



Article

Nanosized Eu^{3+} -Doped $\text{NaY}_9\text{Si}_6\text{O}_{26}$ Oxyapatite Phosphor: A Comprehensive Insight into Its Hydrothermal Synthesis and Structural, Morphological, Electronic, and Optical Properties

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Abstract: Detailed analysis covered the optical and structural properties of Eu^{3+} -doped $\text{NaY}_9\text{Si}_6\text{O}_{26}$ oxyapatite phosphors, which were obtained via hydrothermal synthesis. X-ray diffraction patterns of $\text{NaY}_9\text{Si}_6\text{O}_{26}:\text{xEu}^{3+}$ ($\text{x} = 0, 1, 5, 7, 10$ mol% Eu^{3+}) samples proved a single-phase hexagonal structure ($P6_3/m$ (176) space group). Differential thermal analysis showed an exothermic peak at 995 °C attributed to the amorphous to crystalline transformation of $\text{NaY}_9\text{Si}_6\text{O}_{26}$. Electron microscopy showed agglomerates composed of round-shaped nanoparticles ~53 nm in size. Room temperature photoluminescent emission spectra consisted of emission bands in the visible spectral region corresponding to $^5\text{D}_0 \rightarrow ^7\text{F}_j$ ($j = 0, 1, 2, 3, 4$) f - f transitions of Eu^{3+} . Lifetime measurements showed that the Eu^{3+} concentration had no substantial effect on the rather long $^5\text{D}_0$ -level lifetime. The Eu^{3+} energy levels in the structure were determined using room-temperature excitation/emission spectra. Using the $^7\text{F}_1$ manifold, the Nv-crystal field strength parameter was calculated to be 1442.65 cm^{-1} . Structural, electronic, and optical properties were calculated to determine the band gap value, density of states, and index of refraction. The calculated direct band gap value was 4.665 eV (local density approximation) and 3.765 eV (general gradient approximation). Finally, the complete Judd–Ofelt analysis performed on all samples confirmed the experimental findings.

Keywords: $\text{NaY}_9\text{Si}_6\text{O}_{26}$; oxyapatite; europium ions; nanophosphors; amorphous-to-crystalline transformation



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1. Introduction

Compounds with the general formula $\text{Me}_{10}(\text{TO}_4)_6\text{O}_2$ belong to apatite-type materials with a specific arrangement of metal cations, tetrahedral units, and oxygen atoms. In these materials, Me stands for metal cations, usually alkali and alkaline metals and/or rare earth elements; $(\text{TO}_4)_6$ refers to six tetrahedral units where T is a tetrahedral metal (like silicon or germanium) each surrounded by four oxygen atoms; and O_2 represents two additional oxygen atoms that are not part of the tetrahedral units. Depending on the metal cations and the tetrahedral element T, this group of materials can find applications in: (i) materials science where such compounds might be of interest for their structural properties, which can be useful in high-temperature ceramics or advanced materials; (ii) catalysis where they may be used as catalysts or catalyst supports due to their stable and unique crystal structures; and/or (iii) phosphors for lighting in LEDs, OLEDs, and other display technologies if the material is luminescent. Their multiple combinations lead to the design of complex

materials that are studied for important applications such as high oxide ion conductivity and photoluminescence, immobilizing radioactive waste, laser research, solid-state lighting, oxide fuel cell development, biomaterials, etc. [1–6].

Alkaline metal/rare earth orthosilicates are a family of apatite oxide materials called oxyapatites that have gained interest, especially for their luminescent properties. Among them, sodium yttrium orthosilicate is an oxyapatite of the $\text{NaY}_9\text{Si}_6\text{O}_{26}$ general formula featuring a structure where yttrium is incorporated into the apatite-like framework, and sodium ions are included to balance the charge. The presence of trivalent yttrium ions in the structure makes this host suitable for activation with other rare earths and optically active luminescent materials design. Only a few studies have published the synthesis and characterization of $\text{NaY}_9\text{Si}_6\text{O}_{26}$ doped with activating ions. Chuai et al. investigated the luminescence of Eu^{3+} -, Tb^{3+} -, Dy^{3+} -, and Pb^{2+} -doped $\text{NaY}_9\text{Si}_6\text{O}_{26}$ obtained through the sol–gel technique [7]. The authors concluded that lanthanides occupy both sites in the oxyapatite structure and that white light emission of Dy^{3+} -doped samples improve when combined with Pb^{2+} and Gd^{3+} co-dopants. Kang et al. reported the conventional solid-state synthesis of $\text{NaY}_9\text{Si}_6\text{O}_{26}$ doped with Yb^{3+} , an NIR-emitting material serving as a potential state of the art candidate for advanced anti-counterfeiting utilization [8]. Zheng et al. reported color-tunable emission of Eu^{3+} -, Ce^{3+} -, and $\text{Eu}^{3+}/\text{Ce}^{3+}$ -doped $\text{NaY}_9\text{Si}_6\text{O}_{26}$ obtained with a conventional solid-state reaction [9]. The authors reported emission in the blue wavelength range for the Ce^{3+} -doped sample, and in the reddish-orange wavelength for the Eu^{3+} -doped sample while the emission of the $\text{Eu}^{3+}/\text{Ce}^{3+}$ sample changed from blue to orange-reddish by changing the Eu^{3+} concentration. Zheng et al. also reported color tuning in Bi^{3+} - and Eu^{3+} -doped/co-doped $\text{NaY}_9\text{Si}_6\text{O}_{26}$ obtained via a solid-state reaction as a solution to obtain phosphors with white light emission. The proper concentration and ratio of $\text{Bi}^{3+}/\text{Eu}^{3+}$ activating ions resulted in white light emission, while different concentrations of solely added Bi^{3+} and Eu^{3+} could alter the emission from blue to an orange-red color [10]. In addition, Brgoch et al. reported rapid microwave preparation of blue-emitting cerium-substituted $\text{NaY}_9\text{Si}_6\text{O}_{26}$ using active carbon as a microwave susceptor [11].

