

Synthesis and Characterization of $\text{Li}_2\text{MgGeO}_4:\text{Ho}^{3+}$

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Abstract: In this work, the synthesis and characterization of $\text{Li}_2\text{MgGeO}_4:\text{Ho}^{3+}$ ceramics were reported. The X-ray diffraction measurements revealed that the studied ceramics belong to the monoclinic $\text{Li}_2\text{MgGeO}_4$. Luminescence properties were analyzed in the visible spectral range. Green and red emission bands correspondent to the $^5\text{F}_4, ^5\text{S}_2 \rightarrow ^5\text{I}_8$ and $^5\text{F}_5 \rightarrow ^5\text{I}_8$ transitions of Ho^{3+} were observed, and their intensities were significantly dependent on activator concentration. Luminescence spectra were also measured under direct excitation of holmium ions or ceramic matrix. Holmium ions were inserted in crystal lattice $\text{Li}_2\text{MgGeO}_4$, giving broad blue emission and characteristic 4f-4f luminescent transitions of rare earths under the selective excitation of the ceramic matrix. The presence of the energy transfer process between the host lattice and Ho^{3+} ions was suggested.

Keywords: $\text{Li}_2\text{MgGeO}_4$; Ho^{3+} ions; structure; luminescence



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1. Introduction

Holmium-doped materials are really interesting optical systems due to several 4f-4f electronic transitions operating in the visible and near-IR spectral ranges [1–4]. The energy level diagram of Ho^{3+} ions favors various radiative and non-radiative pathways dependent on the activator concentration, excitation wavelengths, host matrices, and their phonon energies. Trivalent holmium ions were introduced to numerous inorganic glasses [5–9], ceramics [10–12], and other nanoparticles synthesized using the sol–gel method [13]. Special attention has been paid to Ho^{3+} -doped ceramic phosphors with superior luminescence properties. Ho^{3+} -doped (K,Na)NbO₃-based multifunctional ceramics present excellent optical temperature-sensing performance [14]. Such systems possess an optical temperature sensitivity higher than other rare-earth-doped ceramics or glasses, suggesting their attractive applications, especially in temperature-sensing devices. The same situation was also observed for similar Ho^{3+} -doped ceramic compounds [15–18]. These aspects were also reported in the excellent review that was published recently [19]. Holmium-doped $\text{Y}_2\text{Zr}_2\text{O}_7$ ceramics [20] were proposed as a new type of laser materials emitting visible light. The experimental results demonstrate that $\text{Y}_2\text{Zr}_2\text{O}_7:\text{Ho}^{3+}$ ceramics are able to generate efficient down- and upconversion luminescence. Further studies revealed that $\text{Y}_2\text{O}_3\text{-MgO}:\text{Ho}^{3+}$ ceramics are novel IR-transparent nanocomposite ceramics [21] that can be applied to high-power eye-safe near-infrared lasers operating at about 2000 nm.

In this work, we show preliminary results for holmium-doped $\text{Li}_2\text{MgGeO}_4:\text{Ho}^{3+}$ germanate ceramics. In particular, their visible emission properties under different excitation wavelengths were examined in detail. These germanate ceramic systems are less documented in the literature. The previously published works were mainly concentrated on luminescence investigations of $\text{Li}_2\text{MgGeO}_4:\text{Mn}^{2+}$. Germanate ceramic $\text{Li}_2\text{MgGeO}_4:\text{Mn}^{2+}$ was

proposed as a green long-persistent phosphor [22]. Trap-controlled reproducible mechano-luminescent (ML) $\text{Li}_2\text{MgGeO}_4:\text{Mn}^{2+}$ materials were also developed, and their short-term non-decaying ML behavior was reported [23]. Further investigations offering a constructive prospect for developing novel functional mechanoluminescent $\text{Li}_2\text{MgGeO}_4:\text{xMn}^{2+}$ phosphors by defect control are also presented and discussed [24]. Optical properties of rare earths, especially Ho^{3+} ions in $\text{Li}_2\text{MgGeO}_4$ ceramics, have not yet been reported, to the best of our knowledge. Therefore, the synthesis and characterization of $\text{Li}_2\text{MgGeO}_4:\text{Ho}^{3+}$ are exhibited here.

