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Perovskite SrZrO₃:Ho³⁺ phosphors: synthesis, structure, Judd–Ofelt analysis and photoluminescence properties

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A series of SrZrO₃:xHo³⁺ ($x = 0.01, 0.03, 0.05, 0.07, 0.09, \text{ and } 0.11$ mol) perovskite phosphors have been synthesized by using the sol–gel technique. The structural and optical characteristics of the prepared phosphors have been investigated through powder XRD, FT-IR, UV-visible diffuse reflectance, and photoluminescence analysis. The photoluminescence emission spectra showed a bright characteristic peak at 545 nm (⁵F₄ + ⁵S₂ → ⁵I₈) under the 454 nm excitation, which exhibits emission in the green region of the electromagnetic spectrum. The emission intensity of the phosphors starts decreasing slowly beyond 3 mol% Ho³⁺ ions concentration due to concentration quenching, which is attributed to the dipole–dipole interaction between Ho³⁺ ions. The site symmetry of the Ho³⁺ ions has been studied by estimating the relative Judd–Ofelt intensity parameters (Ω_{λ} , where $\lambda = 2, 4, 6$) from the photoluminescence excitation spectrum of the SrZrO₃:0.03Ho³⁺ phosphor. The obtained findings suggest that the synthesized phosphors will be favorable for their bright green emission and thus, can be widely used for different optoelectronic applications.

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1. Introduction

Perovskite materials with the general formula ABO₃ (where A = Ca, Sr, Ba; and B = Zr, Hf, Ti) have great versatility and outstanding chemical, physical, electrical, and thermo-mechanical properties. These host lattices are getting special attention due to their potential applications as catalysts, photocatalysts, fuel cells, in photovoltaic applications, optoelectronics, and solid oxide fuel cells.^{1–3} Perovskite materials possess a fascinating feature in which a slight variation in structure and chemical composition may result in enormous changes in their chemical and physical properties.^{4–7} The doping of a foreign element into these ABO₃ type inorganic oxides influences their optical and magnetic properties by creating various defects.^{8,9} Especially, lanthanide ions as dopants are suitable candidates since they exhibit unique spectroscopic properties.^{10–12} The coordination geometry and oxidation states of uranium ions in the SrZrO₃ perovskite were studied by Gupta *et al.*,¹³ although Li *et al.*¹⁴ investigated the spectral characteristics and intrinsic defects of SrZrO₃ perovskite. The earlier report published by Knight *et al.*¹⁵ reveals the structural and thermoelastic characteristics of SrZrO₃ perovskite.

Perovskites have been reported to be advantageous in high-temperature applications, like hydrogen gas sensors, steam

electrolysis, and fuel cells.^{16–18} Proton conductivity at elevated temperature enables its usage in typical electrochemical devices. Among different perovskite materials, the SrZrO₃ host material has been suggested for use as a potential substrate due to its large single crystals.¹⁹ In recent years, the structural phase transitions of strontium zirconate perovskites have been studied significantly at room temperature and higher temperatures.^{20–22} Initially, the structural investigations revealed that the SrZrO₃ possesses an orthorhombic phase at room temperature, and later Carlsson²³ proposed the presence of additional phases at high temperatures. Mete *et al.*¹⁷ examined the structural and electronic characteristics of 4d-perovskite: the cubic phase of SrZrO₃. The electronic and structural performances of selected surfaces of SrZrO₃ were investigated by Sambrano *et al.*²⁴ Singh *et al.*²⁵ have also published research on the photoluminescence and structural properties of SrZrO₃:Sm³⁺ orange-emitting perovskite phosphors.

Due to long-lived excited states and energy levels, the trivalent lanthanide ions doped luminescent materials (using Tm³⁺, Er³⁺, and Ho³⁺ ions) have been selected as the main subject of interest by several research groups.^{26–28} Holmium belongs to the lanthanides and its electronic configuration becomes [Xe]4f¹⁰ when doped into a crystalline host. Several spectroscopic studies revealed that Ho³⁺ is the most desirable ion for mid-infrared lasers and has excellent green emission properties other than Tb³⁺ (green emission only) ions among the rare earth ions due to its various electronic transitions. Ranjan *et al.*²⁹ reported the enhanced green up-conversion emission of Ho³⁺ doped Gd₂O₃ phosphor by co-doping with Yb³⁺ ions. The luminescence studies of Eu³⁺ and Ho³⁺ doped Sr₂TiO₄ revealed

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that the Sr_2TiO_4 could be a suitable material in favor of high-pressure mercury vapor lamps or white light-emitting diodes.³⁰

A literature survey confirms a lack of reports available on Ho^{3+} doped ABO_3 type zirconate perovskites. The Ho^{3+} is often used as a structural probe because it can be accommodated at the A-place or B-place of perovskite oxides and in-site changes in the optical behavior and local site surrounding these doped oxide materials. Based on these results, our prepared sample possesses excellent thermal and chemical stability, prompting its practical application. Combining trivalent rare-earth metal ions in zirconate perovskites is considered as a promising approach to developing more useful and stable luminescent materials. Shi *et al.*³¹ prepared Yb^{3+} , Ho^{3+} , Li^+ tri-doped TiO_2 up-conversion materials to enhance the efficiency of perovskite solar cells. First, Hou *et al.*³² investigated the impacts of Ho^{3+} ion doping over the surface morphology, crystal phase, and magnetic characteristics of BiFeO_3 thin films synthesized by the sol-gel technique. Sharif *et al.*³³ investigated surface morphology, structural, magnetic, and dielectric properties in

the BiFeO_3 with holmium-doped thin films deposited by the pulsed laser deposition technique. Moreover, Hussain *et al.*³⁴ presented resistive leakage and intrinsic polarization analyses for high-performance piezo/pyroelectric Ho -doped $0.64\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - 0.36PbTiO_3 binary ceramic materials.

