state absorp-

^aUniversity of Silesia, Institute of Chemistry, Szkolna 9 Street, 40-007 Katowice, Poland. E-mail: natalia.pawlik@us.edu.pl

^bUniversity of Silesia, Institute of Materials Engineering, 75. Pułku Piechoty 1A Street, 41-500 Chorzów, Poland

^cUniversity of Hradec Králové, Department of Physics, Rokytanského 62, 50003 Hradec Králové, Czech Republic


tion (ESA, $\lambda_{\text{ex}} = 525 \text{ nm}$) mechanisms on the $^3\text{P}_0 \rightarrow ^3\text{H}_4$ emission, as was performed for $\text{LaF}_3:\text{Pr}^{3+}$ crystals in the temperature range from 273.15 K to 573.15 K.²⁰ Finally, Pr^{3+} -doped luminescent thermometers could also be based on the intensity ratio of the $^3\text{P}_1 \rightarrow ^3\text{H}_5$ and $^3\text{P}_0 \rightarrow ^3\text{H}_5$ transitions. Indeed, the $^3\text{P}_1$ state is thermally populated following the $^3\text{P}_0$ excitation and governed by the Boltzmann statistics, as was described in the literature for $\text{YF}_3:\text{Pr}^{3+}$,²¹ $\text{LaF}_3:\text{Pr}^{3+}$,^{22,23} and $\text{LiYF}_4:\text{Pr}^{3+}$.²³ Their usage could also extend the broad application area of Pr^{3+} -doped materials as scintillators^{24,25} or dye-sensitized solar cells (DSSC).²⁶ Thus, the presented vast fields of practical applications of Pr^{3+} -doped optical materials make them highly needed for the development of modern optoelectronics.

Among the various classes of optical materials doped with Pr^{3+} ions (e.g., glasses^{3–5,27,28} or crystals^{21–23}), many research papers are devoted to oxyfluoride glass-ceramics (OxGCs). Indeed, oxyfluoride GCs are very attractive host materials because Pr^{3+} ions could be effectively insulated from the high-energetically oscillations of the glassy framework by their incorporation inside the low-phonon energy fluoride crystals; nevertheless, the glassy framework provides good chemical, mechanical, and thermal stability of the OxGCs. Most of the Pr^{3+} -doped OxGC materials characterized and described in the current literature are focused on the preparation by high-temperature melt-quenching method, followed by the annealing of parent glasses at controlled and specified time and temperature conditions. Among them, OxGCs containing plentiful fluoride phases classified to AF_x type (CaF_2 ,²⁹ SrF_2 ,^{30,31} BaF_2 ,^{32,33} LaF_3 ,^{2,34–37} YF_3 ,³⁸ or PbF_2 ³⁹) and AMF_x type (NaYF_4 ,¹ NaLaF_4 ,²⁵ BaYF_5 ,⁴⁰ $\text{LiGdF}_4/\text{GdF}_3$,⁴¹ NaGdF_4 ,⁴² KYF_4 ⁴³) have been reported. Interestingly, the spectroscopic behavior of Pr^{3+} ions could be successfully modulated by changing their local environment, i.e., glassy or crystalline. In this matter, C. Koepke *et al.*³² reported that Pr^{3+} photoluminescence in BaF_2 -based OxGCs is strictly correlated to their residing in oxide higher-field (O–Pr–O) or fluorine lower-field (F–Pr–F and/or O–Pr–F) sites. Further, for $\text{KYF}_4:\text{Pr}^{3+}$ -based glass-ceramics, it was proven that the modification in a local field around Pr^{3+} from fully amorphous to crystalline (for the latter with parallel control of the growth of fluoride crystals from 5 nm to 30 nm) resulted in emission color tuning from red *via* warm white, finally to cold white.⁴³ The tunability of Pr^{3+} emission could also be triggered by modifications in their concentration, as presented by H. Lee *et al.*,² who reported that $\text{LaF}_3:\text{Pr}^{3+}$ -based OxGC materials could be used as color converters with a wide color gamut for blue LEDs emitting 450 nm wavelength, dependent on Pr^{3+} concentration (from 1 mol% to 5 mol%). In addition, the elongation in the heat-treatment time (from 1 hour to 10 hours) and elevation of temperature (from 700 °C to 800 °C) also allowed for successfully shifting the chromaticity coordinates of emitted light color from blue regions to white light. Hence, these peculiarities make the Pr^{3+} -doped OxGC materials very attractive both from cognitive and utilitarian points of view.

Despite many undoubted advantages, there is a substantial drawback in the fabrication of OxGCs *via* the melt-quenching technique, which is related to the significant losses of fluor-

ides during processing at high temperatures. Hence, such conditions could contribute to noticeable inhibition in the formation of fluoride crystal fraction, consequently resulting in a significant part of rare earth ions remaining inside the amorphous glassy host.⁴⁴ This limitation, according to the risk of fluorides evaporation, could be overcome by the involvement of sol-gel synthesis as an alternative preparation route because the individual chemical reactions (i.e., hydrolysis of the metal/semi-metal alkoxide and (poly)condensation) are usually performed at relatively low temperatures. However, despite this unquestionable ascendancy, due to the small energy gap of Pr^{3+} between the $^3\text{P}_0$ and the lower-lying $^1\text{D}_2$ states ($\sim 4080 \text{ cm}^{-1}$),²⁷ the luminescence of Pr^{3+} —especially within the NIR scope—is very sensitive to high-vibrational OH groups, which are naturally created during aqueous sol-gel processing.⁴⁵ Due to this limitation, studies on Pr^{3+} luminescence in oxyfluoride sol-gel materials are scarce and, as far as we know, there is only one paper published by the research team of J. J. Velázquez⁴⁶ dedicated to studies of Pr^{3+} spectroscopy in OxGCs with 95 SiO_2 -5 LaF_3 :0.1 mol% Pr^{3+} composition. The paper describes the photoluminescence of singly- (Pr^{3+}) and doubly-doped $(\text{Pr}^{3+}/\text{Yb}^{3+})$ systems within the visible light range. Additionally, it should also be noted that the luminescence of Pr^{3+} ions in NIR scope, according to OxGC materials, has not been explored in the literature, as far as we know. Therefore, due to the reasons mentioned above, an investigation of Pr^{3+} luminescence within both visible and NIR ranges in oxyfluoride sol-gel glass-ceramic systems seems to be highly meaningful and necessary.

The main concept of this research reported here was to prepare the series of Pr^{3+} -doped oxyfluoride glass-ceramics containing LaF_3 nanocrystals and investigate the impact of variable $\text{La}^{3+}:\text{Pr}^{3+}$ molar ratios as well as heat-treatment conditions (500 °C, 700 °C, and 900 °C) on the efficiency of host densification by the removal of OH groups (responsible for quenching luminescence of Pr^{3+}) and efficiency of Pr^{3+} incorporation inside the fluoride crystal lattice. LaF_3 was chosen due to the high similarity of La^{3+} and Pr^{3+} ionic radii, ensuring the efficient incorporation of Pr^{3+} inside the LaF_3 crystal phase, as was stated in the literature.^{2,36} The ATR-IR and XRD techniques as well as TEM microscopy were used to determine the structural changes within the silicate sol-gel host and the crystallization of the $\text{LaF}_3:\text{Pr}^{3+}$ phase. The luminescence properties of the synthesized oxyfluoride glass-ceramic materials were characterized based on the excitation and emission spectra, along with the decay analysis from the $^3\text{P}_0$ and $^1\text{D}_2$ excited states. The results showed that the fabricated series of sol-gel Pr^{3+} -doped nano-glass-ceramics could be potentially used as white light emitters or elements of amplifiers operating at E, S, C, and L bands belonging to the fifth optical telecommunication window.

Experimental

The series of xerogels singly-doped with Pr^{3+} ions were prepared using the sol-gel synthesis described elsewhere.⁴⁷ All



reagents were taken from Sigma Aldrich Chemical Company. The subsequent chemical reactions, which undergo during the sol-gel evolution, *e.g.*, hydrolysis, condensation, and polycondensation of precursor (tetraethoxysilane, TEOS), were carried out in a solution of ethyl alcohol, deionized water, and acetic acid with molar ratio equals to 1:4:10:0.5. Parallelly, the solutions of $\text{La}(\text{CH}_3\text{COO})_3$ and $\text{Pr}(\text{CH}_3\text{COO})_3$ in deionized water and trifluoroacetic acid (TFA) were added dropwise to TEOS-based mixtures. The molar ratio of $\text{TFA}:\text{La}^{3+}:\text{Pr}^{3+}$ was set to $5:(1-x):x$, where $x = 0.003, 0.006, 0.012, 0.03, 0.06$, and 0.12 . The as-prepared sols were dried at 35°C for several weeks to form green-colored rigid xerogels. Afterward, the nano-glass-ceramic materials were obtained during controlled heat-treatment at selected temperatures (500°C , 700°C , and 900°C). The prepared samples were denoted as $\text{GC1Pr}_x\text{-GC6Pr}_x$, where x refers to the temperature conditions of performed heat-treatment and 1–6 expresses the variable $\text{La}^{3+}:\text{Pr}^{3+}$ molar ratios in the following samples from the series.

The fabricated nano-glass-ceramics were characterized by X-ray diffraction analysis using an X'Pert Pro diffractometer supplied by PANalytical with $\text{CuK}\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$). The transmission electron microscopy (TEM) observations were performed using a JEOL high resolution (HR-TEM) JEM 3010 microscope working at 300 kV accelerating voltage and equipped with Gatan $2\text{k} \times 2\text{k}$ OriusTM 833SC200D CCD camera and the Elite T Energy Dispersive Spectroscopy (EDS) silicon drift detector (SDD) from AMETEK EDAX. The sol-gel samples were suspended in isopropanol, and after ultrasonication for 10 minutes in an ultrasonic cleaner, the resulting materials were deposited on a Cu grid coated with amorphous carbon film standardized for TEM observations. Selected area electron diffraction (SAED) patterns were characterized using the ElDyf software (version 2.1). The structural characterization also included the infrared measurements; the experiment was performed with the use of a Nicolet iS50 ATR spectrometer, and the spectra were collected in attenuated total reflectance (ATR) configuration within the $4000\text{--}400 \text{ cm}^{-1}$ as well as $500\text{--}300 \text{ cm}^{-1}$ frequency range (64 scans, 0.1 cm^{-1} resolution). The ATR-IR spectra were decomposed using Fityk software (0.9.8 software, open-source (GPL2+)) based on the analysis of second derivatives, preceded by the appropriate smoothing of the spectra (using the Savitsky-Golay algorithm). The shape of the bands was described by the sum of the Gaussian and Lorentzian functions, and the coefficient of determination was 0.99. The luminescence measurements were performed on a Photon Technology International (PTI) Quanta-Master 40 (QM40) UV/VIS Steady State Spectrofluorometer supplied with a tunable pulsed optical parametric oscillator (OPO) pumped by the third harmonic of a Nd:YAG laser. The laser system was coupled with a xenon lamp, a double 200 mm monochromator, a multimode UV/VIS PMT detector (R928, PTI Model 914), and a Hamamatsu detector (H10330B-75). The excitation and emission spectra were recorded with a resolution of 0.5 nm . The luminescence decay curves were recorded by a PTI ASOC-10 (USB-2500) oscilloscope with an accuracy of $\pm 0.1 \mu\text{s}$.

All structural and optical measurements were carried out at room temperature.

Results and discussion

ATR-IR characterization

The fabricated sol-gel materials, as porous species, could evolve to more condensed stages and create a more dense and continuous silicate network during the gradual elevation of heat-treatment temperature. These peculiarities of sol-gel processing, according to differential structure and texture of prepared materials, were verified based on ATR-IR measurements, whose results were presented in Fig. 1 and 2. To determine the impact of variable temperature conditions (500°C , 700°C , and 900°C) on a dynamically formed sol-gel network, the spectra were recorded within the two frequency intervals: from 4000 cm^{-1} to 400 cm^{-1} (to observe the changes during the



Fig. 1 ATR-IR spectra recorded for individual sol-gel materials heat-treated at 500°C (a), 700°C (b), and 900°C (c). The deconvolution of spectra for representative GC2Pr_{500} , GC2Pr_{700} , and GC2Pr_{900} nano-glass-ceramics in the range from 1400 cm^{-1} to 400 cm^{-1} region is also presented in (d)–(f), respectively.





Fig. 2 The comparison of the ATR-IR spectra within the frequency range from 500 cm^{-1} to 300 cm^{-1} for representative GC2Pr₅₀₀, GC2Pr₇₀₀, and GC2Pr₉₀₀ samples (the spectra of xerogel, as well as reference LaF₃ and PrF₃ are also given) (a). The juxtaposition of the ATR-IR spectra and localization of the La–F band for individual samples from each series: 500 °C (b), 700 °C (c), and 900 °C (d) are also presented.

polycondensation of the silicate skeleton) and from 500 cm^{-1} to 300 cm^{-1} (to visualize the structural changes according to the crystallization of the LaF₃ phase and incorporation of Pr³⁺ inside the fluoride crystallites).