2. Experimental Methods

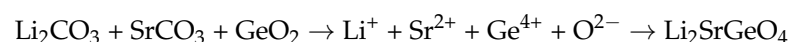
Germanate ceramics were characterized by a SETARAM Labsys thermal analyzer (SETERAM Instrumentation, Caluire, France) using the DSC method. The DSC curve was acquired in the range from room temperature to 1100 °C at the standard rate of 10 °C/min. The X-ray diffraction patterns were measured using an X'Pert-Pro diffractometer (PANalytical, Eindhoven, The Netherlands). The microstructure of germanate ceramics was observed using a JSM6480 scanning electron microscope (Jeol Ltd., Tokyo, Japan) as well as a JSM-7100F TTL LV (Jeol Ltd., Tokyo, Japan). The UV-VIS diffuse-reflectance spectra were collected using a Cary 5000 UV-VIS-NIR spectrophotometer, (Agilent Technology, Santa Clara, CA, USA). Excitation and luminescence measurements were carried out on a Photon Technology International (PTI) Quanta-Master 40 (QM40) UV/VIS Steady State Spectrofluorometer coupled with a tunable pulsed optical parametric oscillator (OPO) pumped by a third harmonic of a Nd:YAG laser (Opotek Opolette 355 LD, OPOTEK, Carlsband, CA, USA). The laser system included a double 200 mm monochromator, a xenon lamp as a light source, and a multimode UVVIS PMT (R928) (PTI Model 914, Horiba Instruments, New York, NY, USA) detector. The spectral resolution was equal to 0.5 nm. The Commission Internationale de l'Éclairage (CIE) chromaticity coordinates (x, y) and chromaticity diagram for $\text{Li}_2\text{MgGeO}_4$ ceramics doped with Ho^{3+} ions were calculated from the emission spectra and plotted using *Color Calculator* software (Osram Sylvania, Inc., Wilmington, MA, USA). Decay curves were recorded by a PTI ASOC-10 [USB-2500] oscilloscope (Horiba Instruments, New York, NY, USA) with an accuracy of $\pm 0.5 \mu\text{s}$. All experiments were carried out at room temperature.

3. Results and Discussion

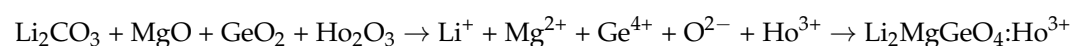
3.1. Synthesis

Holmium-doped germanate ceramics with the following chemical compositions $\text{Li}_2\text{Mg}_{(100-x)}\text{GeO}_4:\text{xHo}^{3+}$ in molar % (where $x = 0, 0.5, 2.5,$ and 5) were prepared by the solid-state reaction method using precursor powders of high purity (Sigma-Aldrich Chemical Co., St. Louis, MO, USA). The initial reagents Li_2CO_3 (99.997%), MgO (99.99%), GeO_2 (99.99%), and optical active dopant Ho_2O_3 (99.999%) were weighed in stoichiometric amounts and mixed together homogeneously in an agate mortar for 1 h with ethanol (POCH Basic 96% pure) as a medium.

After the samples were grounded, the mixtures were calcinated in the muffle furnace (FCF 5 5SHP produced by Czylok, Jastrzębie-Zdrój, Poland) in a non-covered platinum crucible at 1100 °C for 6 h in the ambient air to achieve decarbonization. According to the results for similar $\text{Li}_2\text{SrGeO}_4$ phosphors obtained by Huang and Li [25], the following reaction takes place during calcination:



Thus, it can be assumed that for the synthesized $\text{Li}_2\text{MgGeO}_4:\text{Ho}^{3+}$ ceramics, referred to here as LMG- Ho^{3+} , the following reaction occurs:



The calcination process consisted of two steps. The temperature was increased to $T = 800\text{ }^{\circ}\text{C}$ in 30 min, then the furnace reached $1100\text{ }^{\circ}\text{C}$ in 10 min. The samples were kept at this temperature for 5 h and 20 min.

In the next step, the granulated powders were divided into smaller batches and then mixed with an organic binder for 0.5 h. Among possible binders, polyvinyl alcohol (PVA) can be successfully used to receive germanate ceramic pellets. In general, PVA was often used as a binder [26–29]. The mixtures were uniaxially pressed into pellets of 10 mm diameter under 375 MPa. The prepared pellets were gradually heated to remove the PVA binder at $550\text{ }^{\circ}\text{C}$. The temperature was raised by $3\text{ }^{\circ}\text{C}/\text{min}$ until the appropriate temperature was achieved. The samples were annealed for 2 h under ambient air conditions and naturally cooled to room temperature.

Lastly, the ceramic samples were sintered in a high-temperature furnace (FCF 4/170M produced by Czylok, Jastrzębie-Zdrój, Poland) at $1200\text{ }^{\circ}\text{C}$ for 5 h. The thermal and structural results for olivine-type germanates presented previously and discussed by Koseva et al. [30] indicate that the annealing temperature of 1373 K ($1100\text{ }^{\circ}\text{C}$) is optimal for obtaining well-crystallized phase-pure samples. It is worth noting that germanium dioxide has a low melting point at $1115\text{ }^{\circ}\text{C}$; therefore, the germanate olivines have low sintering temperatures [31]. In our synthesis procedure, the free sintering process consisted of several steps. First, the temperature was increased up to $800\text{ }^{\circ}\text{C}$ for 1 h, and the samples were sintered without increasing the temperature for 15 min. Next, the furnace was heated to $1200\text{ }^{\circ}\text{C}$ at a rate of $9\text{ }^{\circ}\text{C}/\text{min}$. The samples were sintered at the set temperature for 3 h. After this time, the resulting ceramics were cooled down to room temperature in a closed furnace.