The correlation between structure and optical properties is essential when defining the host material and related efficiency for phosphor applications. Therefore, this research aims to investigate and present detailed structural and optical properties of Eu^{3+} -doped $\text{NaY}_9\text{Si}_6\text{O}_{26}$ oxyapatite phosphor obtained by hydrothermal synthesis. The hydrothermal technique offers several advantages over other synthesis methods, such as: (1) a controlled environment—the high temperature and pressure in hydrothermal conditions allow for better control over the reaction environment, leading to more uniform products; (2) higher solubility—unlike the solid-state method that struggles with complex materials or a precipitation method limited to materials that can be precipitated from solution, materials that are difficult to dissolve at room temperature can be effectively synthesized in a hydrothermal setup, enabling the formation of complex compounds; (3) good crystallinity—due to slow growth rates hydrothermal synthesis often results in high crystallinity of the final product compared to room/mild temperature techniques like precipitation; (4) versatility—this method can be used to synthesize a wide range of complex materials, making it more versatile when compared to solid-state or precipitation; (5) eco-friendly—hydrothermal processes often use water as a solvent, reducing the need for harmful organic surfactants usually needed in precipitation; (6) scalability—unlike solid-state and precipitation methods where quality can vary significantly with the batch, hydrothermal synthesis can be scaled up easily for industrial applications, allowing for the production of larger quantities of good quality materials; and (7) low energy consumption—compared to other methods, especially solid-state reactions, hydrothermal synthesis is more energy-efficient.

Thermal analysis was performed to determine the proper calcination temperature for oxyapatite phase transformation. Structural and photoluminescent measurements were analyzed and correlated. Structural, electronic, and optical properties were calculated to determine band gap value, density of states, and index of refraction. Finally, Judd–Ofelt analysis calculated the intensity parameters for electric dipole transitions, allowing

an estimate of their radiative properties. To the extent of our knowledge, there are no data on the temperature needed for the amorphous-to-crystalline transformation of the $\text{NaY}_9\text{Si}_6\text{O}_{26}$ oxyapatite host nor an index of refraction values, both being very important for the potential application of alkaline metal/rare earth orthosilicates.

2. Materials and Methods

2.1. Hydrothermal Synthesis of Undoped and Eu^{3+} -Doped Apatite Samples

A total of five samples of undoped and Eu^{3+} -doped apatite— $\text{NaY}_9\text{Si}_6\text{O}_{26}:\text{xEu}^{3+}$ ($\text{x} = 0, 1, 5, 7, 10$ mol% Eu^{3+} ; molecular formula of each sample is given in Table 1) were synthesized via the hydrothermal method [12,13]. The proper amounts of $\text{Na}_2\text{SiO}_3 \times 9\text{H}_2\text{O}$ (Sigma Aldrich, 98%, St. Louis, MO, USA), $\text{Y}(\text{NO}_3)_3 \times 6\text{H}_2\text{O}$ (Sigma Aldrich, 99.8%), and $\text{Eu}(\text{NO}_3)_3 \times 6\text{H}_2\text{O}$ (Alfa Aesar, 99.9%, Haverhill, MA, USA) were dissolved in deionized water leading to the formation of the aqueous precursor solutions. That way, concentrations of 0.299 mol/dm^3 for the Y and Eu precursors and 0.225 mol/dm^3 for the Si precursor solution were prepared. The Si solution was added in drops under intense magnetic stirring to the Y/Eu solution (molar ratio $\text{Eu/Y:Si} = 1.33:1$), and the pH of the precursor mixture was tuned to 13 by the dropwise addition of sodium hydroxide solution (6 mol/dm^3). The final mixture solution was stirred for another 3 h and then transferred to the PTFE liner of the hydrothermal reactor using a filling ratio of 30%. The hydrothermal reaction was carried out in the hydrothermal autoclave reactor at 230°C for 12 h; the precursor was then separated by centrifugation, washed with water five times, and dried at 80°C for 2 h, resulting in an amorphous material. The crystalline samples were obtained by calcinating the amorphous materials for 12 h at 1100°C .

Table 1. Chemical formulas of the synthesized $\text{NaY}_9\text{Si}_6\text{O}_{26}:\text{xEu}^{3+}$ ($\text{x} = 0, 1, 5, 7, 10$ mol% Eu^{3+}) samples.

Sample Code	Eu^{3+} (mol %)	Molecular Formula
NaYSO	0	$\text{NaY}_9\text{Si}_6\text{O}_{26}$
NaYSO:1Eu	1	$\text{NaY}_{8.91}\text{Eu}_{0.09}\text{Si}_6\text{O}_{26}$
NaYSO:5Eu	5	$\text{NaY}_{8.55}\text{Eu}_{0.45}\text{Si}_6\text{O}_{26}$
NaYSO:7Eu	7	$\text{NaY}_{8.37}\text{Eu}_{0.63}\text{Si}_6\text{O}_{26}$
NaYSO:10Eu	10	$\text{NaY}_{8.1}\text{Eu}_{0.9}\text{Si}_6\text{O}_{26}$