Besides the solid-state reaction process, a conventional synthetic route for preparing phosphor particles, several new synthetic methods have already been developed, for example, co-precipitation, sol-gel, solution combustion, microemulsion, spray pyrolysis, and hydrothermal synthesis. The present work uses the sol-gel method to prepare SrZrO_3 phosphor. Sol-gel is a synthetic route to synthesize ceramic oxides, which provides reasonable control over stoichiometry, high purity, good homogeneity, and reduced sintering temperature. This method may also enable the production of low-temperature phases. A sol-gel method in a liquid includes a polycondensation reaction, which builds the oxide network of a molecular precursor. Although the process consists of several steps, doping concentration positively impacts the luminescence and crystal structural properties of the prepared phosphor. Wurm *et al.*³⁵ prepared sol-gel SrZrO_3 and SrTiO_3 coatings on C and SiC-fibers. Venkatesh *et al.*³⁶ prepared a novel strontium zirconate perovskite coating on an Inconel substrate using the sol-gel synthesis method. Liu *et al.*³⁷ reported sol-gel derived SrZrO_3 memory thin films with resistance switching properties. In this work, the Ho^{3+} doped SrZrO_3 perovskite phosphors were synthesized by using sol-gel synthesis. The prepared phosphors were characterized structurally and optically. To know the spectral characteristics, the measured photoluminescence excitation spectra were used to calculate the Judd-Ofelt intensity parameters, Ω_2 , Ω_4 & Ω_6 . Detailed photoluminescence properties are discussed herein.

Table 1 Detailed information of sample composition and starting materials

Sample compositions	Weight of starting materials (g)			
	$\text{Sr}(\text{NO}_3)_2$	$\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$	$\text{C}_6\text{H}_8\text{O}_7$	$\text{Ho}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$
$\text{SrZrO}_3:0.01\text{Ho}$	0.8464	1.0688	3.0738	0.0176
$\text{SrZrO}_3:0.03\text{Ho}$	0.8464	1.0688	3.0738	0.0592
$\text{SrZrO}_3:0.05\text{Ho}$	0.8464	1.0688	3.0738	0.0882
$\text{SrZrO}_3:0.07\text{Ho}$	0.8464	1.0688	3.0738	0.1243
$\text{SrZrO}_3:0.09\text{Ho}$	0.8464	1.0688	3.0738	0.1578
$\text{SrZrO}_3:0.11\text{Ho}$	0.8464	1.0688	3.0738	0.1940

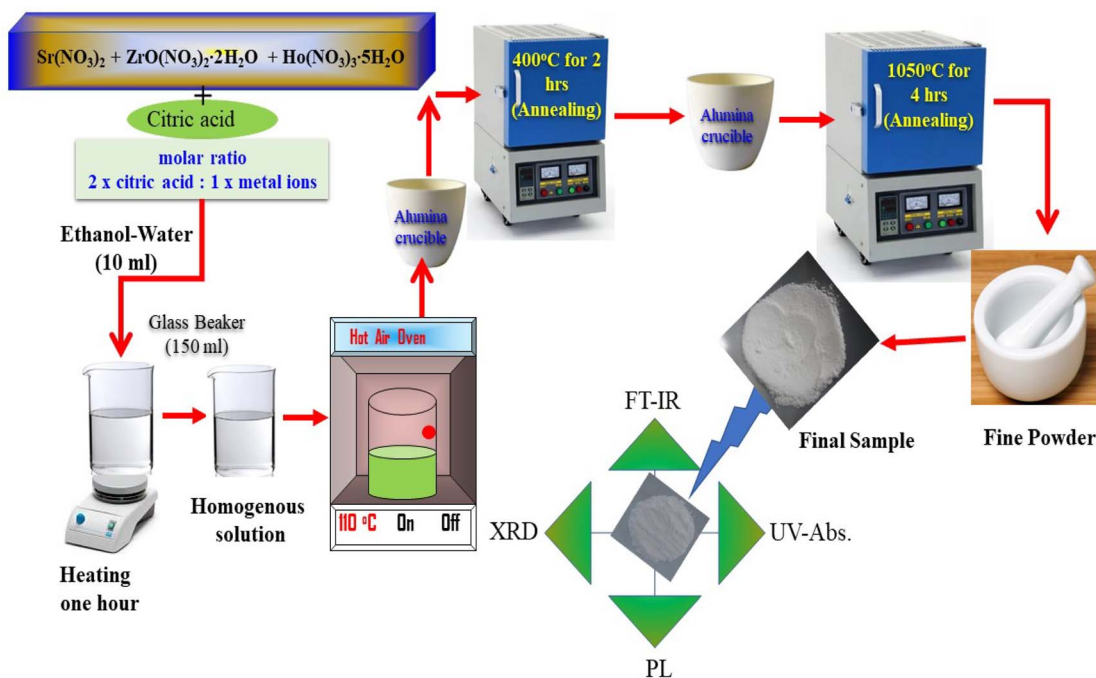


Fig. 1 Systematic diagram of synthesis process of the sample.



2. Materials preparation and analysis

The $\text{SrZrO}_3:x\text{Ho}^{3+}$ ($x = 0.01, 0.03, 0.05, 0.07, 0.09,$ and 0.11 mol) perovskite phosphors were fabricated by sol-gel procedure. The quantity of the employed starting materials is reported in Table 1. As per the chemical formulae, the stoichiometric quantities of strontium nitrate ($\text{Sr}(\text{NO}_3)_2$) (Sigma-Aldrich, purity: 99%), zirconium nitrate oxide dihydrate ($\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$) (Kanto chemical, purity: 99%), holmium(III) nitrate pentahydrate ($\text{Ho}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$) (Sigma-Aldrich, purity: 99.9%), citric acid ($\text{C}_6\text{H}_8\text{O}_7$) (Junsei, purity: 99.5%) and, a mixture of 6 ml of ethanol and 4 ml of water combine in a 150 ml beaker. The molar ratio was kept at 2 : 1 according to citric acid and total metal ions. Next, the mixture was stirred for 1 h to achieve a clear homogeneous solution; after that, put the resultant in the oven until the solution dried. A hot temperature furnace maintained at 400 °C preheated the acquired gels for 2 h in air. After preheating, the samples were granulated and fired for 4 h at 1050 °C in the ambient condition, giving the fine powder samples. Fig. 1 presents a pictorial view of the synthesis process.