The comparison of the IR-ATR spectra, recorded in the frequency region from 4000 cm^{-1} to 400 cm^{-1} for all the samples from the individual series (GCPr₅₀₀, GCPr₇₀₀, and GCPr₉₀₀), is presented in Fig. 1a–c. It should be stated that the shape of the recorded IR spectra for samples from the individual series is practically indistinguishable. These similarities in the spectral profiles clearly prove the formation of equivalent structures of silicate sol-gel host in each series, indicating their high reproducibility. Among the recorded IR signals, a weak and broad band at $\sim 3350 \text{ cm}^{-1}$, assigned to vibrations of unreacted Si–OH groups, was identified. It is worth noticing that the band's intensities of the band are relatively low for all the prepared series of nano-glass-ceramics, indicating the residual amount of OH groups. Further, it was verified that the band slowly disappeared with the simultaneous elevation of heat-treatment temperature, as was shown in the following Fig. 1a–c, which continuously underwent polycondensation reaction within the silicate network. These speculations were also evaluated by the analysis of the spectral profile in the frequency range from 850 cm^{-1} to 1300 cm^{-1} . Generally, a gradual disappearance of the shoulder at $\sim 955 \text{ cm}^{-1}$ and a shift of the infrared signal from $\sim 1045 \text{ cm}^{-1}$ (500 °C and 700 °C) to $\sim 1065 \text{ cm}^{-1}$ (900 °C) could be observed. Therefore,

to interpret the differences in the spectral profiles, deconvolution was implemented. It revealed the existence of the following oscillations inside the silicate sol-gel hosts: $\sim 440 \text{ cm}^{-1}$ (Si–O–Si siloxane bridges), $\sim 560 \text{ cm}^{-1}$ (4-fold siloxane rings), $\sim 620 \text{ cm}^{-1}$ (6-fold siloxane rings), $\sim 730 \text{ cm}^{-1}$ (Si–O bonds), $\sim 800 \text{ cm}^{-1}$ (TO₂ mode of Si–O–Si), $\sim 835 \text{ cm}^{-1}$ (2-fold siloxane rings), $\sim 910 \text{ cm}^{-1}$ (Q¹ units, [Si(O_{1/2})₃]^{3–}), $\sim 970 \text{ cm}^{-1}$ (Q² units, [Si(O_{1/2})₂O₂]^{2–}), $\sim 1030 \text{ cm}^{-1}$ (Q³ units, [Si(O_{1/2})₃O][–]), $\sim 1075 \text{ cm}^{-1}$ (TO₃ mode of Si–O–Si), $\sim 1160 \text{ cm}^{-1}$ (Q⁴ units, [Si(O_{1/2})₄]), and $\sim 1220 \text{ cm}^{-1}$ (TO₄ and/or LO₃ modes of Si–O–Si).⁴⁸ “O_{1/2}” and “O” denote SiO₄ tetrahedral units: the first of them corresponds to each oxygen atom involved in the formation of the Si–O–Si bridge, but the second to each non-bridging oxygen atom. It could be observed that the mutual intensities of individual components change while the annealing temperature increases. Particularly interesting is the change in the intensity of the deconvoluted component assigned to the oscillations inside Q³ units ($\sim 1045 \text{ cm}^{-1}$), which enhanced with elevation of treatment temperature from 500 °C to 700 °C and further reduced with the continuous elevation of temperature from 700 °C to 900 °C. As a result, the component located near $\sim 1075 \text{ cm}^{-1}$ (TO₃ mode of Si–O–Si bridges) determines the subtle but progressive overall position of the entire infrared signal toward higher frequencies, from $\sim 1045 \text{ cm}^{-1}$ (500 °C and 700 °C) up to $\sim 1065 \text{ cm}^{-1}$ (900 °C). Additionally, it is quite good visible that the participation of the component near $\sim 1155 \text{ cm}^{-1}$ (Q⁴ units) gradually increases for nano-glass-ceramics fabricated at higher temperatures. Therefore, it could be concluded that increasing the annealing temperature of silicate xerogels favors the more efficient conversion of SiO₄ units into Q³ and Q⁴ species without non-bridging oxygen atoms, proving the forming of condensed silicate sol-gel hosts. The conclusions mentioned above about the progressive polycondensation of sol-gel hosts could be additionally confirmed by a gradual shift of the signal assigned to the Si–O–Si bending vibration from 440 cm^{-1} (500 °C), through 444 cm^{-1} (700 °C), up to 451 cm^{-1} (900 °C). Similar results for the analogous SiO₂–LaF₃ sol-gel system were elaborated in the work by G. Gorni *et al.*⁴⁹ Indeed, during the studied sol-gel evolution, the maximum of indicated signal noticeably shifted from 425 cm^{-1} (for xerogel) to higher wavenumbers of about 450 cm^{-1} for glass-ceramics prepared at 550 °C at various time intervals ranging from 1 minute to 80 hours. The maxima were compared with the location of the signal for SiO₂ glass ($\sim 460 \text{ cm}^{-1}$). As was also stated in another paper,⁵⁰ the observed shift is characteristic of silicate xerogels as they evolve toward more densified states with decreasing porosity. Moreover, according to the texture of sol-gel hosts, the shift of the signal assigned to the TO₃ mode of Si–O–Si siloxane bridges with increasing treatment temperature is strictly attributed to structural modifications related to the change in the residual porosity of the sol-gel framework.⁴⁸ Indeed, the pores induce deformations of Si–O–Si bridges that give rise to higher bridging angles and longer Si–O silanol bonds compared to bulk SiO₂ glasses. Therefore, the changes in the porosity alter the appropriate modifications in Si–O–Si deformations; thus,



shifts in the infrared signal are expected. This theory was justified by Almeida *et al.*⁵¹ and Parrill *et al.*,⁵² who proved that the maximum of the infrared signal corresponding to the TO₃ mode shifts from 1073 cm⁻¹ (500 °C) to 1083 cm⁻¹ (900 °C) and from 1061 cm⁻¹ (500 °C) to 1072 cm⁻¹ (900 °C), respectively. Also, in our studies, such a shift of the component from 1069 cm⁻¹ (500 °C) through 1075 cm⁻¹ (700 °C) to 1083 cm⁻¹ (900 °C) was denoted, confirming the polycondensation of the host parallelly with an elevation of heat-treatment temperature.

To determine the impact of heat-treatment conditions on the fabrication of the fluoride crystal phase, the ATR-IR spectra were also collected within the 500 cm⁻¹–300 cm⁻¹ frequency region to observe the vibrations originating from the La–F bond (Fig. 2). Indeed, highly visible bands with a maximum in the 360 cm⁻¹–342 cm⁻¹ range assigned to vibrations of fluoride crystal phase were recorded for nano-glass-ceramic samples from all the prepared series. To assess if the recorded infrared signal is associated with fluoride crystal fraction, the spectra of glass-ceramics fabricated at 500 °C, 700 °C, and 900 °C were compared with the spectra of the xerogel before heat-treatment, for which there is no band in this frequency region (Fig. 2a). The differences in the infrared spectra of xerogels and glass-ceramics could be explained by the thermal decomposition of lanthanum(III) trifluoroacetate and the further formation of a fluoride crystal fraction at about 300 °C, as shown in our previous work.⁵³ Thus, the infrared spectra revealed the band ~350 cm⁻¹ only for annealed species. It is quite interesting that the frequency of La–F band was gradually shifted toward lower wavenumbers in the direction GC2Pr₅₀₀ (358.7 cm⁻¹) → GC2Pr₇₀₀ (358.2 cm⁻¹) → GC2Pr₉₀₀ (355.6 cm⁻¹) as heat-treatment temperature increases (Fig. 2a). To perform a more in-depth analysis of the changes in the band's frequency, the ATR-IR spectra were recorded for all glass-ceramic samples from individual series with varied La³⁺:Pr³⁺ molar ratio (Fig. 2b–d). Based on the obtained results, it could be observed that for samples from the series fabricated at 500 °C, the maximum of the La–F band was slightly changed (from 358.2 cm⁻¹ for GC1Pr₅₀₀ to 360.7 cm⁻¹ for GC6Pr₅₀₀). In the case of glass-ceramics produced at 700 °C, it was denoted that the tendency to increase in the La–F band's frequency from 357.2 cm⁻¹ to 358.2 cm⁻¹ up to reaching the La³⁺:Pr³⁺ molar ratio equaled 0.994:0.006 (GC2Pr₇₀₀) and then to decrease with further growing concentration of Pr³⁺ ions (through 354.8 cm⁻¹ for GC3Pr₇₀₀ up to 352.8 cm⁻¹ for GC6Pr₇₀₀). Hence, any significant changes in the frequencies were observed, and the differences are greater than that for glass-ceramics fabricated at 500 °C. For samples annealed at 900 °C, the differences in the La–F band's frequencies parallelly with increasing concentration of Pr³⁺ ions are best visible, and a clear downward trend is observed from 357.0 cm⁻¹ (GC1Pr₉₀₀) to 342.3 cm⁻¹ (GC6Pr₉₀₀). Therefore, it seems to be reasonable to associate the observed differences in the frequencies of the La–F band with the efficiency of Pr³⁺ incorporation within the LaF₃ crystal lattice. The considerations of the observed changes in the profiles of the recorded infrared

spectra were made based on the data from the literature. Indeed, according to a paper by Kadlec *et al.*⁵⁴ that concentrated on studying the structure of (BaF₂)_{1-x}(LaF₃)_x mixed crystals, the gradual entering of La³⁺ cations into the parent BaF₂ crystal lattice with cubic symmetry was manifested by a change in the IR band frequencies. The authors reported that the progressive and significant changes in the profile of infrared spectra could be clearly observed for high *x* values (*x* > 0.13), where LaF₃ formed continuously arranged clusters with tysonite symmetry within the cubic BaF₂ parent crystal lattice. Indeed, the modifications in the (BaF₂)_{1-x}(LaF₃)_x crystals structure (influenced by high-doping level of La³⁺) are highly visible by the appearance of additional infrared signals as well as the shift of the band from 330 cm⁻¹ (for *x* = 0, pure BaF₂ crystal phase) to 402 cm⁻¹ with growing amounts of LaF₃ (*x* = 0.47, mixed BaF₂–LaF₃ crystals). Such a huge shift (Δ = 72 cm⁻¹) in the maximum of the infrared signal is due to the significant difference in the ionic radius of Ba²⁺ (135 pm)⁵⁵ and La³⁺ (122 pm),⁵⁶ resulting in the modification of the lattice parameters and gradual changing of the force constants. Kovács *et al.*⁵⁷ also studied an increase toward higher wavenumbers for selected rare earth trichlorides, *i.e.*, CeCl₃, NdCl₃, SmCl₃, GdCl₃, and DyCl₃. As a result of lanthanides contraction from Ce³⁺ to Dy³⁺, a highly visible increase in the vibrational frequency of the M–Cl bond was denoted from 328 cm⁻¹ (CeCl₃), through 333 cm⁻¹ (NdCl₃), 338 cm⁻¹ (SmCl₃), 343 cm⁻¹ (GdCl₃) up to 346 cm⁻¹ (DyCl₃). The observed shifts are not as radical as for (BaF₂)_{1-x}(LaF₃)_x mixed crystals, and we concluded that it is correlated with noticeable smaller differences in the ionic radius of trivalent rare earths than that for Ba²⁺/La³⁺ cations. Hence, in our experiment, we suppose that the indicated differences in the La–F band frequencies are strictly associated with the efficiency of Pr³⁺ incorporation inside the LaF₃ crystal lattice. Due to the slightly smaller ionic radius of Pr³⁺ (118 pm) than of La³⁺ (122 pm),⁵⁶ the increasing frequency should indicate the growing efficiency of Pr³⁺ entering into the LaF₃ lattice. Indeed, this effect was clearly denoted for GC1Pr₅₀₀–GC6Pr₅₀₀ and GC1Pr₇₀₀–GC2Pr₇₀₀ samples. Unexpectedly, for the remaining GC3Pr₇₀₀–GC6Pr₇₀₀ and GC1Pr₉₀₀–GC6Pr₉₀₀ nano-glass-ceramic systems, the frequency of the infrared signal decreases, and the maximum is localized between the signal from the reference LaF₃ (340.0 cm⁻¹) and PrF₃ phase (345.0 cm⁻¹). In general, the results from XRD analysis, TEM microscopy, and luminescence characterization (presented in the next section) clearly demonstrate that the increase in the heat-treatment temperature and growing activator concentration favor the efficiency of Pr³⁺ incorporation inside the LaF₃ nanocrystal lattice. It allows us to conclude that the initial shift of the IR signal to higher wavenumbers (GC1Pr₅₀₀–GC6Pr₅₀₀ and GC1Pr₇₀₀–GC2Pr₇₀₀) could be correlated with the incorporation of Pr³⁺ into the LaF₃ phase at the dopant level, while for the remaining samples (GC3Pr₇₀₀–GC6Pr₇₀₀ and GC1Pr₉₀₀–GC6Pr₉₀₀), the IR signal “returns” to the frequency range close to the pure PrF₃ phase; thus, we tentatively assumed that this observed nonlinear correlation and highly visible shift of the IR signals near frequency character-



istic for PrF_3 phase might be associated with the creation of PrF_3 clusters inside the LaF_3 lattice. Interestingly, the observed direction of shifting in the IR signal during the expected creation of PrF_3 clusters is opposite to that of the $(\text{BaF}_2)_{1-x}(\text{LaF}_3)_x$ mixed crystals.⁵⁴ However, these differences could be correlated with the fact that both PrF_3 and LaF_3 are isostructural and crystallize in the hexagonal system; in the case of $(\text{BaF}_2)_{1-x}(\text{LaF}_3)_x$ mixed crystals, the formation of LaF_3 tysonite clusters within the cubic BaF_2 parent lattice is responsible for causing significant changes in the symmetry and force constants, which could influence a different direction of change in the frequencies of IR signals.