2.2. Characterization of the Apatite Materials

Thermal stability was examined by non-isothermal thermo-gravimetric analysis (TG) and differential thermal analysis (DTA), simultaneously, using a SETARAM SETSYS Evolution 1750 instrument (heating rate $-20^\circ\text{C}/\text{min}$ in a dynamic air atmosphere; flow rate $-40 \text{ cm}^3/\text{min}$; temperature range $30\text{--}1300^\circ\text{C}$). The mass of the sample was about 5 mg. The crystal structures of the obtained phosphors were looked at carefully with an X-ray diffractometer (XRD) from Rigaku SmartLab ($\text{Cu-K}_{\alpha 1,2}$ radiation, $\lambda = 0.1540 \text{ nm}$) at room temperature. The experimental conditions for measurements were as follows: 2θ range of $20^\circ\text{--}80^\circ$, with a step size of 0.02° , and a counting time of $10^\circ/\text{min}$. Conclusions on the structural study (unit cell parameters, crystal coherence size, micro strain values, and data fit parameters) were attained using the built-in PDXL2 software (v2.1). The average particle size was calculated using ImageJ software (<https://imagej.net>). The morphology was examined by a TESCAN MIRA3 field emission scanning electron microscope (FE-SEM) (TESCAN, Brno, Czechia), with the samples coated using a thin layer of Au, and by transmission electron microscope (TEM) JEOL JEM1011 operated at an accelerating voltage of 100 kV (JEOL, Frenchs Forest, NSW, Australia). The sample's UV–VIS diffuse reflection spectrum was recorded with a Shimadzu UV-3600 UV-VIS-NIR spectrophotometer with BaSO_4 used as the reflectance standard (Shimadzu, Kyoto, Japan). Photoluminescence measurements were carried out using a Fluorolog-3 Model FL3-221 spectrofluorometer system (Horiba Jobin-Yvon, Longjumeau, France) equipped with an R928 PMT detector. Emission

and excitation spectra were corrected for the lamp spectral intensity and detector sensitivity. Excited-state lifetime measurements were carried out using the Rohde&Schwarz RTC1002 two-channel oscilloscope paired with the Hamamatsu H10722-20 photomultiplier tube, and by exciting the samples with a square wave modulated Ocean Insight fiber-coupled LED (LSM-405A LED Light Source, Winter Park, FL, USA) controlled by an Ocean Insight LDC-1 Single Channel LED Controller.

3. Results and Discussion

3.1. Thermal Stability (TGA) and Differential Thermal Analysis (DTA)

The hydrothermal method used to obtain the desired materials resulted in amorphous apatite samples which, under appropriate sintering, transformed to crystalline $\text{NaY}_9\text{Si}_6\text{O}_{26}$. The undoped amorphous precursor was investigated to establish the adequate calcination temperature needed for transformation to the apatite phase. DTA analysis showed an exothermic peak at 995 °C that could be attributed to the transformation of amorphous $\text{NaY}_9\text{Si}_6\text{O}_{26}$ to the crystalline phase $\text{NaY}_9\text{Si}_6\text{O}_{26}$. At the same time, the TG curve showed ~13% total mass loss that could be attributed to the vaporization of adsorbed water and residual molecules. At the same time, the initial TG curve showed a sharp mass loss that could be attributed to the fast vaporization of adsorbed water and residual molecules. The total mass loss was found to be ~13%. According to the TG/DTA analysis results, calcination at 1100 °C was chosen to complete the amorphous-to-crystalline transformation (Figure 1).

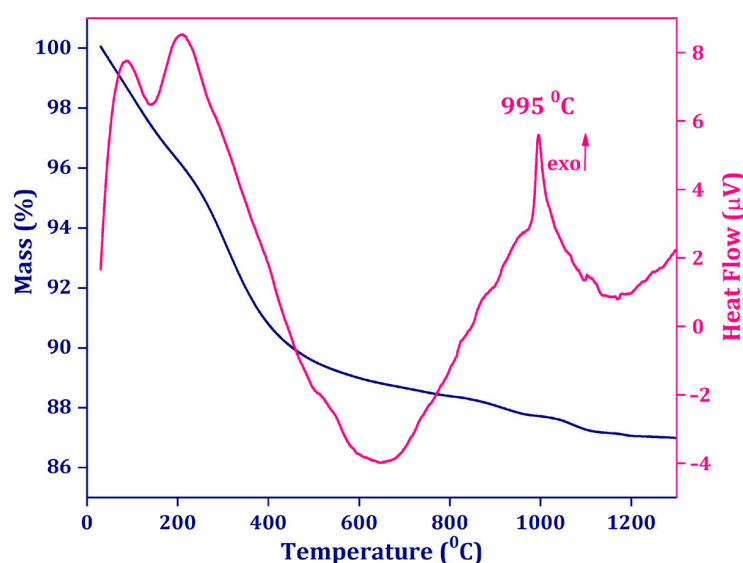


Figure 1. Thermogravimetry (TG, blue) and differential thermal analysis (DTA, pink) curves for undoped $\text{NaY}_9\text{Si}_6\text{O}_{26}$ precursor prepared via the hydrothermal method.

Table 2 presents a comparison of the obtained amorphous-to-crystalline transformation temperature with the values found in the literature for some rare earth silicates.

Table 2. Comparison of the obtained amorphous-to-crystalline transformation temperature with the values found in the literature.

Material	Synthesis	Structure	Total Weight Loss	Crystallization T (°C)	Reference
Y_2SiO_5	Sol-gel	Monoclinic	~29.3%	~1040	[14]
Y_2SiO_5	Sol-gel	Monoclinic	~30%	~1010	[15]
		X1— Y_2SiO_5 X2— Y_2SiO_5		~1360	

Table 2. Cont.