3.2. Characterization

Figure 1 presents a representative DSC curve (a) and X-ray diffraction patterns (b) recorded for the studied LMG- Ho^{3+} ceramic system.

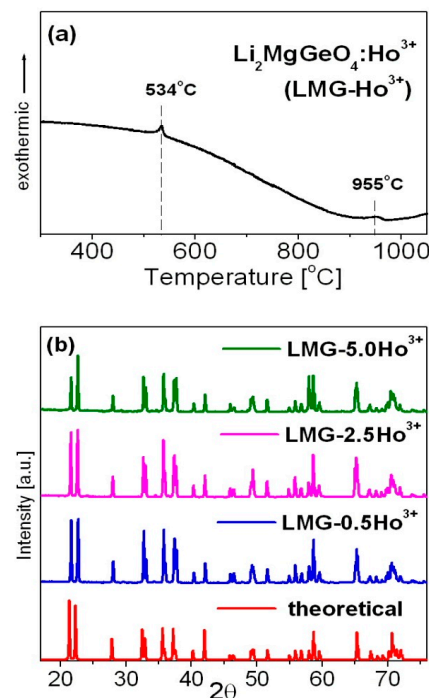


Figure 1. Representative DSC curve (a) and X-ray diffraction patterns (b) of LMG- Ho^{3+} .

$\text{Li}_2\text{MgGeO}_4:\text{Ho}^{3+}$ germanate ceramics (LMG- Ho^{3+}) show two phase transitions [30]. The low-temperature phase transition near $T = 534\text{ }^{\circ}\text{C}$ is related to insignificant changes in the monoclinic symmetry. The high-temperature phase transition at about $955\text{ }^{\circ}\text{C}$ is

assigned to the transition from monoclinic to orthorhombic symmetry. The X-ray diffraction analysis confirmed that the studied LMG-Ho³⁺ ceramic systems crystallize in a monoclinic crystal lattice. The narrow diffraction lines are in a good agreement with the theoretical pattern belonging to the monoclinic Li₂ZnGeO₄ (ICDD PDF-4 database—card no 04-015-4929), which is isostructural to Li₂MgGeO₄ [32]. The schematic crystal structure of Li₂ZnGeO₄ belonging to the same monoclinic crystal system with P2₁/n space group as Li₂MgGeO₄ was presented by Lin et al. [33].

The introduction of Ho³⁺ playing the role of active doping ions to the host matrix Li₂MgGeO₄ do not cause any significant changes in the crystal structure. Independent of the Ho³⁺ concentration (0.5, 2.5, and 5 mol%), the XRD patterns without additional diffraction peaks due to impurities are almost consistent with pure Li₂MgGeO₄ monoclinic phase. This suggests that trivalent holmium ions are well-entered into the Li₂MgGeO₄ crystalline lattice. Furthermore, the Mg²⁺ ions are substituted by Ho³⁺ ions similar to Li₂AGeO₄ compounds, where the atomic positions of A²⁺ ions may be occupied by trivalent rare earth ions such as Ce³⁺, Tb³⁺, or Dy³⁺ [25]. The introduction of rare earth ions to the Li₂MgGeO₄ host matrix due to the substitution of a divalent cation (Mg²⁺) by a trivalent ion (Ho³⁺) can result in charge imbalance. It is well-known that charge compensation can be achieved by creating defects in the crystal lattice. The presence of defects in the ceramic host leads to the weakness of luminescent properties. However, the incorporation of alkali ions (Li⁺ or Na⁺) might compensate for the charge imbalance, reduce the lattice distortion, and enhance luminescence intensity without creating impurities in the host structure [34–38]. It should be also noted that agglomerates are present in the studied germanate ceramics. The diameter of agglomerates is changed from several dozen micrometers to even 150 μm. Most agglomerates have a diameter of around 40 μm. For the LMG-Ho³⁺ system, the grain sizes do not exceed 10 μm, which was verified using scanning electron microscopy (SEM). SEM images of the LMG-Ho³⁺ ceramic host are shown in Figure 2.