XRD measurements

The XRD patterns recorded for fabricated Pr^{3+} -doped sol-gel glass-ceramics are presented in Fig. 3. For all the prepared series, the diffraction lines are highly visible and were attributed to the hexagonal LaF_3 phase crystallized in the $P6_3cm$ space group (ICDD card no. 00-008-0461). Based on the broadening of the XRD lines, the average diameters (D) of the crystallized LaF_3 phase were calculated using the Williamson-Hall theorem⁵⁸

$$\beta_{hkl} \cos \theta = \frac{K\lambda}{D} + 4Z \sin \theta,$$

where β_{hkl} is the broadening of the (hkl) diffraction line, θ is the diffraction angle, λ is the X-ray wavelength, D is the average crystal size, and Z is the effective strain. The lattice strain and the crystallite size were deduced from the intercept of $\beta \cos \theta / \lambda$ versus $\sin \theta / \lambda$. It was found that for all series of sol-gel samples, the LaF_3 phase crystallized in the nanoscale, and the results of performed calculations are collected in Table 1. In general, analyzing the obtained data allows us to notice that the average crystallite sizes assessed for samples from GCPr_{500} and GCPr_{700} series are very similar (the range from 8.6 ± 0.1 nm to 13.5 ± 0.1 nm). In comparison, the treatment at 900 °C clearly contributed to an increase in the crystallite size (from 57.7 ± 0.3 nm to 81.7 ± 5.8 nm).

Table 1 also summarizes the information about the calculated lattice parameters of the $\text{LaF}_3:\text{Pr}^{3+}$ phase for individual sol-gel samples. The crystal lattice parameters were determined using Le Bail method.⁵⁹ Since the ionic radius of Pr^{3+} ($r = 1.179$ Å) is slightly smaller than that of La^{3+} ($r = 1.216$ Å),⁵⁶ it was expected that Pr^{3+} co-doping—parallelly with the elevation of heat-treatment temperature—would result in a progressive decrease in the lattice parameters. Interestingly, according to the representative GC2Pr_x samples, the reverse trend was denoted, and the lattice parameters changed as follows: $a_0 = 7.179(9)$ Å and $c_0 = 7.346(8)$ Å (GC2Pr_{500}), $a_0 = 7.195(4)$ Å and $c_0 = 7.361(7)$ Å (GC2Pr_{700}), as well as $a_0 = 7.179(9)$ Å and $c_0 = 7.346(8)$ Å (GC2Pr_{900}); thus, it could be clearly stated that the lattice parameters increased simultaneously with the increase in the annealing temperature. The observed trend might be correlated with the positive thermal expansion coefficients (along a (α_{\perp}) and c axis (α_{\parallel}) as well as the directionally averaged linear expansion coefficient ($\bar{\alpha}$) of the LaF_3 fluor-

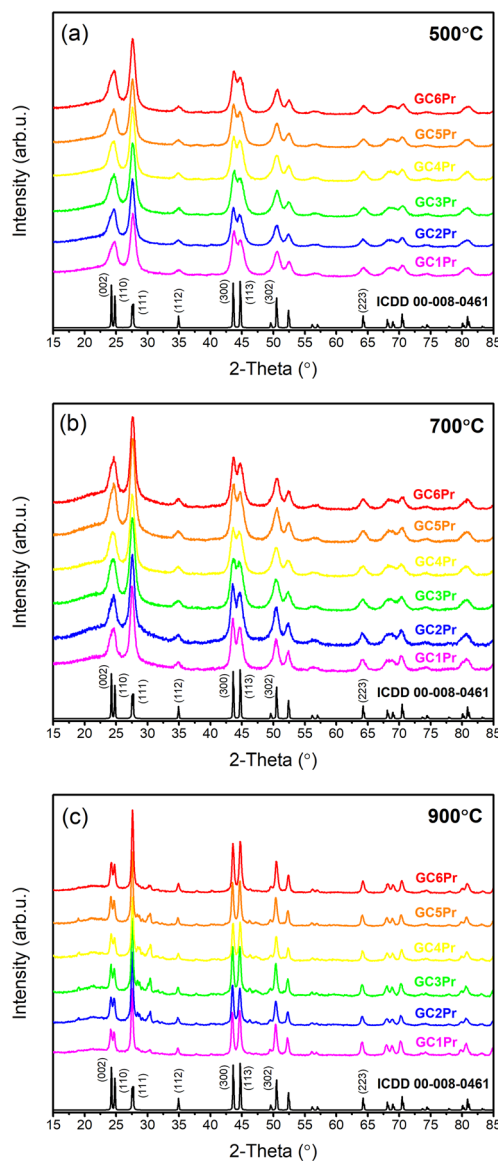


Fig. 3 XRD patterns for the series of the fabricated sol-gel samples at: 500 °C (a), 700 °C (b), and 900 °C (c).

ide phase, as was proved in the work by Korczak *et al.*,⁶⁰ similar to that for other fluoride crystal phases, *i.e.*, CaF_2 , SrF_2 , and BaF_2 .⁶¹ Such a direction of changes in the lattice parameters is consistent with the shift of infrared signals from 358.7 cm^{-1} (GC2Pr_{500}), 358.2 cm^{-1} (GC2Pr_{700}) to 355.6 cm^{-1} (GC2Pr_{900}), as was demonstrated in Fig. 2a. The increase in the lattice parameters were also denoted for $\text{LaF}_3:\text{Pr}^{3+}$ nanocrystals prepared by hydrothermal ($a_0 = 7.201$ Å, $c_0 = 7.432$ Å) and co-precipitation ($a_0 = 7.197$ Å, $c_0 = 7.375$ Å) methods, as presented in a paper by M. S. Pudovkin *et al.*²³

The modification in lattice parameters of the $\text{LaF}_3:\text{Pr}^{3+}$ nanocrystal phase is also correlated with the changes in the Pr^{3+} concentration, resulting from the variable $\text{La}^{3+}:\text{Pr}^{3+}$ molar ratio. In the case of samples fabricated at 500 °C, the lattice parameters remain almost constant (the deviations were



Table 1 Crystal sizes and lattice parameters of the LaF₃ phase for the fabricated Pr³⁺-doped sol–gel samples

Oxyfluoride glass-ceramics	Lattice parameters [Å]		Crystallite size [nm]
	LaF ₃ ^a	Sol–gel sample	
GC1Pr ₅₀₀	$a_0 = 7.184$	$a_0 = 7.176(4)$ $c_0 = 7.345(5)$	10.8 ± 0.1
GC2Pr ₅₀₀		$a_0 = 7.176(9)$ $c_0 = 7.346(8)$	12.5 ± 0.2
GC3Pr ₅₀₀		$a_0 = 7.178(1)$ $c_0 = 7.347(9)$	8.6 ± 0.1
GC4Pr ₅₀₀	$c_0 = 7.351$	$a_0 = 7.184(3)$ $c_0 = 7.348(1)$	9.4 ± 0.1
GC5Pr ₅₀₀		$a_0 = 7.185(8)$ $c_0 = 7.348(9)$	9.7 ± 0.1
GC6Pr ₅₀₀		$a_0 = 7.179(8)$ $c_0 = 7.347(9)$	9.0 ± 0.1
GC1Pr ₇₀₀	$a_0 = 7.184$	$a_0 = 7.194(6)$ $c_0 = 7.362(9)$	13.5 ± 0.1
GC2Pr ₇₀₀		$a_0 = 7.195(4)$ $c_0 = 7.361(7)$	11.6 ± 0.1
GC3Pr ₇₀₀		$a_0 = 7.195(3)$ $c_0 = 7.360(5)$	9.5 ± 0.1
GC4Pr ₇₀₀	$c_0 = 7.351$	$a_0 = 7.192(8)$ $c_0 = 7.358(8)$	9.7 ± 0.1
GC5Pr ₇₀₀		$a_0 = 7.185(2)$ $c_0 = 7.349(8)$	10.2 ± 0.1
GC6Pr ₇₀₀		$a_0 = 7.184(7)$ $c_0 = 7.349(9)$	10.9 ± 0.1
GC1Pr ₉₀₀	$a_0 = 7.184$	$a_0 = 7.203(3)$ $c_0 = 7.367(5)$	79.2 ± 1.0
GC2Pr ₉₀₀		$a_0 = 7.200(5)$ $c_0 = 7.364(1)$	57.7 ± 0.3
GC3Pr ₉₀₀		$a_0 = 7.198(8)$ $c_0 = 7.363(6)$	81.7 ± 5.8
GC4Pr ₉₀₀	$c_0 = 7.351$	$a_0 = 7.197(4)$ $c_0 = 7.361(5)$	68.8 ± 1.4
GC5Pr ₉₀₀		$a_0 = 7.195(5)$ $c_0 = 7.360(1)$	70.0 ± 0.9
GC6Pr ₉₀₀		$a_0 = 7.191(7)$ $c_0 = 7.352(7)$	58.1 ± 0.2

^a Refers to lattice parameters of pure LaF₃ phase assigned to ICDD card no. 00-008-0461.

denoted only for GC4Pr₅₀₀ and GC5Pr₅₀₀ samples; however, an increase in a_0 and c_0 parameters may result from the thermal expansion). For GC1Pr₇₀₀–GC3Pr₇₀₀ nano-glass-ceramic samples, similar lattice parameters were denoted, while from the GC4Pr₇₀₀ sample, a more noticeable decrease in a_0 and c_0 parameter values was observed. Such parameter changes could suggest a particularly efficient Pr³⁺ incorporation into the LaF₃ phase for GC4Pr₇₀₀–GC6Pr₇₀₀ sol–gel samples. The most remarkable differences in the lattice parameters were identified for nano-glass-ceramics fabricated during heat-treatment performed at 900 °C, suggesting the highest efficiency of Pr³⁺ entering into the LaF₃ nanocrystal fraction compared with other series of sol–gel samples. In conjunction with the tentative conclusions from the analysis of the IR spectra according to the possibility of the PrF₃ clusters formation (Fig. 2b–d), the observed changes in the lattice parameters for GC4Pr₇₀₀–GC6Pr₇₀₀ and GC1Pr₉₀₀–GC6Pr₉₀₀ samples seem to confirm this hypothesis.

TEM microscopy

The transmission electron microscopy (TEM) analyses were conducted for selected nano-glass-ceramics with low Pr³⁺ content (GC1Pr_x) and high Pr³⁺ concentration (GC6Pr_x) for each temperature level, *i.e.*, 500 °C, 700 °C, and 900 °C. The resulting micrographs are illustrated in Fig. 4. The TEM investigations unequivocally delineated the nanocrystalline nature of the materials obtained during the controlled heat-treatment of the as-prepared xerogels at the proposed annealing conditions. The TEM micrographs recorded in both the bright and dark fields apparently show that all sol–gel samples comprise crystalline grains embedded within an amorphous host. According to the images from Fig. 4, it could be observed that following the elevation in the heat-treatment temperature, the crystalline phase becomes notably more prominent in size and crystallinity, particularly evidenced by the increase in crystallite sizes for nano-glass-ceramics obtained at 900 °C independent from Pr³⁺ concentration. In other words, the crystal sizes depend on the heat-treatment conditions, without any significant influence of the established La³⁺:Pr³⁺ molar ratio, as was evidenced from XRD analysis. Furthermore, the phase analysis conducted for the selected nano-glass-ceramics also agrees with the XRD results; the identification of the LaF₃ nanophase with *P6₃cm* symmetry was confirmed through electron diffraction measurements. The acquired selected area electron diffraction (SAED) patterns were indexed using phase data sourced from the ICDD database with lattice parameter values obtained from XRD analysis. The implemented heat-



Fig. 4 TEM observations of the GC1Pr_x (left side) and GC6Pr_x (right side) for the nano-glass-ceramics obtained during heat-treatment at 500 °C (a and b), 700 °C (c and d), and 900 °C (e and f). The right part of the columns presents corresponding dark field images and recorded SAED patterns. Red circles indicate theoretical Bragg positions.



treatment process of the as-prepared xerogels led to the fluoride crystalline particles becoming more conspicuous, increasing in size, and transitioning into equiaxial nanoparticles. Moreover, it could be observed that these fluoride particles are dispersed more homogeneously within the amorphous sol-gel host parallelly with an elevation in heat-treatment temperature. Additional microscopic observations were carried out for the GC6Pr₉₀₀ nano-glass-ceramic sample, and the results are collected in Fig. 5. The high-resolution (HR-TEM, Fig. 5c) microscopic image demonstrated the good quality of the formed LaF₃ nanocrystals. The crystallization of the LaF₃ phase inside the silicate sol-gel host was also confirmed by fast Fourier transform (FFT, Fig. 5d) analysis conducted on the acquired images, and the observed interplane distances correlate well with the theoretical values for the reference material. Furthermore, it should be also emphasized that in correlation with our previous assumptions regarding the efficient incorporation of Pr³⁺ ions inside LaF₃ nanocrystals from ATR-IR and XRD analysis, the results from energy-dispersive X-ray spectroscopy (EDS, Fig. 5b) of the edge region presented in Fig. 5a confirmed that the nanocrystals consist primarily of lanthanum and fluorine, with praseodymium admixtures. Simultaneously, EDS analysis revealed that the amorphous part of the host matrix predominantly comprises silicon oxide, confirming the conclusions from ATR-IR spectra interpretation according to the polycondensation reaction of the sol-gel network.