Material	Synthesis	Structure	Total Weight Loss	Crystallization T (°C)	Reference
Y ₂ SiO ₅	Sol-gel	Monoclinic X1—Y ₂ SiO ₅ X2—Y ₂ SiO ₅	~70%	~1025 ~1350	[16]
Y ₂ Si ₂ O ₇	Oxalate gel	Monoclinic α—Y ₂ Si ₂ O ₇	~60%	~1065	[17]
La ₁₀ Si ₆ O ₂₇	Precipitation	Hexagonal	~21.4%	~902	[18]
La ₁₀ Si ₆ O ₂₇	Sol-gel	Hexagonal	~48.4%	~959	[19]
La _{9.5} Si ₆ O _{26.25}	Co-precipitation	Hexagonal	~26.5%	~883	[20]
La _{9.33} Si ₆ O ₂₆	Sol-gel	Hexagonal	~48.4%	~874	[19]
NaY ₉ Si ₆ O ₂₆	Hydrothermal	Hexagonal	~13%	~995	This work

3.2. Structural Characterization

Figure 2a shows the X-ray diffraction pattern of NaY₉Si₆O₂₆:xEu³⁺ (x = 0, 1, 5, 7, 10 mol% Eu³⁺) samples depicted with a corresponding ICDD Card No. 00-035-0404. X-ray diffraction analysis verified a single-phase hexagonal structure (space group: *P63/m* (176)) with no other phase peaks or traces of impurities signifying that dopant Eu³⁺ ions have been efficiently incorporated into the NaY₉Si₆O₂₆ host lattice owing to similar sizes between Y³⁺ and Eu³⁺ ions [21]. PDXL2 software was used to calculate the average crystallite size and structural parameters presented in Table 3. The initial parameters for the evaluation were extracted from Reference [22]. The calculated mean crystallite size for all the samples was in the nanometer region (~14–25 nm).

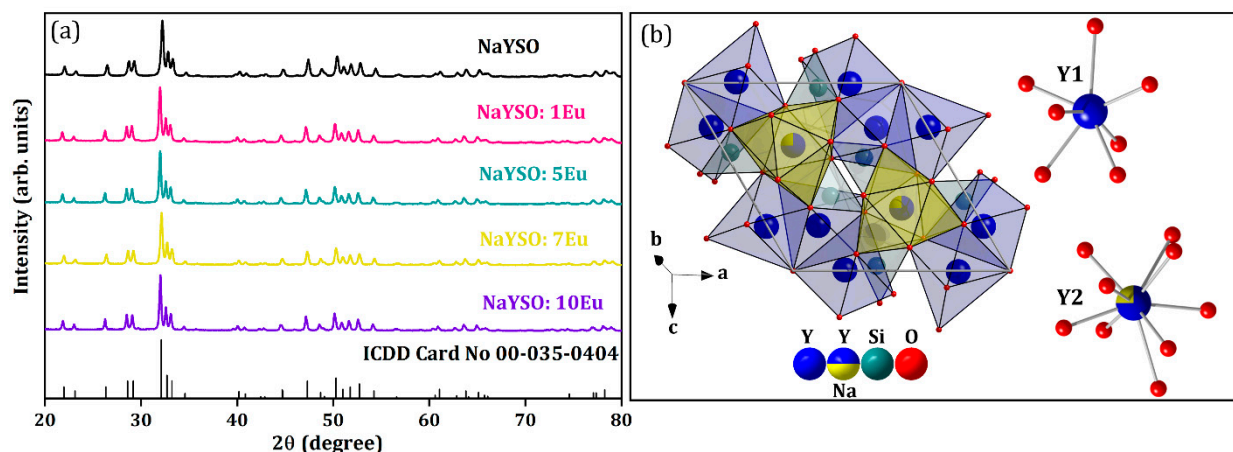


Figure 2. (a) XRD patterns of NaY_{9-x}Eu_xSi₆O₂₆ materials with standard ICDD Card No. 00-035-0404; (b) representation of NaY₉Si₆O₂₆ crystal structure and coordination environment of Y1 and Y2 atoms in the NaY₉Si₆O₂₆ crystal lattice designed with DIAMOND Release 4.6.8. Crystal Impact GbR software (version 4.0).

As seen from Table 3 the value of lattice constant *c* becomes larger with the increase of Eu³⁺ concentration. When Y³⁺ is replaced with Eu³⁺ within the crystal structure, the significant increase in the lattice parameter *c* rather than *a* = *b* can be explained by several factors such as: (a) ionic radius—Eu³⁺ has a larger ionic radius than Y³⁺ which can lead to an expansion of the unit cell in the vertical direction (along the *c*-axis); (b) crystal field effects—the different electronic configurations and interactions of Eu³⁺ compared to Y³⁺ can alter the crystal field, which affects the bond lengths and angles, particularly in the axial direction, which might preferentially expand the *c*-parameter; (c) phase stability—the introduction of Eu³⁺ may stabilize certain orientations within the crystal structure that are

more favorable in the vertical direction, leading to an increase in c without a corresponding increase in $a = b$. So, the significant increase in the c lattice parameter upon replacing Y^{3+} with Eu^{3+} in a hexagonal crystal structure is primarily driven by the larger ionic radius of Eu^{3+} , changes in crystal field interactions, and potentially different bonding characteristics that favor expansion along the c -axis.

Table 3. Selected structural parameters of the synthesized $NaY_{9-x}Eu_xSi_6O_{26}$ samples. CS—Crystallite size; Rwp—the weighted profile factor; Rp—the profile factor; Re—the expected weighted profile factor; and GOF—the goodness of fit.