The X-ray diffraction patterns were monitored by a RIGAKU (Miniflex-II) diffractometer attached to an X-ray source (Cu-K α radiation, $\lambda = 1.5406$ Å); the scan rate was set at 5° per minute between 10°–80° for 2θ angle. To identify the functional group present in the prepared samples, a Fourier transform infrared (6700, Thermo Fisher Nicolet) spectrometer was operated in a range of 400–4000 cm^{-1} . A small quantity of prepared $\text{SrZrO}_3:\text{Ho}^{3+}$ phosphor powder is used to measure diffuse reflectance with A Cary-5000 (UV-VIS-NIR) spectrophotometer coupled to a Praying Mantis diffuse reflectance accessory. Photoluminescence (PL) spectra were analyzed by a Shimadzu (RF-5301PC) spectrofluorophotometer fitted with a Xenon-flash lamp. The emission and excitation spectra were recorded using a spectral slit width of 1.5 nm. The above characterizations were performed at room temperature.

3. Results and discussion

3.1 Crystal structure

The XRD measurement was conducted to study the structural phase and crystallinity of the prepared samples. Fig. 2 displays the XRD patterns of the $\text{SrZrO}_3:x\text{Ho}^{3+}$ powders. For the synthesized phosphors, the major diffraction peaks matched with JCPDS (Joint Committee for Powder Diffraction Standards Card) File No. 76-0167 corresponding to SrZrO_3 . The effect of Ho^{3+} ions (at the studied concentrations *i.e.* 0.01, 0.03, 0.05, 0.07, 0.09, and 0.11 mol) on the structure of the SrZrO_3 lattice seems to be negligible as XRD patterns remain the almost same at different doping concentrations. However, we believe the actual doping level can be clarified by Le Bail method to find the evolution trend of the cell lattice parameters. To calculate the crystalline size, the FWHM (full width at half maximum) of dominant (110) diffraction peaks are considered in leading Scherrer's equation, $D = 0.9\lambda/\beta \cos \theta$, in which the wavelength of incident X-rays is denoted as λ , the corresponding Bragg's diffraction angle is θ , and the FWHM of the (110) peak is β . The

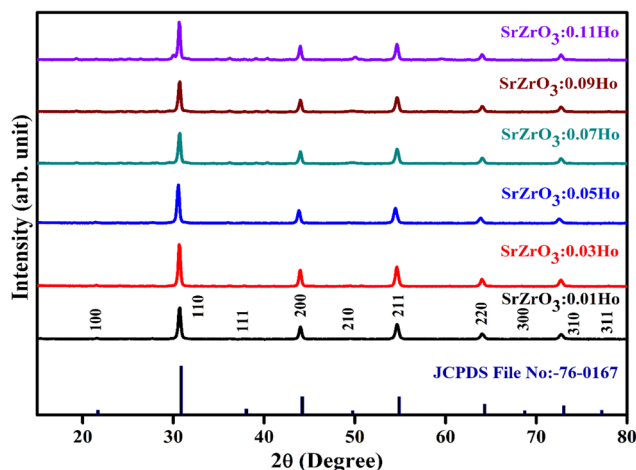


Fig. 2 Powder XRD patterns of $\text{SrZrO}_3:x\text{Ho}^{3+}$ phosphors.

determined crystal sizes were approximately within the range of 24–31 nm. Various oxides with the ABO_3 chemical formula follow the perovskite structure. Fig. 3 showed the simplified crystal lattice of the SrZrO_3 perovskite. The SrZrO_3 has cubic symmetry with a $Pm\bar{3}m[221]$ space group. In the SrZrO_3 perovskite structure, the Sr atoms are situated on the edges of the cubic unit cell, and the 12 closest neighbor O atoms surround the Sr atoms. Similarly, the Zr atom is situated in the centrum of the unit cell and is six-fold integrated with the O closed-neighbor atoms, making an octahedron. The cubic unit cell faces have O atoms, which are two-fold coordinated with Zr neighbor atoms. The Zr-ion and Sr-ion have the coordination numbers 6 and 8, respectively.^{1,11}

3.2 Vibrational analysis

Fig. 4 shows a typical vibrational feature of the $\text{SrZrO}_3:0.03\text{Ho}^{3+}$ powder sample. An intense absorption band at 558 cm^{-1} is attributed to the Zr–O stretching vibration. We have also observed a sharp peak at 857 cm^{-1} . Katyayan and Agrawal¹⁸ studied $\text{SrZrO}_3:\text{Eu}^{3+}, \text{Tb}^{3+}$ system and several peaks reported in the range of 509–895 cm^{-1} were due to the vibrational stretching modes of metal–oxygen bond, *i.e.*, Zr–O bond. However, few peaks lie between 1000 and 1270 cm^{-1} due to the active modes of asymmetric stretching of impurity ions. Further, sharp peaks were reported within 1302–1588 cm^{-1} due to the symmetrical stretching of Sr–O bonds. We have also observed bands at 1018 and 1458 cm^{-1} . The observed bands and their assignments can be confirmed with the previous literature.^{8,38–41}

3.3 Diffuse reflectance spectra and optical band gap

The UV-diffuse reflectance spectra were recorded between the wavelength regions of 200–800 nm for the 3 mol% Ho^{3+} doped SrZrO_3 phosphor. Fig. 5 shows the diffuse reflectance spectrum and extracted absorption coefficient with the Kubelka–Munk function. It can be seen that few bands around 365, 421, 454, 468, 489, 542, and 645 nm are related to the 4f–4f configuration of Ho^{3+} transitions: $^5\text{I}_8 \rightarrow ^5\text{G}_5 + ^3\text{H}_6, ^5\text{I}_8 \rightarrow ^5\text{G}_5, ^5\text{I}_8 \rightarrow ^5\text{G}_6, ^5\text{I}_8 \rightarrow$