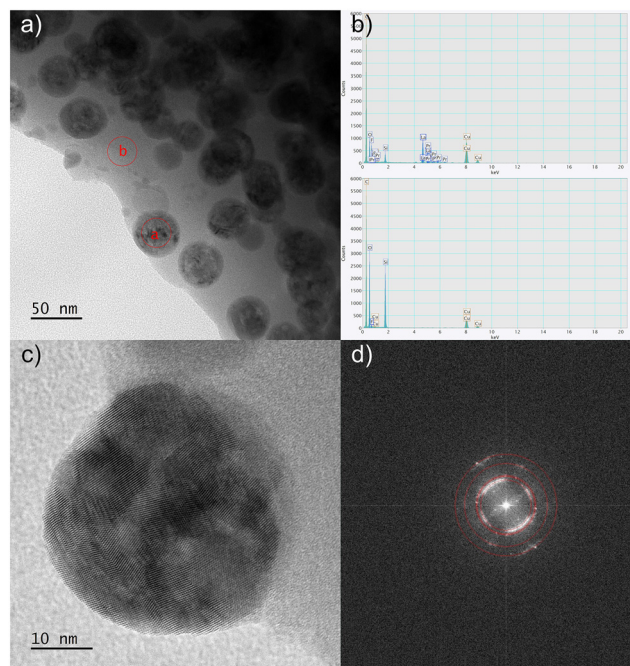


Fig. 5 TEM observations of the GC6Pr₉₀₀ nano-glass-ceramic sample: enlargement of the edge region showing the nanocrystals and the amorphous host regions (a) with red circles, which indicate the area used in the EDS analysis (b). HR-TEM image of the nanocrystals with visible interatomic planes (c) and corresponding FFT with the theoretical lattice distances marked by red rings (d) are also presented.

Excitation spectra

Fig. 6a–c illustrate the excitation spectra (PLE) for the individual series of Pr³⁺-doped oxyfluoride glass-ceramics fabricated at 500 °C, 700 °C and 900 °C, registered by collecting the red emission of the ³P₀ → ³F₂ transition at λ_{em} = 634 nm. The spectra consisted of 4f² → 4f² intra-configurational transitions of Pr³⁺ ions from the ³H₄ ground state to the various excited ³P_J levels, appropriately labeled as the ³P₂ (444 nm), ³P₁ and ¹I₆ (467 nm), as well as ³P₀ (480 nm). Moreover, the weak excitation band within the orange spectral range (592 nm), assigned to the ³H₄ → ¹D₂ transition, was also recorded. It could be observed that for all the fabricated series, independent from the heat-treatment conditions, the intensities of individual excitation bands have grown with increasing Pr³⁺ content from La³⁺:Pr³⁺ molar ratio equal to 0.997:0.003 (GC1Pr_x) up to 0.994:0.006 (GC2Pr_x). However, exceeding this La³⁺:Pr³⁺ molar ratio resulted in a gradual decrease in the band intensities, suggesting that concentration quenching between neighboring Pr³⁺ ions (CQ_{Pr}) takes place.

It should also be noted that for the series of sol-gel glass-ceramics obtained during annealing at 700 °C, the ³H₄ → ³P₂ excitation line at 444 nm is characterized by the highest intensity for GC1Pr₇₀₀–GC4Pr₇₀₀ samples, while with further increase in concentration of optically active dopant (GC5Pr₇₀₀, GC6Pr₇₀₀), the ³H₄ → ³P₁, ¹I₆ as well as the ³H₄ → ³P₀ bands at 467 nm and 480 nm, respectively, became dominant. A similar tendency, according to the mutual alteration in the feeding of



Fig. 6 Excitation spectra recorded for Pr³⁺-doped sol-gel nano-glass-ceramics fabricated at: 500 °C (a), 700 °C (b), and 900 °C (c). The comparison of excitation spectra for the as-prepared xerogels and GC2Pr_x nano-glass-ceramics with La³⁺:Pr³⁺ molar ratio equal 0.994:0.006 (d); the inset in (d) shows an enlargement of the PLE spectra recorded for the as-prepared xerogels.



the 3P_2 , 3P_1 , 1I_6 , and 3P_0 excited levels, was also denoted for samples from GC1–6Pr₉₀₀ series, for which an increase in the intensities of the $^3H_4 \rightarrow ^3P_1$, 1I_6 and the $^3H_4 \rightarrow ^3P_0$ bands were observed from the GC3Pr₉₀₀ sample. A detailed discussion on determining the effect of Pr³⁺ concentration on the excitation bands' intensities was performed in the work.⁶² It was proven that the contribution of the $^3H_4 \rightarrow ^3P_2$ band's intensity according to the overall excitation spectrum gradually decreased parallelly with an increase in the Pr³⁺ concentration; additionally, it was denoted that the shape of the excitation bands became wider. It was assumed that such a spectroscopic behavior, characteristic for higher dopant concentration, could be explained by the reabsorption processes or by the location of the dopant ions in slightly different crystallographic sites of symmetry modified by the high Pr³⁺ concentration. Therefore, the observed changes in the intensities of individual excitation bands for samples from GC1–6Pr₇₀₀ and GC1–6Pr₉₀₀ series could suggest the high efficiency of Pr³⁺ ions embedding into a fluoride environment, especially according to our hypothesis about the possibility of forming PrF₃ clusters within the LaF₃ parent crystalline phase at high Pr³⁺ concentrations. Interestingly, for each nano-glass-ceramics fabricated at 500 °C (with the exception of GC1Pr₅₀₀), the $^3H_4 \rightarrow ^3P_1$, 1I_6 band is more intense than the $^3H_4 \rightarrow ^3P_2$ one. However, it should be noted that the $^3H_4 \rightarrow ^3P_1$, 1I_6 band (~468 nm) coincides with the strong background attributed to the photon recombinations from the defects inside the silicate sol-gel host (~470 nm, similar to that shown for the as-prepared xerogels in the inset in Fig. 6d). According to the studies performed by Kłonkowski *et al.*,⁶³ this effect could be significantly reduced after the thermal treatment at higher temperatures; therefore, it effectively disappeared for samples from the GC1–6Pr₇₀₀ and GC1–6Pr₉₀₀ series. Moreover, according to Fig. 6d, it could be observed that the intensities of whole excitation bands grow up in the following order of the representative samples: GC2Pr₅₀₀ → GC2Pr₇₀₀ → GC2Pr₉₀₀, which could be explained by increasing the segregation of Pr³⁺ ions inside the LaF₃ fluoride crystal phase with low-phonon energy. For the same reason, the $^3H_4 \rightarrow ^1D_2$ (592 nm) weak excitation band appeared only for glass-ceramics fabricated at 900 °C. Additionally, according to the inset in Fig. 6d, none of the PLE bands were recorded for the as-prepared xerogels, indicating a strong influence of OH groups on Pr³⁺ luminescence. Indeed, the observed quenching for xerogels could be explained by the occurrence of plentiful high-vibrational OH groups inside the porous silicate network, which was verified by us earlier by the presence of intense and broad band with a maximum >3000 cm⁻¹ in the IR-ATR spectra.^{47,53}

Emission spectra in VIS range and white light emission

The emission (PL) spectra of the individual series of Pr³⁺-doped glass-ceramic materials are presented in Fig. 7a–c. The spectra were recorded upon excitation at $\lambda_{ex} = 444$ nm ($^3H_4 \rightarrow ^3P_2$ transition) and showed several luminescence bands with maxima located within the greenish-blue and the reddish-orange light regions at 478 nm ($^3P_1 \rightarrow ^3H_4$), 484 nm ($^3P_0 \rightarrow$



Fig. 7 Emission spectra recorded within the VIS range for Pr³⁺-doped sol-gel samples prepared at: 500 °C (a), 700 °C (b), and 900 °C (c). The comparison of the emission spectra for the as-prepared xerogels and GC2Pr_x nano-glass-ceramics with La³⁺:Pr³⁺ molar ratio equal 0.994:0.006 (d); the inset in Fig. 5d shows an enlargement of the PL spectra recorded for the as-prepared xerogels.

3H_4), 520 nm ($^3P_1 \rightarrow ^3H_5$), 535 nm ($^3P_0 \rightarrow ^3H_5$), 578 nm ($^3P_1 \rightarrow ^3H_6$), 593 nm/598 nm ($^1D_2 \rightarrow ^3H_4$), 608 nm ($^3P_0 \rightarrow ^3H_6$), 633 nm/637 nm/648 nm ($^3P_0 \rightarrow ^3F_2$), 668 nm ($^3P_1 \rightarrow ^3F_3$), as was also illustrated in the energy level diagram (Fig. 8). The shape of the recorded emission bands is very similar to those of hexagonal LaF₃:Pr³⁺ nanocrystals synthesized by the hydro-thermal route.⁴ For each series, the greatest emission intensity

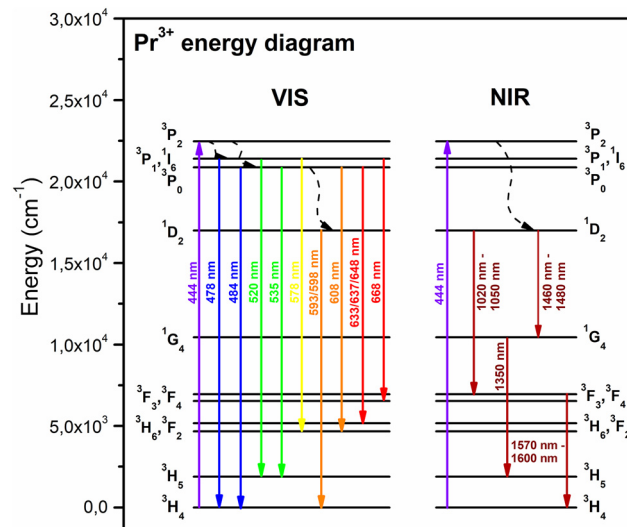


Fig. 8 The energy level scheme of Pr³⁺ in the studied sol-gel samples.

was recorded for glass-ceramics with $\text{La}^{3+}:\text{Pr}^{3+}$ molar ratio of equal 0.994 : 0.006 (GC2Pr₅₀₀, GC2Pr₇₀₀, and GC2Pr₉₀₀). From GC3Pr_x samples with higher content of Pr^{3+} ions, the luminescence started to quench, indicating the occurrence of energy transfer between neighboring Pr^{3+} ions in the host. The possible cross-relaxation (CR) channels involved the following transitions: $\{^3\text{P}_0 + ^3\text{H}_4\} \rightarrow \{^3\text{H}_6 + ^1\text{D}_2\}$ (1), $\{^3\text{P}_0 + ^3\text{H}_4\} \rightarrow \{^1\text{G}_4 + ^1\text{G}_4\}$ (2), $\{^3\text{P}_0 + ^3\text{H}_4\} \rightarrow \{^1\text{D}_2 + ^3\text{H}_6\}$ (3), $\{^1\text{D}_2 + ^3\text{H}_4\} \rightarrow \{^1\text{G}_4 + ^3\text{F}_3\}$ (4), $\{^1\text{D}_2 + ^3\text{H}_4\} \rightarrow \{(^3\text{F}_3 + ^3\text{F}_4) + ^1\text{D}_2\}$ (5), or *via* resonant energy transfer (RET) $\{^1\text{D}_2 + ^3\text{H}_4\} \rightarrow \{^3\text{H}_4 + ^1\text{D}_2\}$ (6).⁶⁴ Similarly, as in the case of the excitation spectra, the intensities of emission bands gradually increase in the following order of representative samples: GC2Pr₅₀₀ → GC2Pr₇₀₀ → GC2Pr₉₀₀ (Fig. 7d). Such a tendency could be associated with the growing tendency to incorporate Pr^{3+} ions inside LaF_3 crystals and the removal of OH groups from the silicate sol-gel host. Moreover, Fig. 7d shows the comparison of PL spectra recorded for the as-prepared xerogels and GC2Pr_x nano-glass-ceramics. As could be seen, for the as-prepared xerogels, the luminescence of Pr^{3+} was not recorded, contrary to various types of Pr^{3+} -doped glasses prepared by the conventional melt-quenching method, as presented in numerous papers published elsewhere.^{1,30,32,33,36,38,40–42} The observed quenching of Pr^{3+} emission in xerogels is strictly correlated with the occurrence of plentiful high-vibrational OH groups inside the silicate pores of the sol-gel network, which are responsible for the fast and efficient quenching of the Pr^{3+} luminescence from the emitting $^3\text{P}_0$ and $^1\text{D}_2$ levels, considering the relatively small $^3\text{P}_0\text{--}^1\text{D}_2$ ($\sim 4080\text{ cm}^{-1}$) and $^1\text{D}_2\text{--}^1\text{G}_4$ ($\sim 6570\text{ cm}^{-1}$) energy gaps. As was presented in the inset in Fig. 7d, upon excitation at $\lambda_{\text{ex}} = 444\text{ nm}$, only a broad band originating from defects inside the sol-gel host was registered.⁶³ Thus, the PL results clearly proved that only heat-treated samples revealed the characteristic $4f^2\text{--}4f^2$ visible luminescence lines of Pr^{3+} , and the appearance of emission characteristic for Pr^{3+} ions could be associated with their favorable cumulation inside precipitated fluoride nanocrystals as well as with the removal of OH groups.