ICDD Card 00-035-0404	NaYSO	NaYSO: 1Eu	NaYSO: 5Eu	NaYSO: 7Eu	NaYSO: 10Eu
a = b (Å)	9.3398 (10)	9.3539 (13)	9.3504 (7)	9.3483 (15)	9.3511 (5)
c (Å)	6.7508 (8)	6.7571 (10)	6.7610 (5)	6.7611 (11)	6.7769 (5)
CS (Å)	181 (2)	212 (3)	233 (3)	219 (2)	282 (3)
Strain	0.28 (5)	0.23 (6)	0.21 (4)	0.22 (4)	0.17 (3)
Rwp	12.56	12.37	10.69	9.86	9.69
Rp	8.86	8.60	7.46	7.0	6.78
Re	3.35	3.17	3.13	3.13	2.99
GOF	3.7449	3.8971	3.4905	3.2399	3.2399

There are two distinct crystallographic positions for the Y^{3+} in the $NaY_9Si_6O_{26}$ crystal structure (Figure 2b): one is coordinated by seven oxygen atoms (Y1), and the other one by nine (Y2), while the silicon atom is positioned in a tetrahedral site. In the nine-coordinated site, one quarter of the Y^{3+} position is occupied by Na^+ atoms, thus preserving the charge balance [23].

3.3. Microstructural Characterization by Electron Microscopy (SEM and TEM)

It is generally acknowledged that in nanoparticles with a large specific surface area, luminescence characteristics are affected by the particles' size, which ultimately influences excitation efficiency and emission. The SEM images captured at low magnification illustrate that the representative NaYSO:1Eu powder sample tends to form agglomerates (Figure 3a). At higher magnification, the surface morphology shows that the particles can be classed as round-shaped nano-sized particles (Figure 3b). Figure 3c illustrates the microstructure at a local scale, examined through transmission electron microscopy, and shows the presence of sphere-like nanoparticles. The TEM images used for the average particle size analysis considered over 70 particles, using the largest axis of the grain. From the inset in Figure 3c, it can be concluded that the most frequent nanoparticle size is in the 45 to 60 nm range with an average particle size of ~53 nm in diameter. The upper inset in Figure 3c shows a ring electron diffraction pattern as evidence of the polycrystalline nature of the material. At the same time, the rings' grainy form is linked to the finding that the constituent crystallites have a size of ~20 nm. The ring pattern is formed due to diffraction from polycrystalline material because diffracting planes are oriented randomly in all possible directions. This agrees with the crystallite size obtained from XRD measurements (~20 nm) and particle size obtained from TEM (45–60 nm range) showing that each particle is composed of approximately 2–3 crystallites.

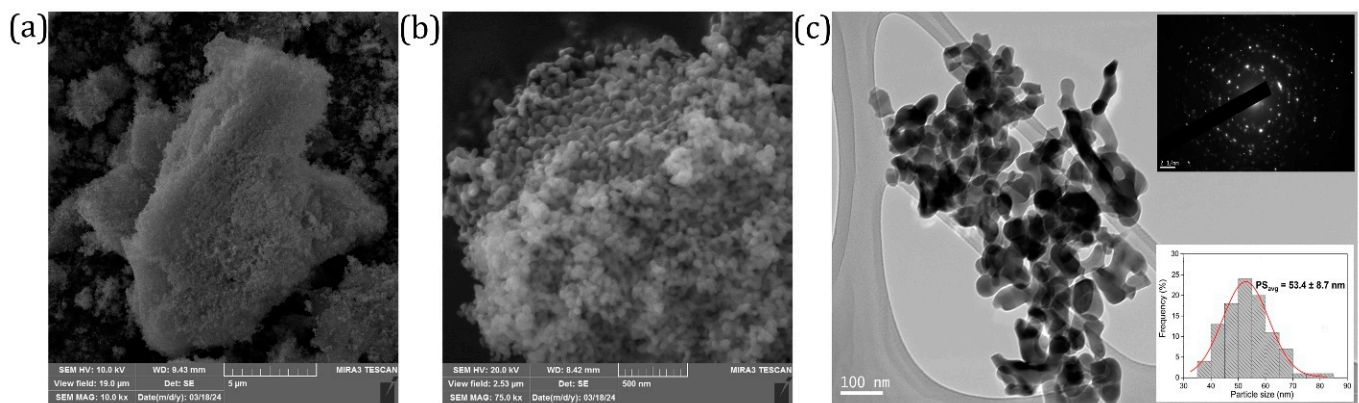


Figure 3. SEM images of the representative NaYSO:1Eu powder sample at different magnifications: (a) $\times 10,000$, (b) $\times 75,000$, (c) TEM image of the representative NaYSO:1Eu powder sample with electron diffraction pattern and particle size distribution histogram as insets.

3.4. Calculations of the Structural and Electronic Properties

Calculations of the structural and electronic properties of NaY₉Si₆O₂₆ were performed using the CASTEP module of Materials Studio [24]. The general gradient approximation (GGA) [25] and local density approximation (LDA) [26] were used to treat the exchange-correlation effects. The plane wave basis set cut-off was 370 eV; the k-points grid was $3 \times 3 \times 4$. The electronic configurations for the atoms in the unit cell were $2s^2 2p^6 3s^1$ for Na, $3s^2 3p^2$ for Si, $4s^2 4p^6 4d^1 5s^2$ for Y, and $2s^2 2p^4$ for O.

Figure 4a,b show the calculated (in both approximations) band structure of the studied material. The calculated direct band gap values are 4.665 eV (LDA) and 3.765 eV (GGA).