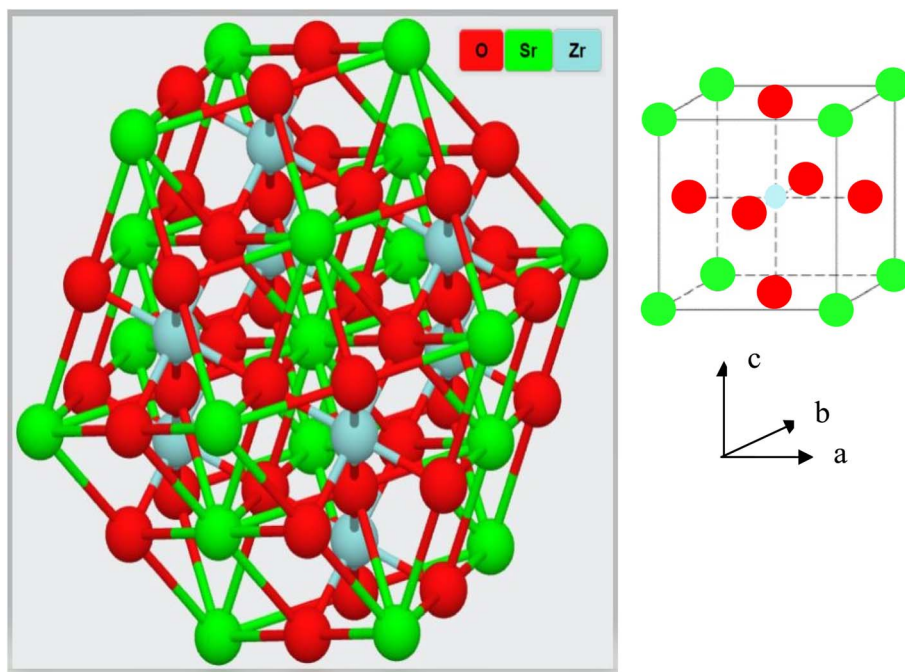


Fig. 3 Crystal structure of the SrZrO₃ perovskite.

5F_1 , $^5I_8 \rightarrow ^5F_2 + ^3K_8$, and $^5I_8 \rightarrow ^5F_3$, respectively. The extracted optical-absorption coefficient ($\alpha \text{ cm}^{-1}$) was calculated by the consecutive expression:⁴²

$$F(R) = \frac{(1 - R)^2}{2R} = \alpha \quad (1)$$

where R stands for sample reflectance. The E_g (optical band gaps) for the Ho³⁺ doped SrZrO₃ phosphor can be estimated with the Tauc relation:⁴³

$$F(R)\hbar\omega \approx A(\hbar\omega - E_g)^n \quad (2)$$

where A is a constant, $F(R)$ is the absorption coefficient with photon energy ($\hbar\omega$) and n represents the power factor: $n = 1/2$ allowed direct transitions, and $n = 2$ allowed an indirect transition. Fig. 6 shows plots of $(F(R)\hbar\omega)^n$ as a function of $\hbar\omega$ (eV). After assuming $(F(R)\hbar\omega)^2 = 0$ and $(F(R)\hbar\omega)^{1/2} = 0$ for the linear region within the plot, the energy band gaps of the direct allowed and indirectly allowed transitions were observed to be 5.21 eV and 5.43 eV, correspondingly for the SrZrO₃:0.03Ho³⁺ phosphor.

3.4 Photoluminescence analysis

Fig. 7(a) demonstrates the photoluminescence excitation (PLE) spectra for the produced Ho³⁺ doped SrZrO₃ phosphors. The

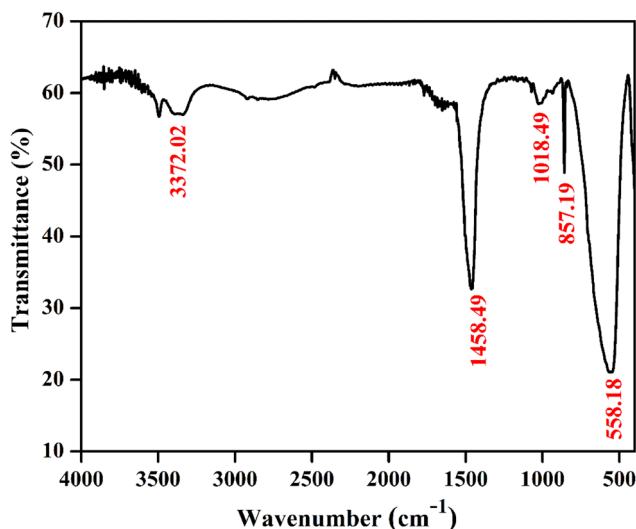


Fig. 4 FTIR spectrum of SrZrO₃:0.03Ho³⁺ phosphor.

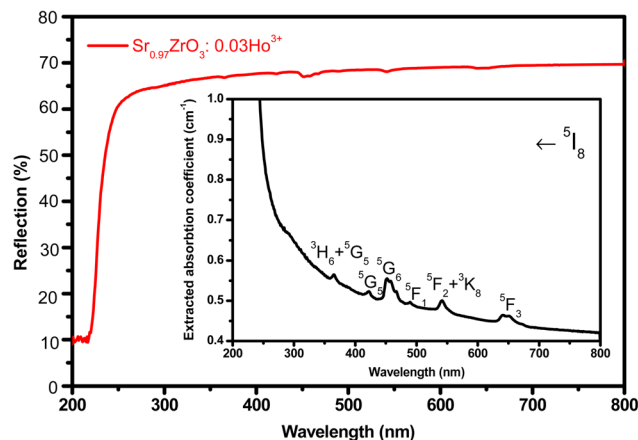


Fig. 5 UV-visible diffuse reflectance spectrum of SrZrO₃:0.03Ho³⁺ phosphor. Inset of the figure shows extracted absorption spectrum.