The further characterization of luminescent properties involved the analysis of emission intensities from the $^3\text{P}_0$ as well as the $^1\text{D}_2$ states of Pr^{3+} . Indeed, the population of these two excited levels strongly depends on the concentration of Pr^{3+} ions^{3,8} and their distribution between the oxide amorphous host and the fluoride crystal lattice.⁶⁵ Generally, according to the literature, at relatively low concentrations of Pr^{3+} ions, the multiphonon relaxation from the $^3\text{P}_2$ state through the $^3\text{P}_1$, $^1\text{I}_6$, $^3\text{P}_0$ up to the $^1\text{D}_2$ level favors the orange luminescence assigned to the $^1\text{D}_2 \rightarrow ^3\text{H}_4$ transition. For higher dopant concentrations, the non-radiative energy transfer processes from excited Pr^{3+} to nearby unexcited Pr^{3+} ion become more efficient, and the luminescence associated with the $^1\text{D}_2 \rightarrow ^3\text{H}_4$ transition is gradually quenched by cross-relaxation (CR) mechanisms. Concentration quenching (CQ_{Pr}) does not occur at low Pr^{3+} concentrations because the average distance among the neighboring dopants is relatively long; thus, the $\text{Pr}^{3+}\text{--}\text{Pr}^{3+}$ interaction is very weak. This effect was particularly well-observable in a paper by C. Y. Morassuti *et al.*³ concen-

trated on the characterization of Pr^{3+} -doped calcium aluminosilicate glasses, for which the emissions from the $^3\text{P}_0$ multiplet (into the lower-lying $^3\text{H}_4$, $^3\text{H}_5$, and $^3\text{F}_{2,3,4}$ states) gradually increased with growing content of Pr^{3+} from 0.2 wt% Pr^{3+} up to 2.0 wt%; meanwhile, the luminescence from the $^1\text{D}_2$ level was simultaneously quenched from 0.5 wt% Pr^{3+} . Thus, the authors suggest that concentration quenching is strongly influenced by the cross-relaxation (CR) mechanisms between Pr^{3+} ions located in the immediate vicinity in the glassy host by involving the following transitions: $\{^1\text{D}_2 + ^3\text{H}_4\} \rightarrow \{^1\text{G}_4 + ^3\text{F}_3\}$ and $\{^1\text{D}_2 + ^3\text{H}_4\} \rightarrow \{(^3\text{F}_3 + ^3\text{F}_4) + ^1\text{D}_2\}$. Similar results were denoted by F. Zhang *et al.*⁸ for $\text{TeO}_2\text{--BaF}_2\text{--NaF--PrF}_3$ glasses, for which the orange emission from the $^1\text{D}_2$ manifold was successfully quenched from 0.5 mol% Pr^{3+} , while the luminescence from the $^3\text{P}_0$ level started to quench beyond 1.5 mol% Pr^{3+} . In the case of our experiment, as presented in Fig. 7, the emissions from the $^3\text{P}_0$ and the $^1\text{D}_2$ states are well-observed, and the intensity of the $^1\text{D}_2 \rightarrow ^3\text{H}_4$ band is higher for samples with lower concentrations of Pr^{3+} ions; however, for higher concentrations its intensity is reduced, suggesting the activation of cross-relaxation channels from the $^1\text{D}_2$ manifold. Thus, these dependencies in the luminescence intensity as a function of Pr^{3+} concentration and heat-treatment conditions are graphically represented in Fig. 9. The luminescence intensity coefficients were calculated as ratios of the $^3\text{P}_0 \rightarrow ^3\text{H}_4$ band intensity to the sum of the $^1\text{D}_2 \rightarrow ^3\text{H}_4$ and $^3\text{P}_0 \rightarrow ^3\text{H}_6$ bands intensities (blue-to-reddish-orange emission, B/(RO)). For each series of prepared Pr^{3+} -doped sol-gel materials, the calculated B/(RO)-ratio values gradually increase with growing Pr^{3+} ions concentration: from 0.66 (GC1Pr₅₀₀) to 1.68 (GC6Pr₅₀₀), from 0.87 (GC1Pr₇₀₀) to 1.39 (GC6Pr₇₀₀), and finally from 1.26



Fig. 9 The B/(OR)-ratios calculated for the prepared Pr^{3+} -doped sol-gel materials heat-treated at 500 °C, 700 °C, and 900 °C.



(GC1Pr₉₀₀) to 1.65 (GC6Pr₉₀₀). It could be observed that the B/(RO)-ratio values for samples with higher Pr³⁺ concentration from the series annealed at 500 °C are very close to those for samples from the series fabricated at 900 °C. However, we assumed that it is associated with a huge overlapping of characteristic emissions of Pr³⁺ with a background band from the silicate sol-gel host, which is highly visible for samples heat-treated at 500 °C. Hence, overlapping does not allow for a reliable assessment of the B/(RO) coefficients, especially for the GC4Pr₅₀₀–GC6Pr₅₀₀ samples.

It is also well-observed that the calculated B/(RO)-ratio values are generally higher as the annealing temperature increase from 500 °C to 900 °C. These differences in the B/(RO) coefficient could be explained by the vibration energies in the nearest framework around the Pr³⁺:LaF₃ crystal lattice (340 cm^{−1}) or the silicate sol-gel host (~3350 cm^{−1} due to the presence of OH groups or ~1050 cm^{−1} due to the Q³ [SiO₄] units). The energy gap between the ³P₀ and the ¹D₂ multiplets equals about ~4080 cm^{−1},²⁷ and it could be covered by 12 La–F phonons from the fluoride lattice, as well as by 4 or 1 phonon (s) of Q³ [SiO₄] units or OH groups, respectively. As a consequence of the above-mentioned differences in vibrational energies, the ³P₀ state is depopulated very quickly if Pr³⁺ ions are incorporated inside an amorphous silicate sol-gel host, and the excitation energy is transferred non-radiatively from the ³P₀ multiplet to the lower-lying ¹D₂ state. The analysis of the available literature confirms the abovementioned considerations. For OxGCs-containing BaF₂ nanocrystals, the calculated B/(RO)-ratio values are substantially higher (2.30 for the sample annealed at 600 °C/4 hours and 2.36 for the sample obtained during heat-treatment at 600 °C/24 hours) than for the parent amorphous glass (0.91).³³ Therefore, the B/(RO)-ratio values increase with a growing degree of ceramization in the immediate vicinity around Pr³⁺ ions, confirming that an elevation in heat-treatment temperature promotes the cumulation of Pr³⁺ inside the LaF₃ crystal phase.

Since the fabricated Pr³⁺-doped sol-gel nano-glass-ceramic materials emit greenish-blue and reddish-orange light (due to the ³P_{0,1} → ³H₄₋₆, ¹D₂ → ³H₄, ³P₀ → ³F₂, and ³P₁ → ³F₃ transitions), the chromaticity coordinates (x|y) were calculated and graphically presented in the CIE diagrams. The results are collected in Table 2, as well as Fig. 10 and 11. It should be noted that for the series of samples fabricated at 500 °C, the high background (associated with the photon recombinations from defects inside the silicate sol-gel hosts) does not allow for a faithful rendering of the actual color emitted by the samples. Thus, chromaticity coordinates were analyzed only for glass-ceramic samples fabricated at 700 °C and 900 °C. For the samples from the GC1Pr₇₀₀–GC6Pr₇₀₀ series (Fig. 10), the evaluated chromaticity coordinates shift slightly to red-tone color with the modification in the La³⁺:Pr³⁺ molar ratio from 0.997:0.003 (GC1Pr₇₀₀) to 0.994:0.006 (GC2Pr₇₀₀), as the content of Pr³⁺ ions increases. With the further growth of Pr³⁺ content (defined by the La³⁺:Pr³⁺ molar ratio from 0.988:0.012 (GC3Pr₇₀₀) to 0.94:0.06 (GC5Pr₇₀₀)), it is observed that the chromaticity coordinates shift and lie—especially for the

Table 2 CIE coordinates and CCT values for Pr³⁺-doped sol-gel samples

Type of material/sample	CIE (x y)	CCT [K] ^a	Ref.
YF ₃ :1%Pr ³⁺	(0.441 0.390)	2814 ^b	11
BaWO ₄ :0.01Pr ³⁺	(0.284 0.311)	8680 ^b	26
BaWO ₄ :0.03Pr ³⁺	(0.291 0.325)	7847 ^b	
BaWO ₄ :0.05Pr ³⁺	(0.320 0.340)	6073 ^b	
BaWO ₄ :0.07Pr ³⁺	(0.297 0.337)	7294 ^b	
60PbGeO ₃ -20PbF ₂ -20CdF ₂ :0.5Pr ³⁺	(0.38 0.33)	3623 ^b	70
60PbGeO ₃ -20PbF ₂ -20CdF ₂ :0.75Pr ³⁺	(0.34 0.33)	5153 ^b	
β-NaYF ₄ :0.1Pr ³⁺	(0.354 0.339)	4563	71
β-NaYF ₄ :0.5Pr ³⁺	(0.323 0.338)	5951	
β-NaYF ₄ :1.0Pr ³⁺	(0.307 0.335)	6767	
Lu _{1.94} Pr _{0.06} MoO ₆	(0.315 0.312)	6485 ^c	72
Lu _{1.92} Pr _{0.08} MoO ₆	(0.352 0.316)	4499 ^c	
GC1Pr ₇₀₀	(0.419 0.364)	2977 ^b	This work
GC2Pr ₇₀₀	(0.429 0.346)	2581 ^b	
GC3Pr ₇₀₀	(0.405 0.340)	3032 ^b	
GC4Pr ₇₀₀	(0.372 0.338)	3962 ^b	
GC5Pr ₇₀₀	(0.375 0.344)	3917 ^b	
GC6Pr ₇₀₀	(0.390 0.355)	3577 ^b	
GC1Pr ₉₀₀	(0.408 0.339)	2948 ^b	
GC2Pr ₉₀₀	(0.400 0.337)	3124 ^b	
GC3Pr ₉₀₀	(0.434 0.353)	2567 ^b	
GC4Pr ₉₀₀	(0.399 0.355)	3343 ^b	
GC5Pr ₉₀₀	(0.402 0.359)	3309 ^b	
GC6Pr ₉₀₀	(0.405 0.403)	3608 ^b	

^a CCT was calculated using the following McCamy's formula: CCT = $an^3 + bn^2 + cn + d$. ^b $a = -449$, $b = 3525$, $c = -6823$, $d = 5520.33$. ^c $a = -437$, $b = 3601$, $c = -6861$, $d = 5514.21$.

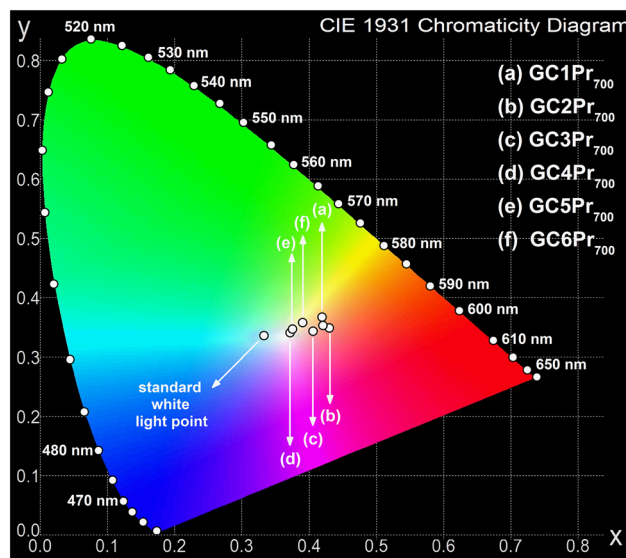


Fig. 10 CIE chromaticity diagram with coordinates assigned for Pr³⁺-doped nano-glass-ceramics prepared at 700 °C.