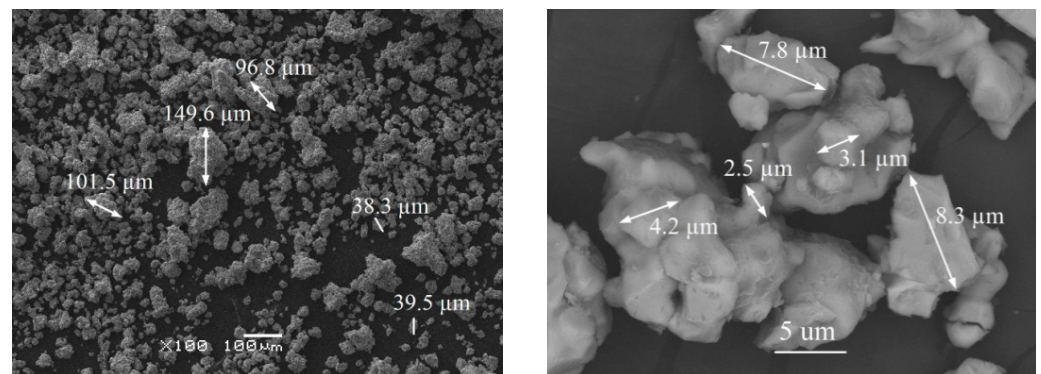


Figure 2. SEM images of LMG-Ho³⁺.

Figure 3 presents the UV-VIS diffuse-reflectance spectra for LMG-Ho³⁺ ceramics with different concentrations of holmium ions (0.5, 2.5, and 5 mol%) that were registered at room temperature in the 225–800 nm spectral region. Several narrow absorption peaks corresponding to intra-configurational 4f-4f electronic transitions from ground state ⁵I₈ to higher-lying excited states of trivalent holmium are quite well observed. The registered absorption peaks are centered at about ~360 nm, ~415 nm, ~450 nm, ~535 nm, and ~635 nm and originated from the ⁵I₈→³H_{5,6}; ⁵I₈→³G_{4,5}; ⁵I₈→⁵G₆,⁵F₂,³K₈; ⁵I₈→⁵F₃; ⁵I₈→⁵S₂,⁵F₄; and ⁵I₈→³F₅ transitions, respectively [39]. The strongest absorption, located at 450 nm, is attributed to the ⁵I₈→²G₆,⁵F₂,³K₈ transition of Ho³⁺ ions. The obtained results clearly show that with increasing optically active dopants the intensity of absorption peaks also increases, keeping the same intensity ratios between the recorded peaks.

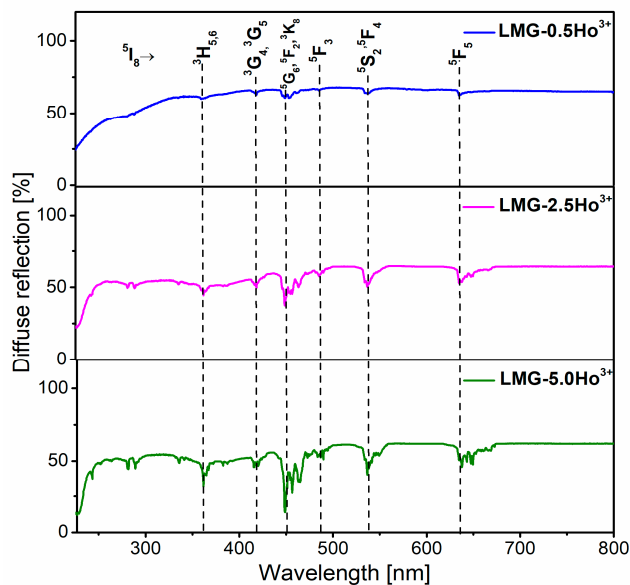


Figure 3. Reflectance spectra of LMG-0.5Ho³⁺, LMG-2.5Ho³⁺, and LMG-5.0Ho³⁺.

The crucial aspect of analyzing the optical properties of transparent glass-ceramics, ceramics, and various phosphors is the characterization of the luminescence, which results from the 4f-4f electronic transitions of rare earth ions [40–47]. It is worth noting that studies of ceramic samples containing trivalent holmium ions are focused on characterizing the efficient green visible emission [6,18,48]. In general, as a result of the excitation of Ho³⁺ ions, the energy is transferred via non-radiative decay from higher-lying excited levels such as ³H₅, ³H₆, ⁵G₄, ⁵G₅, ⁵G₆, ⁵F₂, and ⁵F₃ to levels ⁵F₄, ⁵S₂, and ⁵F₅ of trivalent holmium ions. Afterward, the excitation energy is transferred to the ground state and causes emitting radiation due to characteristic transitions of Ho³⁺ ions. The emission spectra in the visible range, measured for the LMG-Ho³⁺ ceramic samples under the direct excitation of Ho³⁺ ions ($\lambda_{exc} = 453 \text{ nm}$), consist of two well-separated bands (Figure 4).