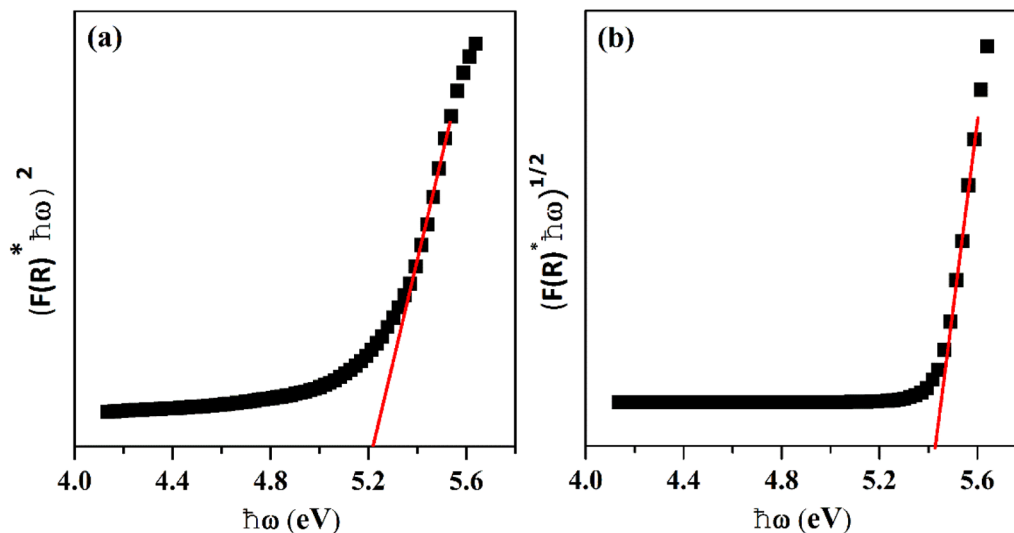


Fig. 6 Plots of $(F(R)\hbar\omega)^n$ versus $\hbar\omega$ (eV): (a) direct allowed transition and (b) indirect allowed transition.

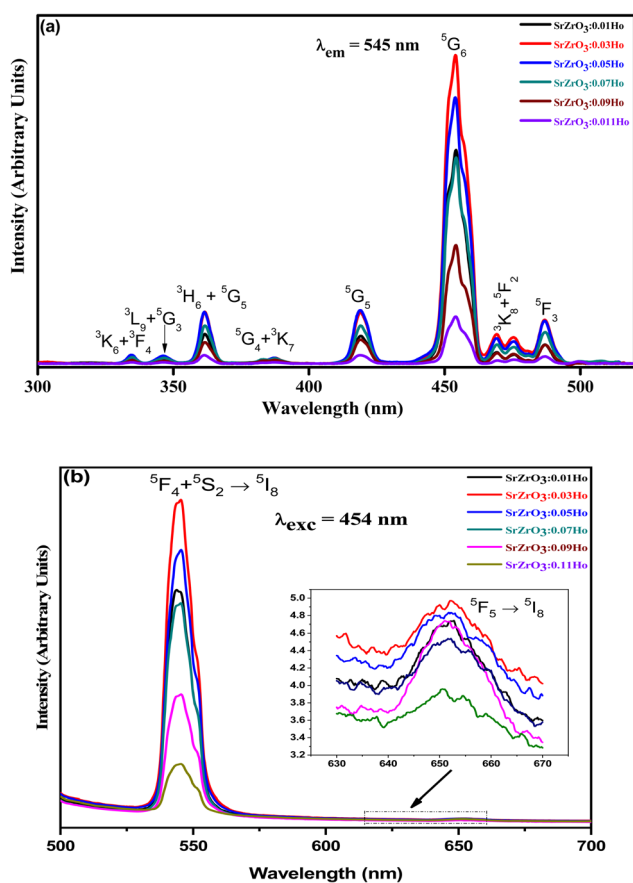


Fig. 7 (a) Photoluminescence excitation spectra of $\text{SrZrO}_3:\text{xHo}^{3+}$ phosphors ($\lambda_{\text{em}} = 545$ nm) and (b) photoluminescence emission spectra of $\text{SrZrO}_3:\text{xHo}^{3+}$ phosphors ($\lambda_{\text{exc}} = 454$ nm).

PLE spectra were acquired using the emission band at 545 nm. It can be read that the narrow bands owing to the $4f-4f$ transitions of Ho^{3+} ions and originated from $^5\text{I}_8$ to $^3\text{K}_6 + ^3\text{F}_4$ (334 nm), $^3\text{L}_9 + ^5\text{G}_3$ (346 nm), $^3\text{H}_6 + ^5\text{G}_5$ (361 nm), $^3\text{K}_7 + ^5\text{G}_4$ (387 nm), $^5\text{G}_5$

(418 nm), $^5\text{G}_6$ (454 nm), $^5\text{F}_2 + ^3\text{K}_8$ (472 nm) and $^5\text{F}_3$ (486 nm). The highest PLE intensity was observed at 454 nm; this would be suitable as the excitation wavelength for all prepared phosphors. The PLE band intensity is saturated at 3 mol% of Ho^{3+} ions in the SrZrO_3 phosphor. Usually, the doping of Ho^{3+} ions in place of Sr^{2+} ions will create positive charge defects that would negatively affect luminescence. Therefore, the expected emission intensity is maximum for 3 mol% of Ho^{3+} ions, and then the subsequent decrease of emission intensity is due to the $\text{Ho}_{\text{Sr}^{2+}}$ defects.⁴⁴

The emission spectra were monitored using 454 nm as the excitation wavelength for all phosphors and are presented in

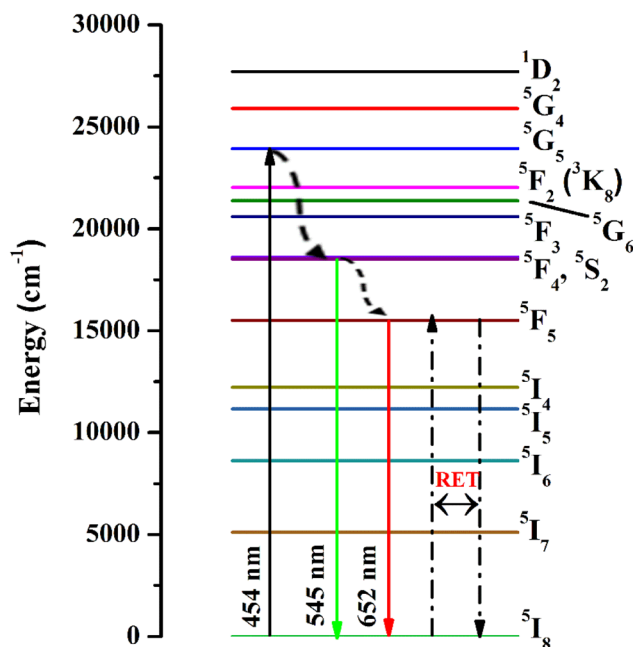


Fig. 8 Schematic energy level diagram for Ho^{3+} ions with possible radiative and non-radiative transitions.