GC4Pr₇₀₀ sample—near the standard point for the illuminant. For the sample with the highest concentration of Pr³⁺ ions in the series (La³⁺:Pr³⁺ molar ratio equals 0.880:0.120), it is observed that the chromaticity coordinates shift into yellow-tone color. For the samples from GC1Pr₉₀₀–GC6Pr₉₀₀ series, the chromaticity coordinates shift from red-tone to yellow-tone





Fig. 11 CIE chromaticity diagram with coordinates assigned for Pr^{3+} -doped nano-glass-ceramics prepared at 900 °C.

color region with the increasing content of Pr^{3+} ions (simultaneously to decrease in the $\text{La}^{3+}:\text{Pr}^{3+}$ molar ratio from 0.997:0.003 to 0.88:0.1, Fig. 11). Nevertheless, similar to that in the case of nano-glass-ceramics prepared during heat-treatment at 700 °C, all samples from the GC1–6Pr₉₀₀ series emit white light. The quality of generated white light by the individual sol-gel sample was examined by the correlated color temperature (CCT) using McCamy's analytical relation given by the below equation⁶⁶

$$\text{CCT} = -449n^3 + 3525n^2 - 6832n + 5520.33,$$

where $n = (x - x_e)/(y - y_e)$ is from the inverse slope line, $x_e = 0.332$ and $y_e = 0.186$ are the coordinates in the epicenter and are evaluated using chromaticity coordinates.⁶⁷ The CCT values determined for GC4Pr₇₀₀–GC6Pr₇₀₀ glass-ceramics, but especially for GC4Pr₇₀₀, inform about the ability to generate nearly neutral white light (CCT \approx 4000 K), while for the remaining samples (GC1Pr₇₀₀–GC3Pr₇₀₀), the CCT values fall in the warm white light region (CCT < 4000 K).^{68,69} The CCT values below 4000 K were also estimated for all glass-ceramics from the GC1–6Pr₉₀₀ series, suggesting that their emissions are also within the warm white light range. Therefore, it could be stated that the fabricated Pr^{3+} -doped glass-ceramics may satisfy the requirements defined for the white light emitters. White light emission originating from Pr^{3+} ions was also reported for BaWO_4 nanophosphors,²⁶ fluorogermanate $60\text{PbGeO}_3\text{--}20\text{PbF}_2\text{--}20\text{CdF}_2$ nano-structured phosphors,⁷⁰ $\beta\text{-NaYF}_4$,⁷¹ or Lu_2MoO_6 phosphors,⁷² as also depicted in Table 2. Furthermore, another important parameter, color purity (CP), was also calculated based on the following equation⁷³

$$\text{CP} = \frac{\sqrt{(x - x_i)^2 + (y - y_i)^2}}{\sqrt{(x_d - x_i)^2 + (y_d - y_i)^2}} \times 100\%,$$

in which (x, y) are the chromaticity coordinates for individual Pr^{3+} -doped sample, (x_i, y_i) are the coordinates of standard white light (0.333|0.333), and (x_d, y_d) are the chromaticity coordinates of the dominant wavelength (determined from the straight line connecting the white light point and the (x, y) coordinates of a sample, as presented in the paper).⁷³ Generally, the CP for standard white light equals 0%; thus, it is preferred if the CP values for the prepared Pr^{3+} -doped sol-gel samples would be as low as possible. The calculated CP values for the individual samples in the prepared series are changed as follows: 33.3%, 24.0%, 12.8%, 16.2%, and 24.0% for GC1–6Pr₇₀₀, as well as 24.5%, 21.5%, 36.6%, 26.6%, 28.7%, and 43.2% for GC1–6Pr₉₀₀. The results clearly indicate that GC3Pr₇₀₀ (CP = 12.8%) and GC4Pr₇₀₀ (CP = 16.2%) samples exhibit bright white light, which could make them potential and interesting candidates for use in the development of white light emitters. Comparably low CP values (CP \approx 10%, as for GC3Pr₇₀₀ sample) were denoted for the Dy^{3+} -doped $\text{CaSrAl}_2\text{SiO}_7$ phosphors prepared by high-temperature solid-state reaction.⁷⁴

Emission spectra in the NIR region

The photoluminescence emission spectra inside the near-infrared (NIR) region for the synthesized Pr^{3+} -doped oxyfluoride sol-gel materials were also recorded and are presented in Fig. 12. In the result of excitation using $\lambda_{\text{ex}} = 444$ nm wavelength from blue-light scope, the emission bands for the transitions $^1\text{D}_2 \rightarrow ^3\text{F}_4$ (with maximum at ~ 1020 nm for GC1–6Pr₅₀₀ and GC1–6Pr₇₀₀ series to ~ 1050 nm for GC1–6Pr₉₀₀ series), $^1\text{G}_4 \rightarrow ^3\text{H}_5$ (~ 1350 nm), $^1\text{D}_2 \rightarrow ^1\text{G}_4$ (1460–1480 nm), and $^3\text{F}_{3,4} \rightarrow ^3\text{F}_4$



Fig. 12 Emission spectra recorded within the NIR range for Pr^{3+} -doped sol-gel samples prepared at 500 °C (a), 700 °C (b), and 900 °C (c). The comparison of emission spectra for the as-prepared xerogels and GC2Pr_x nano-glass-ceramics with $\text{La}^{3+}:\text{Pr}^{3+}$ molar ratio equal to 0.994:0.006 is also presented (d).



$^3\text{H}_4$ (shifted from 1570 nm for GC1-6Pr₅₀₀ series up to 1600 nm for GC1-6Pr₉₀₀ series) were clearly observed. These three latter emissions overlap and form one less-resolved band. Such NIR emissions are essential for telecommunication applications, covering E, S, C, and L bands.¹⁶

Similarly, as in the case of luminescence within the visible light scope, the modification in the La³⁺:Pr³⁺ molar ratio from 0.997:0.003 (GC1Pr_x) to 0.994:0.006 (GC2Pr_x) caused an increase in emission within the NIR region, while the further growing concentration of Pr³⁺ ions resulted in a substantial decrease in photoluminescence intensity. Additionally, as can be seen from Fig. 12d, the NIR emissions are enhanced with the gradual elevation in heat-treatment temperature of the parent xerogels from 500 °C up to 700 °C and 900 °C, clearly illustrating that the entry of Pr³⁺ into the LaF₃ phase as well as the removal of residual OH groups from the sol-gel host are crucial factors determining the NIR luminescence. This hypothesis could be additionally confirmed by the fully quenched NIR luminescence for the as-prepared xerogels, as shown in Fig. 12d. Similar to the PL spectra recorded in the VIS range (Fig. 7d), the presence of high-vibrational OH groups in the porous structure of the as-prepared xerogels determines the effective share of non-radiative transitions from the emitting levels, *i.e.*, $^1\text{D}_2$, $^1\text{G}_4$, and $^3\text{F}_{3,4}$, strongly quenching the NIR luminescence.

Independent from heat-treatment temperature, it should also be pointed out that the NIR luminescence for the prepared GC4Pr_x nano-glass-ceramics is strongly inhibited, and for samples with the highest content of Pr³⁺ ions (GC5Pr_x and GC6Pr_x), the emission is wholly quenched. The mechanism, which is responsible for the observed photoluminescence behavior, is according to the cross-relaxation (CR) processes involving the following channels: $\{^1\text{D}_2 + ^3\text{H}_4\} \rightarrow \{^1\text{G}_4 + (^3\text{F}_3, ^3\text{F}_4)\}$ and $\{^1\text{D}_2 + ^3\text{H}_4\} \rightarrow \{(^3\text{F}_3, ^3\text{F}_4) + ^1\text{G}_4\}$. Thus, the obtained results clearly indicate that NIR emissions are particularly sensitive to the shortening of the Pr³⁺-Pr³⁺ interionic distance. Indeed, for comparison, the luminescence from the $^3\text{P}_0$, $^3\text{P}_1$, and the $^1\text{D}_2$ excited states in the VIS range is well-observable even for the GC5Pr_x and GC6Pr_x samples with the highest Pr³⁺ concentration. Additionally, it could be observed that for the samples from the series heat-treated at 500 °C and 700 °C, the intensity of the wide band in the NIR region with a maximum located near 1470 nm ($^1\text{G}_4 \rightarrow ^3\text{H}_5$, $^1\text{D}_2 \rightarrow ^1\text{G}_4$, $^3\text{F}_{3,4} \rightarrow ^3\text{H}_4$ transitions) is dominant compared with the luminescence recorded at ~1050 nm ($^1\text{D}_2 \rightarrow ^3\text{F}_4$ transition). Interestingly, a gradual change in the mutual intensities of these emissions is well-observable for samples with the same La³⁺:Pr³⁺ molar ratio but fabricated at varied temperature conditions. The most prominent change in the bands' intensities was denoted for samples from the series prepared at 900 °C, especially for the GC3Pr₉₀₀ material, for which the intensity of the $^1\text{D}_2 \rightarrow ^3\text{F}_4$ emission line noticeably increased in comparison with a wide band according to the $^1\text{G}_4 \rightarrow ^3\text{H}_5$, $^1\text{D}_2 \rightarrow ^1\text{G}_4$, $^3\text{F}_{3,4} \rightarrow ^3\text{H}_4$ transitions. Therefore, such changes in the NIR luminescence profile of the studied sol-gel samples may indicate that the expected shortening in the Pr³⁺-Pr³⁺ distances

promotes the $\{^1\text{D}_2 + ^3\text{H}_4\} \rightarrow \{^1\text{G}_4 + (^3\text{F}_3, ^3\text{F}_4)\}$ cross-relaxation (CR) channel.

Luminescence decay analysis of the $^3\text{P}_0$ and the $^1\text{D}_2$ excited states of Pr³⁺

The further evaluation of the luminescence from Pr³⁺ ions in the series of prepared nano-glass-ceramic samples was carried out based on the analysis of the luminescence decay curves from $^3\text{P}_0$ ($\lambda_{\text{ex}} = 444$ nm, monitoring the $^3\text{P}_0 \rightarrow ^3\text{H}_4$ transition) as well as the $^1\text{D}_2$ excited states ($\lambda_{\text{ex}} = 444$ nm, monitoring the $^1\text{D}_2 \rightarrow ^1\text{G}_4$ transition). The resultant curves are presented in Fig. 13; all of them follow the second-order exponential nature, and the average lifetimes were calculated using the formula given below

$$\tau_{\text{avg}} = \frac{A_1\tau_1^2 + A_2\tau_2^2}{A_1\tau_1 + A_2\tau_2},$$

in which A_1 and A_2 are percentage residual weighting factors, and τ_1 and τ_2 are decay components. The bi-exponential character of the recorded curves is associated with the distribution of Pr³⁺ ions either between a silicate amorphous sol-gel host and LaF₃ nanocrystals, but it is also correlated with the involvement of cross-relaxation (CR) processes between neighboring Pr³⁺ ions if the critical interionic distance would be exceeded. It

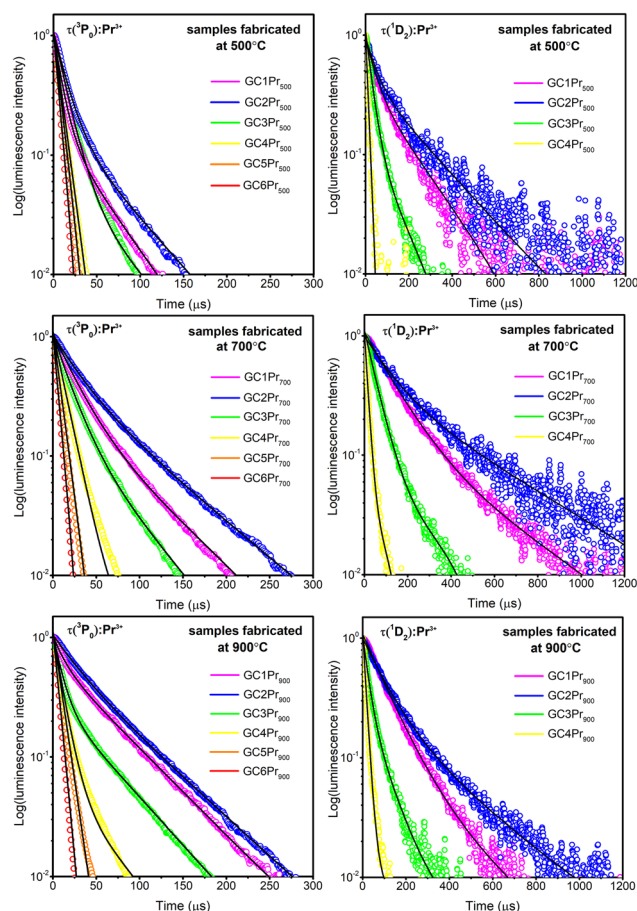


Fig. 13 Luminescence decay curves recorded for the $^3\text{P}_0$ and the $^1\text{D}_2$ states of Pr³⁺ ions in the fabricated nano-glass-ceramic samples.