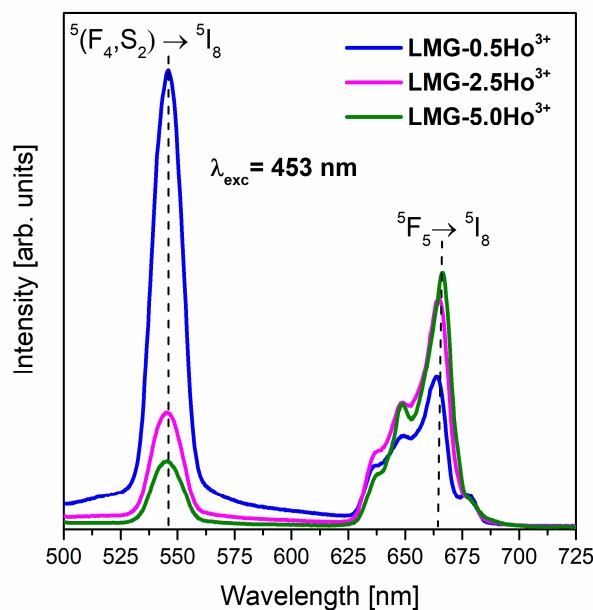


Figure 4. Luminescence spectra for LMG-Ho³⁺ ceramics with different contents of holmium ions.

Independent of the concentration of holmium ions in LMG ceramics, the emission bands located at 546 nm and 666 nm, corresponding to electronic transitions originating

from the 5F_4 , 5S_2 , and 5F_5 states to the ground state, 5I_8 , were recorded, respectively. Both the band originating from the $^5F_4, ^5S_2 \rightarrow ^5I_8$ transitions and the band associated with the $^5F_5 \rightarrow ^5I_8$ transition of Ho^{3+} ions are characterized by considerable emission intensity.

Our investigations clearly indicate that the relative integrated emission intensities due to the $^5F_4, ^5S_2 \rightarrow ^5I_8$ (green) and $^5F_5 \rightarrow ^5I_8$ (red) transitions of Ho^{3+} ions in $\text{Li}_2\text{MgGeO}_4$ ceramics depend critically on activator concentration. The emission intensity of the green transition decreases, whereas the emission intensity of red transition is enhanced, with increasing Ho^{3+} ion concentrations. The observed intensities of green (546 nm) and red (666 nm) emissions for our ceramic samples are opposite in comparison to the $\text{CaLa}_{4-x}\text{Si}_3\text{O}_{13}:\text{Ho}^{3+}$ phosphors reported by Singh et al. [49]. In this study, the $\text{CaLa}_{4-x}\text{Si}_3\text{O}_{13}$ ceramics doped with holmium ions exhibited an intense green emission at 546 nm attributed to the $^5F_4, ^5S_2 \rightarrow ^5I_8$ transitions, whereas the red emission from the $^5F_5 \rightarrow ^5I_8$ transition was significantly weaker. Moreover, Li et al. [50] registered dominant green emission under the direct excitation of Ho^{3+} ions in potassium sodium niobate-based ceramics. However, the emission intensity of the band corresponding to the $^5F_4, ^5S_2 \rightarrow ^5I_8$ transitions decreased with increasing contents of optical active dopants (Ho^{3+}) in ceramic compositions. This phenomenon is attributed to the so-called the concentration luminescence quenching effect, which was also observed for holmium-doped LiPbB_5O_9 [51]. The results obtained for $\text{LiPbB}_5\text{O}_9:\text{Ho}^{3+}$ indicated that the intensity of visible emission was increased for samples with low contents of Ho^{3+} (from 0.04 mol% to 0.08 mol%) and then decreased with further increases in the holmium ion concentration. Consequently, once the content of optical active dopants exceeds a critical value, the mechanism of concentration quenching is triggered [51]. The origin of this phenomenon is due to non-radiative energy transfer interactions between emitting activator ions. Energy transfer between them is more effective at high concentrations because the average distance between the activator ions is shorter, and the energy transfer probability is higher. Thus, the coupled excited states 5F_4 and 5S_2 (Ho^{3+}) are quite easy depopulated, and green emission is effectively quenched in the case of highly holmium-concentrated systems. These effects are due to cross-relaxation channels, i.e., the resonant cross relaxation processes ($^5S_2 + ^5F_4: ^5I_8 \rightarrow ^5I_4: ^5I_7$) and ($^5S_2 + ^5F_4: ^5I_8 \rightarrow ^5I_7: ^5I_4$) as well as the phonon-assisted cross-relaxation ($^5S_2 + ^5F_4: ^5I_8 \rightarrow ^5I_6: ^5I_7$). It was presented well and discussed earlier for $\text{LiPbB}_5\text{O}_9:\text{Ho}^{3+}$ [51].

Additionally, the CIE chromaticity coordinates (x, y) for the studied LMG ceramic samples excited at 453 nm were calculated from the registered emission spectra in the visible range. The results are given in Table 1. It is clearly seen that the increasing concentrations of holmium ions in $\text{Li}_2\text{MgGeO}_4$ germanate ceramics caused changes in the x and y coordinates of the chromaticity parameters.