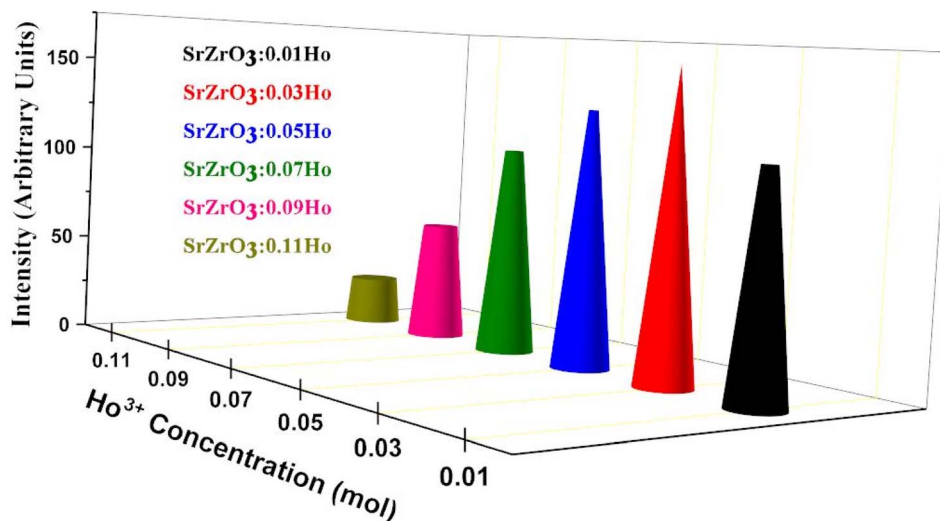


Fig. 9 Variation of emission intensity ($I_{545 \text{ nm}}$) as a function of Ho^{3+} ions in the $\text{SrZrO}_3:\text{Ho}^{3+}$ phosphor.

Fig. 7(b). Strong green and weak red emission bands have been seen around 545 nm and 652 nm. The obtained bands are possibly defined as transitions of Ho^{3+} ions for $^5\text{F}_4 + ^5\text{S}_2 \rightarrow ^5\text{I}_8$ and $^5\text{F}_5 \rightarrow ^5\text{I}_8$, respectively. The intensity of green emission at 545 nm is ~ 35 times more substantial than the red emission at 652 nm. Upon excitation of 454 nm, the ions are excited from $^5\text{I}_8$ to $^5\text{G}_4$, then most of the excited ions decay the lower levels $^5\text{F}_4 + ^5\text{S}_2$ and $^5\text{F}_5$ levels non-radiatively, and subsequently, radiatively transit to $^5\text{I}_8$ level with emission of green ($^5\text{F}_4 + ^5\text{S}_2 \rightarrow ^5\text{I}_8$) and red ($^5\text{F}_5 \rightarrow ^5\text{I}_8$), respectively. The energy gap difference for the $^5\text{F}_4$ and $^5\text{F}_5$ to the next lower levels are around 3400 cm^{-1} and 2400 cm^{-1} , thus the observed difference of green and red emission intensities depends on the population of excited states and multiphonon relaxation rates (W_{mpr}) since the W_{mpr} is increasing with the decrease of the energy gap between excited state to the next lower state. Fig. 8 shows a schematic energy level diagram for Ho^{3+} ions with possible radiative and non-radiative relaxation processes.

As seen in Fig. 9, the highest emission intensity was noticed when the Ho^{3+} ions concentration was 3 mol%, and it was decreased according to the increasing concentration of Ho^{3+} ions in the SrZrO_3 phosphor because of concentration quenching. Generally, it is recognized that the Ho–Ho distance reduces with an enhancement of Ho^{3+} ion concentration, leading to fluorescence quenching that comes from an increase in the resonant transfer probability between Ho^{3+} ions. The chances of energy transmission distance between Ho–Ho ions are termed the critical distance (R_c) obtained by the Blasse expression:⁴⁵

$$R_c \approx 2 \left[\frac{3V}{4\pi\chi_c N} \right]^{1/3} \quad (3)$$

where V is the unit cell volume, critical ion concentration is χ_c and N is the number of Zr ions of a unit cell. For our Ho^{3+} doped SrZrO_3 phosphor, $V = 552.175 \text{ (\AA)}^3$,⁴⁶ $N = 4$, and $\chi_c = 0.03$. The calculated critical transfer distance (R_c) is $\sim 20 \text{ \AA}$, far greater than 5 \AA that favors exchange interaction; thus, it can be

established that the observed concentration quenching in Ho^{3+} doped SrZrO_3 samples is attributed to the multipole–multipole interaction.⁴² In addition, the interaction strength can also be calculated using the following equation:⁴⁷

$$\frac{1}{x} = K \left\{ 1 + \beta(x)^{Q/3} \right\}^{-1} \quad (4)$$

where K and β are constants, I is emission intensity, and x is activator ion concentration. The dipole–dipole (d–d), dipole–quadrupole (d–q), quadrupole–quadrupole (q–q) interactions take place with $Q = 6, 8$, and 10 , respectively. Fig. 10 shows the $\log(I/x)$ based on $\log(x)$ for the $\text{SrZrO}_3:0.03\text{Ho}^{3+}$ phosphor. It can be observed that $-Q/3 = -2.24$, so $Q = 6.72$. Thus, the quenching in emission intensity of Ho^{3+} doped SrZrO_3 host lattices is due to dipole–dipole interactions. The concentration quenching of Ho^{3+} doped SrZrO_3 phosphor that occurred beyond the optimized concentration (3 mol%) is most useful for emitting green light in optoelectronic devices.

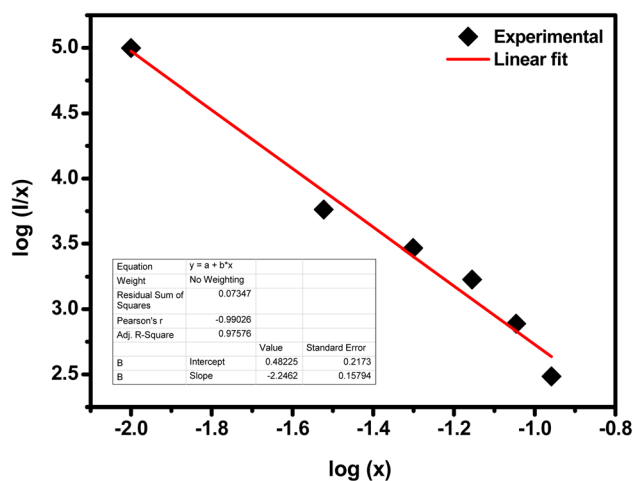


Fig. 10 Plot of $\log(I/x)$ as a function of $\log(x)$ of the $\text{SrZrO}_3:0.03\text{Ho}^{3+}$ phosphor (where I is the green emission peak intensity, and x is the Ho^{3+} ion concentration).