should also be noted that the lifetimes of the 1D_2 state have been designated only for GC1Pr_x-GC3Pr_x glass-ceramics from each series. Although the NIR luminescence has been recorded for GC4Pr_x samples, but its intensity is very low; thus, the lifetimes would be calculated with a huge error. The resultant $\tau_{\text{avg}}(^3P_0):Pr^{3+}$ and $\tau_{\text{avg}}(^1D_2):Pr^{3+}$ average lifetimes, compared with the literature data for other Pr³⁺-doped oxyfluoride glass-ceramics, are collected in Tables 3 and 4, respectively. Generally, it

should be noticed that the lifetimes of the 1D_2 excited state are longer compared with those of the 3P_0 level, and similar observations were also reported for Pr³⁺-doped OxGCs containing BaF₂,³³ PbF₂,³⁹ and LaF₃ crystals.⁴¹

From the analysis of the obtained data, it could be assumed that the $\tau_{\text{avg}}(^3P_0):Pr^{3+}$ lifetimes are prolonged with changing La³⁺:Pr³⁺ molar ratio from 0.997:0.003 (24.9 μs (500 °C), 42.6 μs (700 °C), 53.4 μs (900 °C)) to 0.994:0.006 (31.8 μs (500 °C), 52.9 μs (700 °C), 58.4 μs (900 °C)). A similar tendency was observed for the $\tau_{\text{avg}}(^1D_2):Pr^{3+}$ lifetimes, whose values were changed from 106.0 μs (500 °C), 238.3 μs (700 °C), and 174.5 μs (900 °C) (for samples with La³⁺:Pr³⁺ molar ratio of 0.997:0.003) to 127.4 μs (500 °C), 274.5 μs (700 °C), and 195.3 μs (900 °C) (for La³⁺:Pr³⁺ molar ratio of 0.994:0.006). Further changes in the La³⁺:Pr³⁺ molar ratios resulted in a progressive and strong reduction in the $\tau_{\text{avg}}(^3P_0):Pr^{3+}$ and $\tau_{\text{avg}}(^1D_2):Pr^{3+}$ decay times to values of about ~5 μs (3P_0) and 35.5–58.1 μs (1D_2), respectively. Such optical behavior of the fabricated Pr³⁺-doped oxyfluoride sol-gel materials clearly indicates that a La³⁺:Pr³⁺ molar ratio of 0.994:0.006 determines the critical Pr³⁺-Pr³⁺ interionic distance, beyond which the concentration quenching process (CQ_{Pr}) is well-observable in each of the prepared series.

According to the $\tau_{\text{avg}}(^3P_0):Pr^{3+}$ lifetimes, it could be stated that their values undergo a progressive prolongation for the individual samples with the same La³⁺:Pr³⁺ molar ratio along with the simultaneous elevation of the heat-treatment temperature (500 °C, 700 °C, and 900 °C) of the initial amorphous xerogels. This behavior clearly reveals the beneficial impact of the efficient migration of Pr³⁺ into the lattice of LaF₃ nanocrystals characterized by low-phonon energy (~340 cm⁻¹) and the removal of OH groups from the sol-gel host on the photoluminescent properties. However, for the $\tau_{\text{avg}}(^1D_2):Pr^{3+}$ lifetimes, the observed tendency is slightly different because the longest decay times were denoted for the series of glass-ceramics heat-treated at 700 °C. In comparison with the samples from GC1-3Pr₅₀₀ series, the lifetimes of the 1D_2 level are noticeably extended for the GC1-3Pr₇₀₀ materials, indicating the favorable influence of the partial elimination of OH groups, which are mainly responsible as quenching channels for suppressing the photoluminescence in the NIR region; the observed elongation of $\tau_{\text{avg}}(^1D_2):Pr^{3+}$ lifetimes is also caused by the more efficient incorporation of Pr³⁺ ions inside the LaF₃ crystal lattice during annealing performed at 700 °C than at 500 °C. In contrast to the lifetimes from the 3P_0 state, the further elevation in the heat-treatment temperature (900 °C) led to the shortening of the decay times from the 1D_2 excited level, suggesting the progressive shortening of the Pr³⁺-Pr³⁺ distances, which is sufficient to quench the NIR luminescence. According to the differences mentioned above in the luminescence decay kinetics from the 3P_0 and the 1D_2 levels, it could be suggested that cross-relaxation (CR) processes occur in divergent ways for each of these two states. For this purpose, we compared the cross-relaxation efficiencies (η_{CR}) from the 3P_0 and the 1D_2 levels for the

Table 3 Luminescence lifetimes of the 3P_0 state for the prepared Pr³⁺-doped sol-gel samples

Oxyfluoride glass-ceramics	Type of crystalline phase	$\tau(^3P_0)$ [μs]	Ref.
GC1Pr ₅₀₀	LaF ₃	24.9	This work
GC2Pr ₅₀₀		31.8	
GC3Pr ₅₀₀		21.5	
GC4Pr ₅₀₀		7.9	
GC5Pr ₅₀₀		6.7	
GC6Pr ₅₀₀		5.3	
GC1Pr ₇₀₀	LaF ₃	42.6	This work
GC2Pr ₇₀₀		52.9	
GC3Pr ₇₀₀		31.0	
GC4Pr ₇₀₀		12.6	
GC5Pr ₇₀₀		7.9	
GC6Pr ₇₀₀		5.4	
GC1Pr ₉₀₀	LaF ₃	53.5	This work
GC2Pr ₉₀₀		58.4	
GC3Pr ₉₀₀		40.0	
GC4Pr ₉₀₀		20.4	
GC5Pr ₉₀₀		8.7	
GC6Pr ₉₀₀		4.9	
48.8TeO ₂ -30ZnO-10YF ₃ -10NaF-0.2Pr ₂ O ₃	NaYF ₄	24–62	1
41SiO ₂ -10Al ₂ O ₃ -25.5LiF-23SrF ₂ -0.5Pr ₂ O ₃	SrF ₂	12.0	30
67.7SiO ₂ -14.9BaF ₂ -12.9K ₂ CO ₃ -3La ₂ O ₃ -1.0Sb ₂ O ₃ -0.5Pr ₂ O ₃	BaF ₂	40–54	33
50GeO ₂ -45PbO-5PbF ₂ :2 mol% Pr ³⁺	PbF ₂	8.5	39
45SiO ₂ -15Al ₂ O ₃ -10Na ₂ O-24BaF ₂ -6Y ₂ O ₃ :0.1 mol% Pr ³⁺	BaYF ₅	30.1	40
40SiO ₂ -20Al ₂ O ₃ -20LiF-19GdF ₃ -1.0PrF ₃	LiGdF ₄ /GdF ₃	57.0	41

Table 4 Luminescence lifetimes of the 1D_2 state for the prepared Pr³⁺-doped sol-gel samples

Oxyfluoride glass-ceramics	Type of crystalline phase	$\tau(^1D_2)$ [μs]	Ref.
GC1Pr ₅₀₀	LaF ₃	106.0	This work
GC2Pr ₅₀₀		127.4	
GC3Pr ₅₀₀		99.3	
GC4Pr ₅₀₀		35.5	
GC1Pr ₇₀₀		238.3	
GC2Pr ₇₀₀		274.5	
GC3Pr ₇₀₀	LaF ₃	151.6	This work
GC4Pr ₇₀₀		58.1	
GC1Pr ₉₀₀		174.8	
GC2Pr ₉₀₀		195.3	
GC3Pr ₉₀₀		132.2	
GC4Pr ₉₀₀		49.2	
67.7SiO ₂ -14.9BaF ₂ -12.9K ₂ CO ₃ -3La ₂ O ₃ -1.0Sb ₂ O ₃ -0.5Pr ₂ O ₃	BaF ₂	51–78	33
50GeO ₂ -45PbO-5PbF ₂ :2 mol% Pr ³⁺	PbF ₂	109.0	39
SiO ₂ -Al ₂ O ₃ -AlF ₃ -Na ₂ CO ₃ -NaNO ₃ -BaCO ₃ -Ba(NO ₃) ₂ -LaF ₃ :Pr ³⁺ (x = 0.01–0.5 mol%)	LaF ₃	525–25	41



studied glass-ceramic samples based on estimations from the below equation.³

$$\eta_{\text{CR}} = \left(1 - \frac{\tau_{\text{GCxPr}}}{\tau_{\text{GC2Pr}}}\right) \times 100\%,$$

where τ_{GCxPr} is the decay time of the $^3\text{P}_0$ or $^1\text{D}_2$ state of Pr^{3+} for individual samples from the series ($\text{GC3Pr}_x\text{-GC6Pr}_x$), and τ_{GC2Pr} is the appropriate lifetime for samples with $\text{La}^{3+}:\text{Pr}^{3+}$ 0.994:0.006 molar ratio, beyond which concentration quenching (CQ_{Pr}) occurred. For the $^3\text{P}_0$ level, the η_{CR} values are 32%, 75%, 79%, and 83% for $\text{GC3Pr}_{500}\text{-GC6Pr}_{500}$ samples, 41%, 76%, 85%, and 90% for $\text{GC3Pr}_{700}\text{-GC6Pr}_{700}$ series, as well as 32%, 65%, 85%, and 92% for $\text{GC3Pr}_{900}\text{-GC6Pr}_{900}$ glass-ceramics. Therefore, it could be observed that the $\eta_{\text{CR}}(^3\text{P}_0)$ values for the samples with the same $\text{La}^{3+}:\text{Pr}^{3+}$ molar ratio but fabricated at different temperature conditions are quite similar; however, $\eta_{\text{CR}}(^3\text{P}_0) \geq 90\%$ values were achieved only for samples from the series obtained at 700 °C and 900 °C. The η_{CR} values for the $^1\text{D}_2$ state changed for GC3Pr_x as follows: 22% (GC3Pr_{500}), 45% (GC3Pr_{700}), and 32% (GC3Pr_{900}). It is quite interesting that $\eta_{\text{CR}}(^3\text{P}_0) > \eta_{\text{CR}}(^1\text{D}_2)$ for GC3Pr_{500} , and $\eta_{\text{CR}}(^3\text{P}_0) \approx \eta_{\text{CR}}(^1\text{D}_2)$ for GC3Pr_{700} and GC3Pr_{900} . Additionally, based on the NIR spectra (Fig. 12) and completely quenched luminescence for GC5Pr and GC6Pr samples from the series fabricated at 700 °C and 900 °C (it should be noted that for the GC5Pr_{500} sample, weak NIR emission is still detectable), we assumed that further differences in the $\eta_{\text{CR}}(^1\text{D}_2)$ values would be highly visible, indicating that the luminescence from the $^1\text{D}_2$ state is strongly sensitive to $\text{Pr}^{3+}\text{-Pr}^{3+}$ interionic distances in the studied sol-gel materials. Therefore, based on the performed luminescence measurements, we could suppose that the effect of cross-relaxation (CR) processes from the $^1\text{D}_2$ excited state of Pr^{3+} on the overall luminescence – compared to the cross-relaxation (CR) processes from the $^3\text{P}_0$ state – is particularly dependent on the heat-treatment temperature of initial xerogels, which influences the preferable cumulation of Pr^{3+} ions inside the LaF_3 phase, resulting in the probability of formation of continuously arranged PrF_3 clusters for samples fabricated at 700 °C and 900 °C (as was tentatively assumed from the performed ATR-IR and XRD measurements). In addition, it seems that the size of the precipitated fluoride nanocrystals obtained for individual series of sol-gel samples could also influence the involvement of CR processes, which might be potentially correlated with uniformity in Pr^{3+} distribution inside the fluoride crystal phase.

Conclusions

In this work, we have synthesized and investigated the series of oxyfluoride Pr^{3+} -doped nano-glass-ceramics fabricated by sol-gel method and annealed at different temperatures, *i.e.*, 500 °C, 700 °C, and 900 °C. Based on the performed structural measurements (XRD, ATR-IR) and TEM microscopy, it was

proven that the gradual elevation of annealing temperature favors the densification of the silicate sol-gel host by the efficient removal of OH groups and crystallization of the LaF_3 phase in the nanometer range, with preferable cumulated Pr^{3+} optically active ions. Additionally, the observed changes in the localization of the IR signal assigned to the vibrations of the fluoride crystal lattice allowed for the tentative assumption that the incorporation of Pr^{3+} ions inside the LaF_3 phase is so effective that increasing the Pr^{3+} concentration in the samples from the series fabricated at 700 °C and 900 °C favors the formation of continuously arranged PrF_3 clusters within the LaF_3 parent crystal phase. All of the prepared $\text{LaF}_3:\text{Pr}^{3+}$ -based oxyfluoride nano-glass-ceramic samples exhibit strong luminescence in the VIS range from greenish-blue to reddish-orange light, whose combination allows for successfully obtaining warm or neutral white light emissions with CCT values ranging from 2567 K to 3962 K. Additionally, the luminescence of Pr^{3+} ions within the NIR region was also recorded, and it covers E, S, C, and L bands belonging to the fifth optical telecommunication window. Based on the luminescence decay analysis, it was verified that the longest lifetimes of the $^3\text{P}_0$ excited state were attributed to glass-ceramics fabricated by the controlled heat-treatment of initial xerogels at 900 °C, while the longest lifetimes of the $^1\text{D}_2$ level was attributed to samples from the series annealed at 700 °C. Independently from the heat-treatment conditions, the longest decay times, both for the $^3\text{P}_0$ and the $^1\text{D}_2$ levels, were estimated for samples with $\text{La}^{3+}:\text{Pr}^{3+}$ molar ratio of 0.994:0.006, beyond which the concentration quenching (CQ_{Pr}) process between neighboring Pr^{3+} ions takes place. Further analysis of the decay kinetics showed that the involvement of cross-relaxation (CR) channels from the $^1\text{D}_2$ state is particularly sensitive to the heat-treatment conditions, which could be correlated with the size of the fluoride crystals and the possible creation of PrF_3 clusters within the parent LaF_3 fluoride crystal lattice. The obtained results suggest that the fabricated Pr^{3+} -doped oxyfluoride sol-gel nano-glass-ceramics could be predisposed for applications as white light emitters and optical elements of NIR amplifiers.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The research activities are co-financed by the funds granted under the Research Excellence Initiative of the University of Silesia in Katowice.