Table 1. The values of CIE chromaticity coordinates for LMG- Ho^{3+} ceramic systems.

| Ceramic Code | CIE Coordinates | |
|--------------------------|-----------------|-------|
| | x | y |
| LMG-0.5 Ho^{3+} | 0.338 | 0.627 |
| LMG-2.5 Ho^{3+} | 0.427 | 0.523 |
| LMG-5.0 Ho^{3+} | 0.468 | 0.488 |

The chromaticity diagram shows the luminescence color modification from green through yellowish to nearly orange for ceramic systems doped with 0.5, 2.5, and 5 mol% Ho^{3+} concentrations, respectively. It is illustrated in Figure 5.

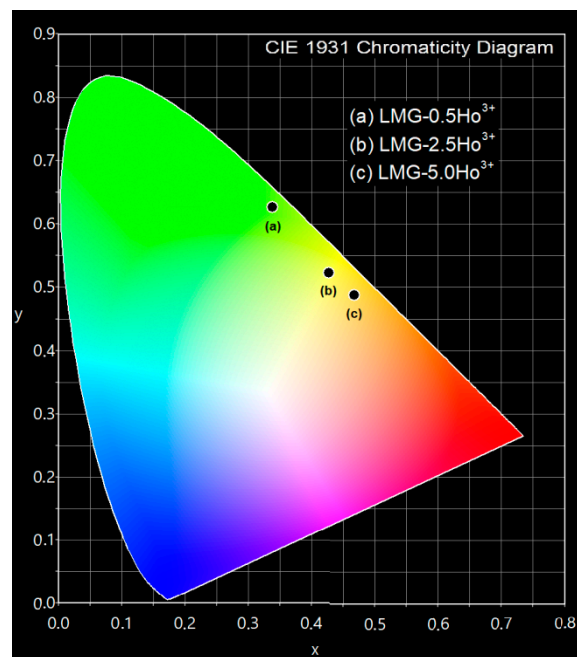


Figure 5. The influence of Ho^{3+} concentration on chromaticity coordinates for $\text{Li}_2\text{MgGeO}_4$ ceramics.

Luminescence decays from the excited states of holmium ions in $\text{Li}_2\text{MgGeO}_4$ ceramics were carried out to fully characterize the studied systems. It is clearly seen in Figure 6 that all registered decay profiles are nearly exponential, independent of the content of optically active dopants. Based on the decays, the luminescence lifetimes for the ${}^5\text{F}_4 + {}^5\text{S}_2$ ($\lambda_{\text{em}} = 546 \text{ nm}$) and ${}^5\text{F}_5$ ($\lambda_{\text{em}} = 666 \text{ nm}$) levels of Ho^{3+} were evaluated. The τ_{m} values for LMG- Ho^{3+} ceramics are nearly $10 \mu\text{s}$ (${}^5\text{F}_4 + {}^5\text{S}_2$) and $6 \mu\text{s}$ (${}^5\text{F}_5$). Moreover, it was observed that this spectroscopic parameter is practically independent of the concentration of Ho^{3+} ions in ceramic samples. The measured emission lifetimes for the ${}^5\text{F}_4 + {}^5\text{S}_2$ states of Ho^{3+} in the LMG host are similar to fluorophosphate glass [6], but they are relatively lower compared to other reported glasses [7], ceramics [52], and crystals [53].

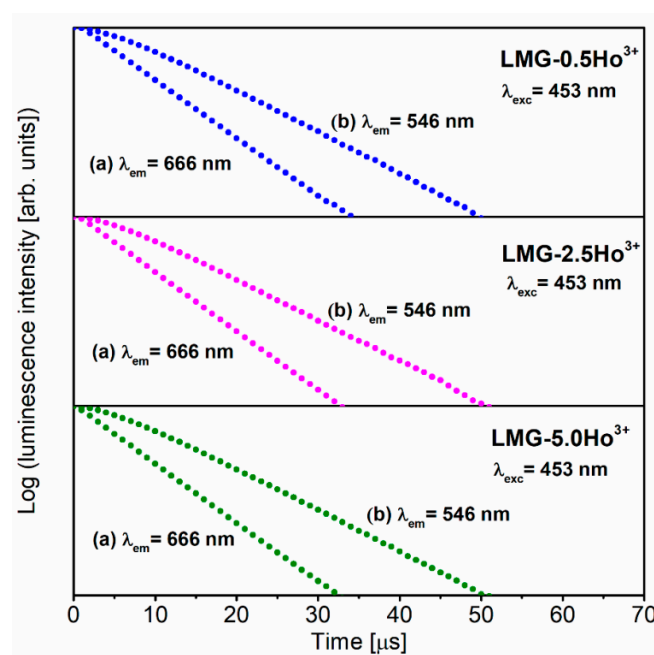


Figure 6. Decay curves for LMG- Ho^{3+} ceramics with different contents of holmium ions.