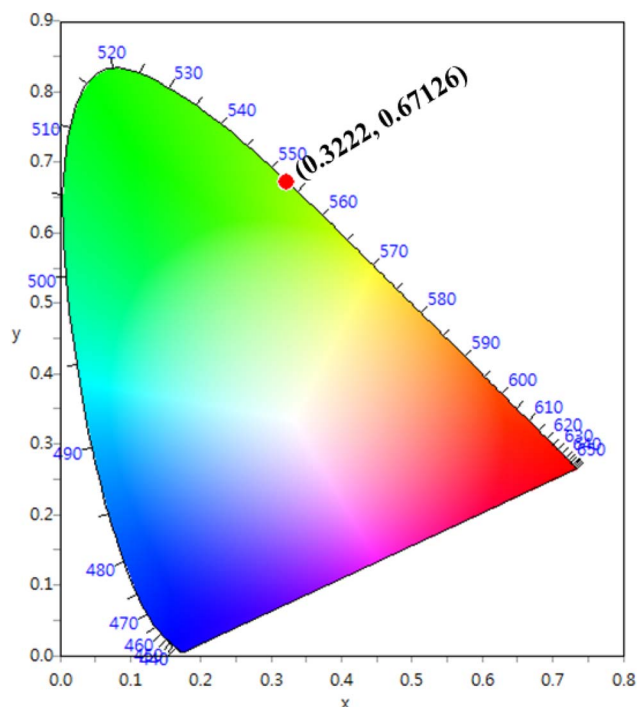


Fig. 11 CIE chromaticity diagram of SrZrO₃:0.03Ho³⁺ phosphor.

The CIE chromaticity coordinates were determined by the emission spectrum ($\lambda_{\text{exc}} = 454 \text{ nm}$) of optimized Ho³⁺ (3 mol%) doped SrZrO₃ phosphor using 1931 CIE (Commission Internationale de l'Eclairage France) technology, which is an accepted standard for the LED industry in matters related to colors, such as color mixing and color rendering. The chromaticity coordinates were found to be (0.322, 0.671) and this is situated in the green region of the CIE chromaticity diagram (see Fig. 11). The correlated color temperature (CCT) was also estimated by the McCamy experimental equation:⁴⁸

$$\text{CCT} = -437n^3 + 3601n^2 - 6861n + 5514.31 \quad (5)$$

where $n = \frac{(x - x_e)}{(y - y_e)}$ with chromaticity epicenter being $x_e = 0.3320$ and $y_e = 0.1858$. The obtained CCT is 5654 K for the Ho³⁺ (3 mol%) doped SrZrO₃ phosphor. Thus, this could be useful for w-LEDs because a CCT < 5000 K gives warm-white LEDs for home gadgets.

3.5 Judd–Ofelt intensity parameters from PLE and radiative properties

The familiar Judd–Ofelt intensity parameters (Ω_λ with $\lambda = 2, 4,$ and 6) were adopted to figure out the fluorescence branching ratios, spontaneous emission probabilities, and radiative lifetimes of the excited multiplets to assess the undertaking of lasers and luminescent materials. As per Judd–Ofelt (J–O) theory,^{49,50} the J–O intensity parameters (Ω_λ with $\lambda = 2, 4,$ and 6) can be examined conventionally from absorption spectra by evaluating the measured and computed spectral line strengths of the excited 4f–4f electronic transitions using least-square or chi-square fit methods. However, in recent decades,^{42,51,52}

Table 2 Doubly reduced matrix elements $\|U^2\|^4$ ($\lambda = 2, 4$ and 6), relative line strengths (S^{red}) ($\times 10^{-20} \text{ cm}^2$) for the observed excitation/absorption bands of Ho³⁺ doped various host matrices

Transitions from ⁵ I ₈ →	Excitation band wavenumber ($\nu \text{ cm}^{-1}$)	^a SrZrO ₃ :0.03Ho ³⁺		YLIF ⁵⁵		GdLiF ₄ (ref. 55)		LuLiF ₄ (ref. 55)	
		$\ U^2\ ^4$	S^{red}	$\ U^2\ ^4$	S^{red}	$\ U^2\ ^4$	S^{red}	$\ U^2\ ^4$	S^{red}
³ K ₆ + ³ F ₄	29 922	0.0026	0.0073	0.101	0.024	0.309	0.341	0.251	
³ L ₉ + ⁵ G ₃	28 902	0.0185	0.1169	0.080	0.031	0.394	0.379	0.300	
³ H ₆ + ³ H ₅	27 685	0.254	0.1609	0.059	0.173	1.310	4.377	1.276	
⁵ G ₄ + ³ K ₇	25 846	0.0058	0.0697	0.012	0.021	0.325	0.345	0.307	
⁵ G ₅	23 872	0	0.0002	0.087	0.085	1.161	1.199	1.120	
⁵ G ₆	22 020	1.5201	0.1535	0.809	0.791	3.893	4.177	4.014	
⁵ F ₂ + ³ K ₆	21 186	0.0208	0.3576	0.094	0.083	0.392	0.446	0.248	
⁵ F ₃	20 542	0	0.3464	0.084	0.067	0.716	0.811	0.375	
δ_{rms}				± 0.011		± 0.117	± 0.114	± 0.108	

^a Present work.



a simple approach has been proposed to evaluate J–O intensity parameters from the assessment of excitation spectra. This approach is successfully applied to Nd³⁺, Er³⁺ and Dy³⁺ doped various phosphor powders.