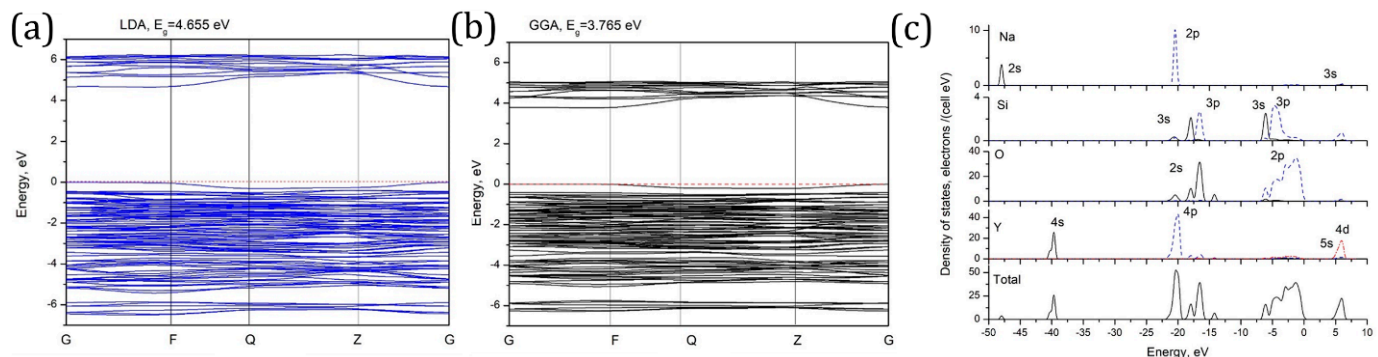


Figure 4. (a,b) Calculated band structure of NaY₉Si₆O₂₆. The coordinates of the special points of Brillouin zone are (in units of the reciprocal lattice unit vectors): G (0, 0, 0); F (0, $\frac{1}{2}$, 0); Q (0, $\frac{1}{2}$, $\frac{1}{2}$); Z (0, 0, $\frac{1}{2}$), and (c) calculated density of states diagrams for NaY₉Si₆O₂₆.

Very low dispersion of the calculated electronic states, which follows from nearly flat electronic bands, indicates low mobility of the charge carriers. The origin of the calculated bands can be clarified with the help of the density of states diagrams (Figure 4c). The conduction band consists mainly of the Y 4d and Na 3s states. The upper part of the valence band is made by the oxygen 2p states, and highly hybridized 3s-3p states of silicon in four-fold coordination (sp^3 hybridized states) are mainly at the bottom of the valence band. Several narrow bands between -22 eV and -13 eV are made by the oxygen 2s and the same highly hybridized Si 3s-3p states. Finally, at about -48 eV and -40 eV very deep Na 2s and Y 4s states, respectively, can be identified.

3.5. Optical Spectroscopy

The diffuse reflectance spectrum of the NaYSO:10Eu sample given in Figure 5a is recorded in the 220–700 nm range. A broad absorption below 250 nm is attributed to the charge transfer band while peaks at longer wavelengths are attributed to the f - f transition of Eu^{3+} ions.