3.3. Luminescence Properties under Different Excitation Wavelengths

In order to study the luminescence properties of LMG- Ho^{3+} ceramics, the excitation spectra were registered at selected monitoring wavelengths. The results are presented in Figure 7. The excitation spectrum for LMG monitored at $\lambda_{\text{em}} = 500$ nm shows a broad band located at about 385 nm. Based on previous investigations, it was found that this phenomenon is related to the occurrence of magnesium in ceramics. It was proposed that the band in this spectral region is assigned to the excitation band of MgO [54–57]. On the other hand, the excitation spectrum for the LMG- Ho^{3+} ceramic monitored at the emission wavelength $\lambda_{\text{em}} = 660$ nm consists of several narrow and well-resolved bands. These bands were assigned to characteristic electronic transitions originating from the ground state, $^5\text{I}_8$, to the higher-lying states of trivalent Ho^{3+} . The following transitions of Ho^{3+} ions centered at about 453 nm, 485 nm, and 543 nm were identified as $^5\text{I}_8 \rightarrow ^5\text{G}_6$, $^5\text{I}_8 \rightarrow ^5\text{F}_{2,3}$, and $^5\text{I}_8 \rightarrow ^5\text{S}_2, ^5\text{F}_4$, respectively. Among the registered bands, the most intense band is located near 453 nm, corresponding to the $^5\text{I}_8 \rightarrow ^5\text{G}_6$ ($\lambda_{\text{em}} = 453$ nm) transition of Ho^{3+} . Moreover, it was also observed in the 350–430 nm spectral region that bands assigned to the $^5\text{I}_8 \rightarrow ^3\text{H}_{5,6}$ and $^5\text{I}_8 \rightarrow ^5\text{G}_{4,5}$ transitions of Ho^{3+} overlapped with the excitation of the ceramic matrix. Therefore, it is possible to obtain the characteristic luminescence associated with trivalent Ho^{3+} ions by the direct excitation of the LMG host. This hypothesis was verified using the emission spectra measurements at selected excitation wavelengths. The ceramic samples were excited at the appropriate wavelengths assigned directly to the transitions of Ho^{3+} as well as the LMG ceramic matrix, and they are referred to by diamonds and asterisks in Figure 7.

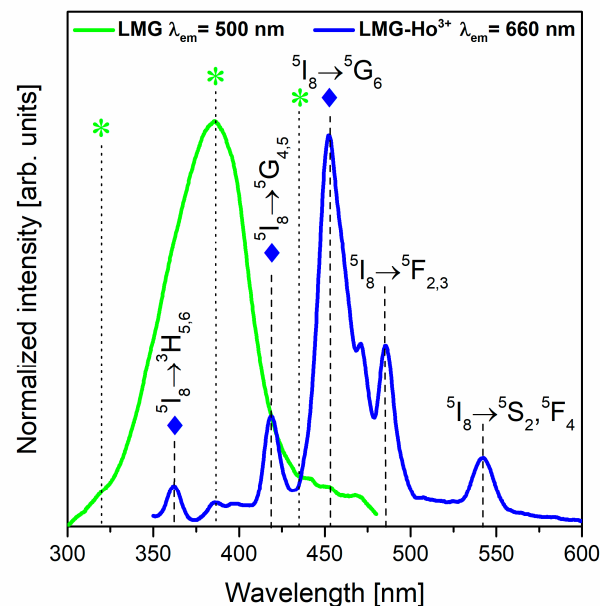


Figure 7. Excitation spectra of LMG and LMG- Ho^{3+} ceramics.

Figure 8 presents the emission spectra of LMG-0.5 Ho^{3+} ceramics measured under the direct excitation of holmium ions (on the left) and the ceramic matrix (on the right). In the spectra, a broad luminescence band with a tail extending to about 700 nm could be distinguished as originating from the ceramic matrix. It is also worth emphasizing that the broad band from the LMG ceramic matrix overlapped with the narrow emission bands characteristic of Ho^{3+} ions. Depending on the excitation wavelengths, blue or greenish-blue broad emission was observed, similar to the excellent results obtained previously for MgO films, and these phenomena are related to the occurrence of defects and oxygen vacancies in MgO assigned to F-type centers [57]. After analyzing the literature data, it is suggested that the broad blue emission band is due to the presence of magnesium in the LMG ceramic matrix.