Normally, the excitation and absorption spectral difference lies in the intensity ratio of the fluorescence excitation to the absorption (*i.e.*, relative fluorescence quantum efficiency). Therefore, the excitation and absorption spectra will coincide exactly while relative fluorescence quantum efficiency maintains to be constant at different wavelengths. Once the experimental excitation spectrum is corrected to the corresponding absorption spectrum in which the excited states are followed by a very fast non-radiative relaxation to the monitored level.^{53,54} In this work, the excited multiplets of Ho³⁺: ⁵G₅, ⁵F₂(³K₈), ⁵G₆, ⁵F₃ levels are nonradiatively relaxed to ⁵F₄ + ⁵S₂ monitored level may satisfy the above statement, and excited multiplets chosen as ideal ones for the determination Judd–Ofelt parameters. The calculated and measured relative excited line strength for the attended electric-dipole transitions across the *aJ* and *bJ'* levels are determined using the following expressions,^{55,56}

$$S_{\text{cal}}^{\text{ed}}(aJ; bJ') = \sum_{\lambda=2,4,6} \Omega_{\lambda} |\langle [\alpha SL]J \| U^{(\lambda)} \| [\alpha' S' L']J' \rangle|^2 \quad (6)$$

$$S_{\text{meas}}^{\text{ed}}(aJ; bJ') = \frac{3ch(2J+1)}{8\pi^3 \bar{\lambda}^2 N_0} \frac{9n}{(n^2+2)^2} I_{\text{exc}} \quad (7)$$

where Ω_{λ} is the J–O intensity parameter, which is used in the environmental field effect of intermixing states, *i.e.*, 4f^N–15d and 4f^N–15g. $U^{(\lambda)}$ is the doubly reduced matrix tensor operator and it is found in the coupling approximations approach, which is taken from the literature.⁵⁶ The term $n \sim 2.12$ is the refractive index of SrZrO₃ material.⁵⁷ The average wavelength of the excitation band is denoted as $\bar{\lambda}$, N_0 is the ion concentration and \bar{I} is the integrated relative excitation intensity of each band. Ω_{λ} parameters were predicted by a least square fitting technique.⁴³ Table 2 shows relative spectral line strengths of excited transitions for Ho³⁺ ions (3 mol%) in the SrZrO₃ phosphor.⁵⁵ The root average square deviation (δ_{rms}) between experimental line strengths is,

$$\delta_{\text{rms}} = \sqrt{\frac{\sum (S_{\text{exp}}^{\text{ed}} - S_{\text{meas}}^{\text{ed}})^2}{(q-p)}} \quad (8)$$

where q and p are fitting parameters as transition number, and it has been used in our case as $q = 8$ and $p = 3$ in the best least square fitting procedure. The observed small δ_{rms} value (see Table 2) is indicative of the validity and fit quality in J–O theory.

Table 3 describes the J–O intensity parameters considering various host matrices.^{58–62} The Ω_2 parameter indicates ionicity (or covalence) of RE–O bonds and is related to the local structure. Ω_4 and Ω_6 are non-sensitive to the dependence structure and are attributed to the stiffness of the host; however, the various active ions alter the characteristics of the evaluated spontaneous emission transitions. For example, from Table 3, the Ho³⁺ doped SrZrO₃ phosphor shows a lower ionic nature between Ho–O bonds compared with other oxide-based host

Table 3 Relative Judd–Ofelt intensity parameters, ($\Omega_{\lambda} \times 10^{-20} \text{ cm}^2$, $\lambda = 2, 4$ and 6) of various host matrices

Host	Ω_2	Ω_4	Ω_6	Order
^a SrZrO ₃ :0.03Ho ³⁺	0.41	0.16	0.19	$\Omega_6 > \Omega_4 > \Omega_2$
Y ₃ Al ₅ O ₁₅ (YAG) ⁵⁸	0.04	2.67	1.89	$\Omega_4 > \Omega_6 > \Omega_2$
Lu ₃ Al ₅ O ₁₂ (ref. 59)	0.17	2.08	1.92	$\Omega_4 > \Omega_6 > \Omega_2$
LaF ₃ (ref. 60)	1.16	1.38	0.88	$\Omega_2 > \Omega_4 > \Omega_6$
LiYF ₄ (ref. 61)	1.01	1.71	1.21	$\Omega_4 > \Omega_6 > \Omega_2$
LiYF ₄ (ref. 62)	0.96	2.05	1.43	$\Omega_4 > \Omega_6 > \Omega_2$

^a Present work.

matrices. On the other hand, when compared with a fluoride-based host, the Ho³⁺ doped SrZrO₃ phosphor shows a higher ionic nature between the Ho–O bonds because of the lesser values of the J–O intensity parameter, Ω_2 .

4. Conclusions

The SrZrO₃:Ho³⁺ phosphors were produced by a sol–gel system and were analyzed by X-ray diffraction, FTIR, UV-visible and photoluminescence spectroscopic techniques. We have identified absorption bands around 365, 421, 454, 468, 489, 542, and 645 nm from the UV-visible diffuse reflectance spectrum of the 4f–4f configuration of Ho³⁺ transitions. The optical band gaps (E_{opt}) were found to be 5.21 eV (direct transition), 5.43 eV (indirect transition), respectively for the Ho³⁺ doped SrZrO₃ phosphor. Upon 454 nm excitation, the Ho³⁺ doped SrZrO₃ phosphor exhibits high green and low red emission bands that are connected to the respective ⁵F₄ + ⁵S₂ → ⁵I₈ (545 nm) and ⁵F₅ → ⁵I₈ (652 nm) transitions of Ho³⁺ ions. The fluorescence quenching of the studied phosphor samples was evaluated by looking at the critical distance between Ho–Ho ions as well as the strength of dipole–dipole (d–d), dipole–quadrupole (d–q) and quadrupole–quadrupole (q–q) interactions. The obtained CCT was 5654 K for the optimum concentration of Ho³⁺ (3 mol%) doped in the SrZrO₃ phosphor suggesting that it may be useful for w-LEDs. In addition, using excitation spectrum of the optimized phosphor, the Judd–Ofelt intensity parameters (Ω_{λ} with $\lambda = 2, 4$ and 6) for Ho³⁺ were estimated and compared with other hosts. The observed results of photoluminescence properties suggested that the SrZrO₃:0.03Ho³⁺ phosphor may be advantageous for green emitting optoelectronic applications.

Conflicts of interest

There are no conflicts to declare.

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