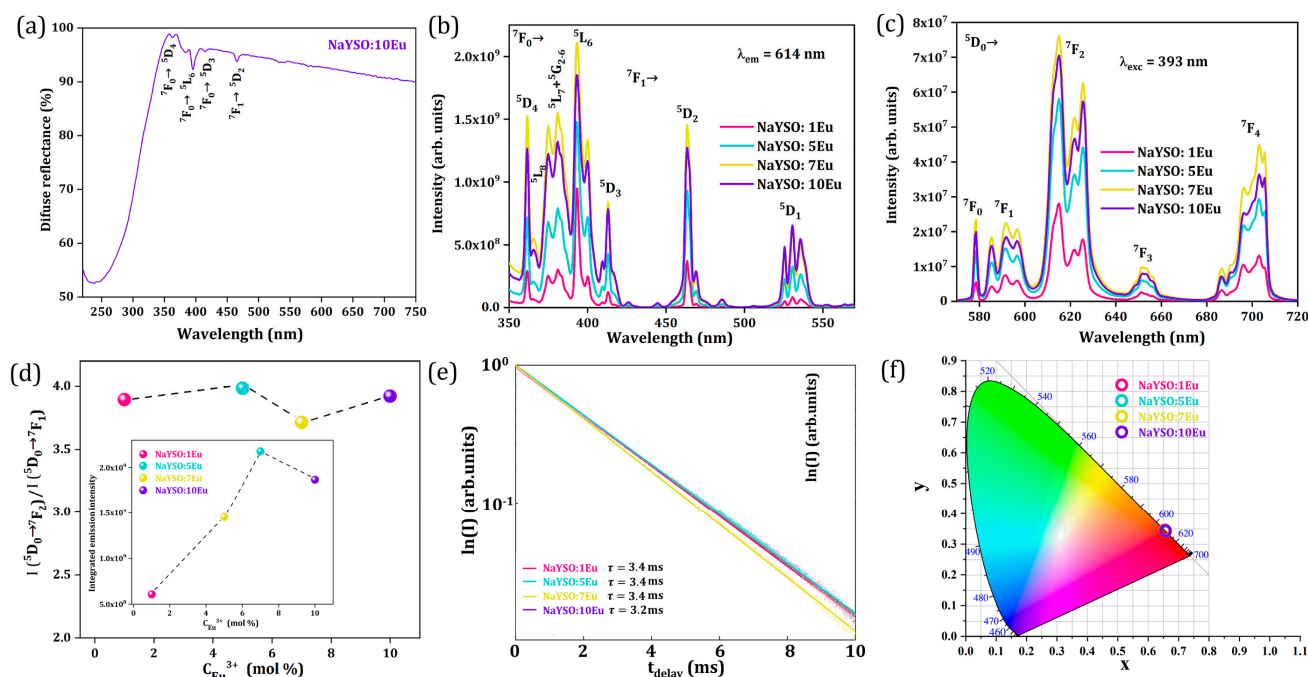


Figure 5. (a) Diffuse reflectance spectrum of NaYSO:10Eu sample. Ambient temperature photoluminescence of $\text{NaY}_9\text{Si}_6\text{O}_{26}:\text{xEu}^{3+}$ ($\text{x} = 1, 5, 7, 10$ mol% Eu^{3+}) samples: (b) excitation spectra under $\lambda_{\text{em}} = 614$ nm; (c) emission spectra under $\lambda_{\text{exc}} = 393$ nm; (d) asymmetry ratio as a function of Eu ions concentration with integrated emission intensity as a function of Eu^{3+} ions concentration given as Inset; (e) lifetime decay curves as a function of Eu^{3+} ions concentration; (f) CIE diagram with calculated coordinates.

The photoluminescence excitation spectra of all $\text{NaY}_9\text{Si}_6\text{O}_{26}:\text{xEu}^{3+}$ ($\text{x} = 1, 5, 7, 10$ mol% Eu^{3+}) samples, recorded in the 350–575 nm ($\lambda_{\text{em}} = 614$ nm) range, are given in Figure 5b, showing emission lines of typical transitions within the $4f^6$ configuration of Eu^{3+} . Excitation into the $^5\text{L}_6$ (393 nm) energy level of Eu^{3+} is picked for observing the emission spectra since it is the most intense peak in the excitation spectra. Upon excitation, distinct emission bands in the visible spectral region corresponding to $^5\text{D}_0 \rightarrow ^7\text{F}_j$ ($j = 0, 1, 2, 3$, and 4) f - f transitions, placed around 578 nm, 592 nm, 615 nm, 652 nm, and 703 nm, respectively, are visible (see Figure 5c).

As mentioned above, there are two different Y^{3+} sites with unequal coordination numbers in the silicate apatite structure [7], one having nine-coordination with C_3 symmetry and the other having seven-coordination with C_s symmetry, both being non-centrosymmetric. Such low symmetry stimulates the splitting of energy levels into a large number of Stark sublevels [27]. According to the Laport rule, the Eu^{3+} ion, with an $[\text{Xe}]4f^6$ electronic configuration, has only magnetic-dipole transitions in a centrosymmetric site, whereas if in a non-centrosymmetric site, both magnetic-dipole and induced electric-dipole transitions are probable.

The $^5\text{D}_0 \rightarrow ^7\text{F}_1$ is a magnetic-dipole transition that does not depend on the local environment. However, the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ electric-dipole transition is hypersensitive and highly dependent on changes in the local environment around the Eu^{3+} ions. Theoretically, when the Eu^{3+} ions occupy non-centrosymmetric sites, the emission spectrum shows a more intense $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition than the $^5\text{D}_0 \rightarrow ^7\text{F}_1$, which agrees with our experimental

observations. In addition, the ratio of the integrated intensity of the $^5D_0 \rightarrow ^7F_2$ and $^5D_0 \rightarrow ^7F_1$ transitions, known as the asymmetry ratio, can be considered indicative of the reduction of symmetry of the coordination environment around the Eu^{3+} ion and is given by Equation (1):

$$R = \frac{I(^5D_0 \rightarrow ^7F_2)}{I(^5D_0 \rightarrow ^7F_1)} \quad (1)$$

The asymmetry ratio values obtained from the emission spectra are presented in Figure 5d showing no significant change with Eu^{3+} concentration. The high value of the asymmetry ratio as a function of dopant ion concentration indicates low symmetry of the Eu^{3+} surroundings in the $\text{NaY}_9\text{Si}_6\text{O}_{26}$ apatite host. Also, no significant change with Eu^{3+} concentration reveals that the degree of distortion of the local symmetry around Eu^{3+} is similar in all the samples in the series produced, as indicated by XRD analysis. The inset in Figure 5d presents the integrated emission intensity as a function of Eu^{3+} concentration showing that 7 mol% Eu^{3+} is the optimal doping concentration in the $\text{NaY}_9\text{Si}_6\text{O}_{26}$ host lattice.

The photoluminescent lifetime decay curves of all Eu^{3+} -doped NaYSO samples recorded at ambient temperature can be seen in Figure 5e. The values of the lifetime (τ) were obtained after the data were fitted to a simple single exponential function. Even though two distinct crystallographic positions for Y^{3+} can host Eu^{3+} ions, our experimental data reveal single exponential decay curves. This can be explained either by both Y sites being non-centrosymmetric and having similar C_3 and C_s symmetry or, most likely, by the similar lifetime values for each of the two Y sites that are not distinguishable by our integrated intensity decay measurement. All samples have similar, rather long lifetime values calculated to be in the 3.2 to 3.4 ms range.

Chromaticity coordinates (x , y) on the CIE chromaticity diagram, which represents a two-dimensional color space encompassing all colors visible to the human eye, can be utilized to quantify apparent color. We derived the CIE chromaticity coordinates from the photoluminescent spectra to evaluate the color of the synthesized samples, as shown in Figure 5f. For all the samples, CIE coordinates are almost identical ($x = 0.65$, $y = 0.34$; $\lambda_{\text{dom}} = 614 \text{ nm}$; color purity = 93.6%) and placed in the orange-red portion of the diagram, confirming that there is no significant change in the local symmetry around Eu^{3+} across the series and consequently in the emission spectra.