References

- 1 D. Rajesh, *Opt. Mater.*, 2018, **86**, 178.
- 2 H. Lee, W. J. Chung and W. B. Im, *J. Lumin.*, 2021, **236**, 118064.



- 3 C. Y. Morassuti, L. H. C. Andrade, J. R. Silva, M. L. Baesso, F. B. Guimarães, J. H. Rohling, L. A. O. Nunes, G. Boulon, Y. Guyot and S. M. Lima, *J. Lumin.*, 2019, **210**, 376.
- 4 T. Q. H. Tran, M. H. Hoang, T. A. T. Do, A. T. Le, T. H. Nguyen, T. D. Nguyen and M. T. Man, *J. Lumin.*, 2021, **237**, 118162.
- 5 N. Deopa, A. S. Rao Dr., S. k. Mahamuda, M. Gupta, M. Jayasimhadri, D. Haranath and G. Vijaya Prakash, *J. Alloys Compd.*, 2017, **708**, 911.
- 6 Z. He, C. Zhu, S. Huang and X. Wu, *Vacuum*, 2019, **159**, 269.
- 7 Z. Chen, X. Wang, S. Pan and J. Pan, *J. Lumin.*, 2021, **236**, 118141.
- 8 F. Zhang, Z. Bi, A. Huang and Z. Xiao, *J. Lumin.*, 2015, **160**, 85.
- 9 W. Wang, J. Tian, N. Li, J. Dong, Q. Wang, Y. Xu, X. Xu, H. Tang, H. Lin, D. Li and J. Xu, *J. Alloys Compd.*, 2021, **887**, 161327.
- 10 M. Venkateswarlu, M. V. V. K. S. Prasad, K. Swapna, Sk. Mahamuda, A. S. Rao, A. M. Babu and D. Haranath, *Ceram. Int.*, 2014, **40**, 6261.
- 11 A. Jusza, L. Lipińska, M. Baran, A. Olszyna, A. Jastrzębska, M. Gil, P. Mergo and R. Piramidowicz, *Opt. Mater.*, 2019, **95**, 109247.
- 12 A. K. Bedyal, D. D. Ramteke, V. Kumar and H. C. Swart, *Mater. Res. Bull.*, 2018, **103**, 173.
- 13 L. R. R. Nunes, H. P. Labaki, F. J. Caixeta and R. R. Gonçalves, *J. Lumin.*, 2022, **241**, 118485.
- 14 M. Y. Tsang, P. Fałat, M. A. Antoniuk, R. Ziniuk, S. J. Zelewski, M. Samoć, M. Nyk, J. Ou, T. Y. Ohulchansky and D. Wawrzyńczyk, *Nanoscale*, 2022, **14**, 14770.
- 15 Y. Fan, P. Wang, Y. Lu, R. Wang, L. Zhou, X. Zheng, X. Li, J. A. Piper and F. Zhang, *Nat. Nanotechnol.*, 2018, **13**, 941.
- 16 L. F. Shen, B. J. Chen, H. Lin and E. Y. B. Pun, *J. Alloys Compd.*, 2015, **622**, 1093.
- 17 D. Wei, H. J. Seo, Y. Liu and X. Yang, *J. Lumin.*, 2023, **253**, 119488.
- 18 S. Wang, J. Zhang, Z. Ye, H. Yu and H. Zhang, *Chem. Eng. J.*, 2021, **414**, 128884.
- 19 R. Shi, L. Lin, P. Dorenbos and H. Liang, *J. Mater. Chem. C*, 2017, **5**, 10737.
- 20 J. Stefanska, K. Maciejewska and L. Marciniak, *New J. Chem.*, 2021, **45**, 11898.
- 21 M. Runowski, P. Woźny, I. R. Martín, V. Lavín and S. Lis, *J. Lumin.*, 2019, **214**, 116571.
- 22 M. S. Pudovkin, O. A. Morozov, V. V. Pavlov, S. L. Korableva, E. V. Lukinova, Y. N. Osin, V. G. Evtugyn, R. A. Safiullin and V. V. Semashko, *J. Nanomater.*, 2017, 3108586.
- 23 M. S. Pudovkin, S. L. Korableva, D. A. Koryakovtseva, E. V. Lukinova, A. V. Lovchev, O. A. Morozov and V. V. Semashko, *J. Nanopart. Res.*, 2019, **21**, 266.
- 24 J. P. Zuniga, S. K. Gupta, M. Pokhrel and Y. Mao, *New J. Chem.*, 2018, **42**, 9381.
- 25 E. Elsts, G. Krieke, U. Rogulis, K. Smits, A. Zolotarjovs, J. Jansons, A. Sarakovskis and K. Kundzins, *Opt. Mater.*, 2016, **59**, 130.
- 26 R. Kamal and H. Hafez, *Novel, Opt. Mater.*, 2021, **121**, 111646.
- 27 P. Singh and J. Joshi, *J. Lumin.*, 2018, **203**, 331.
- 28 M. Kuwik, C. K. Jayasankar, W. A. Pisarski and J. Pisarska, *J. Alloys Compd.*, 2020, **842**, 155801.
- 29 L. P. Naranjo, N. T. C. Oliveira, L. R. P. Kassab and C. B. de Araújo, *J. Lumin.*, 2021, **238**, 118225.
- 30 C. R. Kesavulu, C. S. Dwaraka Viswanath, S. Karki, P. Aryal, H. J. Kim and C. K. Jayasankar, *Ceram. Int.*, 2018, **44**, 1737.
- 31 T. Murakami and S. Tanabe, *J. Ceram. Soc. Jpn.*, 2007, **115**, 605.
- 32 C. Koepke, M. Środa, A. Marczevska, K. Wisniewski and P. Pichniarczyk, *J. Lumin.*, 2016, **179**, 139.
- 33 K. Biswas, A. D. Sontakke, J. Ghosh and K. Annapurna, *J. Am. Ceram. Soc.*, 2010, **93**, 1010.
- 34 H. Zheng, X.-J. Wang, S.-X. Qu, M. J. Dejneka and R. S. Meltzer, *J. Lumin.*, 2006, **119–120**, 153.
- 35 X.-J. Wang, S. H. Huang, R. Reeves, W. Wells, M. J. Dejneka, R. S. Meltzer and W. M. Yen, *J. Lumin.*, 2001, **94–95**, 229.
- 36 Y. Xu, X. Zhang, S. Dai, B. Fan, H. Ma, J.-L. Adam, J. Ren and G. Chen, *J. Phys. Chem. C*, 2011, **115**, 13056.
- 37 H. Zheng, X.-J. Wang, M. J. Dejneka, W. M. Yen and R. S. Meltzer, *J. Lumin.*, 2004, **108**, 395.
- 38 Y. Yu and X. Li, *Mater. Res. Bull.*, 2016, **73**, 96.
- 39 B. Klimesz, G. Dominiak-Dzik, P. Solarz, M. Żelechower and W. Ryba-Romanowski, *J. Alloys Compd.*, 2004, **382**, 292.
- 40 M. Gu, Q.-C. Gao, S.-M. Huang, X.-L. Liu, B. Liu and C. Ni, *J. Lumin.*, 2012, **132**, 2531.
- 41 G. Lakshminarayana and J. Qiu, *Phys. B*, 2009, **404**, 1169.
- 42 J. J. Velázquez, R. Balda, J. Fernández, G. Gorni, L. Pascual, G. Chen, M. Sundararajan, A. Durán and M. J. Pascual, *J. Lumin.*, 2018, **193**, 61.
- 43 Y. Sun, M. Wu, S. Tian, Z. Shi, Z. Lun, Q. Jiang, Y. Zhao, D. Chen, P. Xiong and Z. Yang, *J. Mater. Chem. C*, 2022, **10**, 5266.
- 44 P. P. Fedorov, A. A. Luginina and A. I. Popov, *J. Fluor. Chem.*, 2015, **172**, 22.
- 45 A. E. Danks, S. R. Hall and Z. Schnepf, *Mater. Horiz.*, 2016, **3**, 91.
- 46 J. J. Velázquez, A. C. Yanes, J. del-Castillo, J. Méndez-Ramos and V. D. Rodríguez, *J. Non-Cryst. Solids*, 2010, **356**, 1349.
- 47 N. Pawlik, B. Szpikowska-Sroka, T. Goryczka, M. Zubko, J. Lelątko and W. A. Pisarski, *J. Eur. Ceram. Soc.*, 2019, **39**, 5010.
- 48 P. Innocenzi, *J. Non-Cryst. Solids*, 2003, **316**, 309.
- 49 G. Gorni, M. J. Pascual, A. Caballero, J. J. Velázquez, J. Mosa, Y. Castro and A. Durán, *J. Non-Cryst. Solids*, 2018, **501**, 145.
- 50 C. Kinowski, M. Bouazaoui, R. Bechara, L. L. Hench, J. M. Nedelec and S. Turrell, *J. Non-Cryst. Solids*, 2001, **291**, 143.
- 51 R. M. Almeida, H. C. Vasconcelos and L. M. Ilharco, *SPIE Sol-gel Optics III*, 1994, **2288**, 678.
- 52 T. M. Parrill, *J. Mater. Res.*, 1992, **7**, 2230.



- 53 N. Pawlik, B. Szpikowska-Sroka, E. Pietrasik, T. Goryczka and W. A. Pisarski, *J. Am. Ceram. Soc.*, 2018, **101**, 4654.
- 54 F. Kadlec, P. Simon and N. Raimboux, *J. Phys. Chem. Solids*, 1998, **60**, 861.
- 55 X. Chen and Y. Wu, *J. Alloys Compd.*, 2020, **817**, 153075.
- 56 P. D'Angelo, A. Zitolo, V. Migliorati, G. Chillemi, M. Duvail, P. Vitorge, S. Abadie and R. Spezia, *Inorg. Chem.*, 2011, **50**, 4572.
- 57 A. Kovács, R. J. M. Konings and A. S. Booij, *Vib. Spectrosc.*, 1995, **10**, 65.
- 58 S. Devesa, A. P. Rooney, M. P. Graça, D. Cooper and L. C. Costa, *Mater. Sci. Eng., B*, 2021, **263**, 114830.
- 59 A. Le Bail, *Powder Diff.*, 2005, **20**, 316.
- 60 W. Korczak and P. Mikołajczak, *J. Cryst. Growth*, 1983, **61**, 601.
- 61 R. B. Roberts and G. K. White, *J. Phys. C: Solid State Phys.*, 1986, **19**, 7167.
- 62 J. Stefanska and L. Marciniak, *Adv. Photonics Res.*, 2021, 2100070.
- 63 A. M. Klonkowski, W. Wiczak, J. Ryl, K. Szczodrowski and D. Wileńska, *J. Alloys Compd.*, 2017, **724**, 649.
- 64 V. H. Rao, P. S. Prasad and K. S. Babu, *Opt. Mater.*, 2020, **101**, 109740.
- 65 M. Y. A. Yagoub, H. C. Swart and E. Coetsee, *Mater. Res. Bull.*, 2017, **93**, 170.
- 66 C. S. McCamy, *Color Res. Appl.*, 1992, **17**, 142.
- 67 D. Ramachari, L. Rama Moorthy and C. K. Jayasankar, *Ceram. Int.*, 2014, **40**, 11115.
- 68 I. Golasi, F. Salata, E. de Lieto Vollaro and A. Peña-García, *Energy Build.*, 2019, **185**, 112.
- 69 C. Liu, L. Sun, X. Jing, Y. Zhang, X. Meng, C. Jia and W. Gao, *J. Build. Eng.*, 2022, **45**, 103573.
- 70 A. S. Gouveia-Neto, N. P. S. M. Rios and L. A. Bueno, *Opt. Mater.*, 2012, **35**, 126.
- 71 W. Tang, B. Wang, Y. Chen, Y. Chen, J. Lin and Q. Zeng, *Opt. Mater. Express*, 2019, **9**, 223.
- 72 D. Zeng, Y. Chen, K. Cai, C. Peng and S. Peng, *J. Lumin.*, 2019, **206**, 376.
- 73 Y.-F. Wu, Y.-T. Nien, Y.-J. Wang and I.-G. Chen, *J. Am. Ceram. Soc.*, 2012, **95**, 1360.
- 74 S. Sharma, N. Brahme, D.P. Bisen and P. Dewangan, *Opt. Express*, 2018, **26**, 29495.