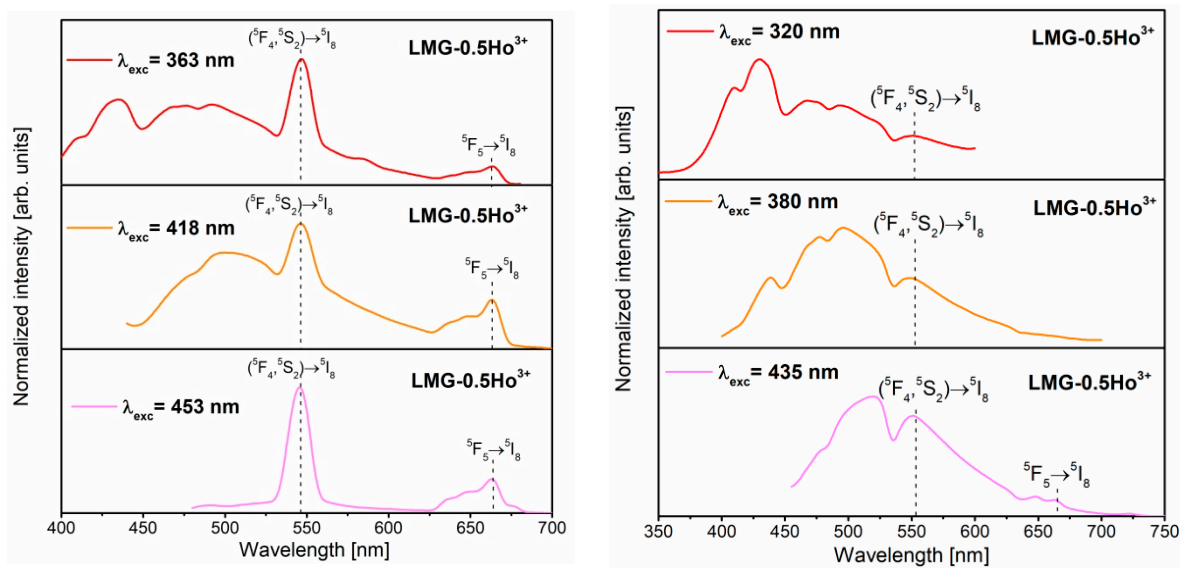


Figure 8. Emission spectra of LMG- Ho^{3+} under direct excitation of holmium ions (**left**) and host matrix (**right**).

The spectroscopic analysis indicates that the relative intensities of the emission bands attributed to the LMG host and Ho^{3+} ions are significantly dependent on the excitation wavelength. The green and red emission bands associated with ${}^5\text{F}_4, {}^5\text{S}_2 \rightarrow {}^5\text{I}_8$ and ${}^5\text{F}_5 \rightarrow {}^5\text{I}_8$ transitions are the most intense for ceramic samples during the direct excitation of Ho^{3+} ions. Additionally, the emission spectra of LMG- 0.5Ho^{3+} samples excited at 363 nm and 418 nm contain broad blue band characteristic for the ceramic matrix. This is due to the fact that these excitation lines of Ho^{3+} overlap with the excitation spectrum of the matrix, as mentioned above. The characteristic band corresponding to the emission of the ceramic matrix becomes insignificant in the spectrum recorded upon the excitation by the 453 nm line.

Interesting results were obtained for LMG- 0.5Ho^{3+} samples under the direct excitation of the ceramic matrix. The samples were excited at 320, 380, or 435 nm. The luminescence intensities of the broad band characteristic for the ceramic matrix were considerably higher in reference to the results obtained for the same LMG- 0.5Ho^{3+} samples but measured under the direct excitation of holmium. Additionally, green emission bands at 550 nm, due to the ${}^5\text{F}_4, {}^5\text{S}_2 \rightarrow {}^5\text{I}_8$ transitions of Ho^{3+} , are also well-observed during the excitation of the ceramic matrix. The presence of characteristic bands for trivalent holmium ions may indicate the energy transfer between the LMG ceramic matrix and the optical active dopants. Further investigations are in progress.

4. Conclusions

In this work, preliminary results for $\text{Li}_2\text{MgGeO}_4:\text{Ho}^{3+}$ ceramics, referred to as LMG- Ho^{3+} , are presented and discussed. The X-ray diffraction analysis confirmed the presence of crystalline phase belonging to the monoclinic $\text{Li}_2\text{MgGeO}_4$. The luminescence spectra consisted of characteristic narrow bands in the green and red spectral regions, which correspond to the ${}^5\text{F}_4, {}^5\text{S}_2 \rightarrow {}^5\text{I}_8$ and ${}^5\text{F}_5 \rightarrow {}^5\text{I}_8$ transitions of Ho^{3+} ions. Their relative integrated emission intensities depend significantly on activator concentration. The emission intensity of the green band decreased rapidly, whereas the intensity of the red emission was enhanced by increasing Ho^{3+} concentrations. In particular, the emission spectra of $\text{Li}_2\text{MgGeO}_4:\text{Ho}^{3+}$ were examined under different excitation wavelengths. The emission spectra were measured under the direct excitation of Ho^{3+} ions and the ceramic matrix. The spectroscopic analysis revealed the presence of broad blue luminescence, which was assigned to the ceramic matrix, and narrow emission bands characteristic of the 4f-4f transi-

tions of Ho^{3+} . Further studies suggest an energy transfer between the LMG ceramic matrix and the Ho^{3+} ions.

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