The energy levels of trivalent Eu^{3+} ions in the structure were determined using room temperature excitation and emission spectra and are given in Table 4. Based on the whole luminescence spectra and the ratio of the $^5D_0 \rightarrow ^7F_J$ ($J = 0-4$) transitions, it is assumed that the Eu^{3+} ion occupies both sites. Also, using the $^7F_1$ manifold, we carried out a simplified phenomenological crystal field calculation by considering only the second-order crystal field B_{20} (51.46 cm^{-1}), and B_{22} (-642.6 cm^{-1}) parameters to calculate the crystal field strength parameter N_v (1442.65 cm^{-1}) [28], using the simplified Equation (2) given by Monteil and Zhu [29,30].

$$N_v(B_{2q}) = \sqrt{4\pi(B_{20}^2 + 2B_{22}^2)}/5 \quad (2)$$

Table 4. Energy levels of Eu^{3+} in the hexagonal $\text{NaY}_9\text{Si}_6\text{O}_{26}$.

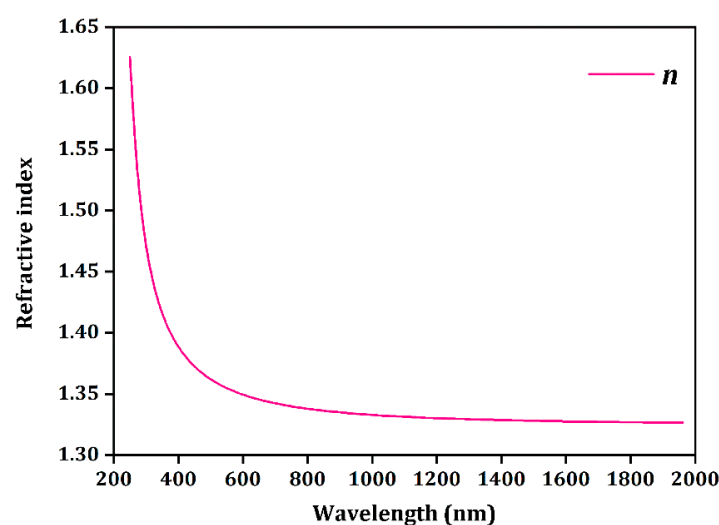
	$^7F_0$	$^7F_1$	$^7F_2$	$^7F_3$	$^7F_4$
	0	207	1026	1854	2719
		380	1209	1937	2804
[cm^{-1}]		522	1299	1984	2928
				2042	3061
					3112

Table 4. Cont.

	${}^7F_0$	${}^7F_1$	${}^7F_2$	${}^7F_3$	${}^7F_4$	
${}^5D_0$	${}^5D_1$	${}^5D_2$	${}^5D_3$	${}^5L_6$	${}^5L_7 + G_{2-6}$	${}^5L_8, {}^5D_4$
17,286	18,657	21,322	24,213	25,000	26,110	27,322
	18,850	21,575	24,420	25,413	26,247	27,662
	19,029				26,667	

3.6. The Judd–Ofelt Calculation

To perform Judd–Ofelt calculations, the refractive index of $\text{NaY}_9\text{Si}_6\text{O}_{26}$ is determined using the structural and electronic property calculations given above. Figure 6 presents the calculated index of refraction values as a function of wavelength.

Figure 6. Calculated refractive index of $\text{NaY}_9\text{Si}_6\text{O}_{26}$.

The Judd–Ofelt theory is a framework for understanding the optical behavior of rare earth ions in different host materials. It allows for the calculation of intensity parameters for electric dipole transitions, aiding in the prediction of their absorption and emission spectra. In the case of the Eu^{3+} ion, these parameters can be derived from the emission spectrum of Eu^{3+} using the formula [31]:

$$\Omega_\lambda = \frac{D_1}{e^2 U^\lambda} \left(\frac{\bar{\lambda}_\lambda}{\bar{\lambda}_1} \right)^3 \frac{9n_1^3}{n_\lambda(n_\lambda^2 + 2)^2} \frac{I_\lambda}{I_1}, \quad \lambda = 2, 4 \quad (3)$$

Here, e denotes the elementary charge, U^λ represents the squared reduced matrix elements, n is the refractive index at the wavelength of the transition, and I is the integrated intensity. The transition ${}^5D_0 \rightarrow {}^7F_1$ is a purely magnetic dipole transition, meaning its dipole strength D_{MD} remains unaffected by the host matrix. The term $\bar{\lambda}$ corresponds to the average wavelength of the emission. The subscripts λ indicate electric dipole transitions.

The Judd–Ofelt Ω_6 parameter can be best determined from the excitation spectrum of Eu^{3+} using the formula [32]:

$$\Omega_6 = \frac{n_6 n_1}{(n_6^2 + 2)^2} \frac{\bar{\lambda}_6}{\bar{\lambda}_1} \frac{D_1}{e^2 U^6} \frac{I_6}{I_1} \quad (4)$$

In this context, index 6 corresponds to excitation from the ground level to ${}^5L_6$, and 1 for the pure magnetic dipole transition to ${}^5D_1$.

Using the Judd–Ofelt parameters, we can derive key quantities relevant to the practical applications of luminescent materials. The radiative transition probabilities, or rates of spontaneous emission, are given by [33]:

$$A_{\lambda} = \frac{64\pi^4}{3h} \frac{10^7}{\lambda_{\lambda}^3} \frac{n_{\lambda}(n_{\lambda}^2 + 2)^2}{9} e^2 \Omega_{\lambda} U^{\lambda} \quad (5)$$

$$A_{MD} = \frac{64\pi^4}{3h} \frac{10^7}{\lambda_{MD}^3} n_{MD}^3 D_{MD} \quad (6)$$

where h stands for the Planck constant. The emission branching ratio is defined as:

$$\beta_{\lambda} = \frac{A_{\lambda}}{A_1 + A_2 + A_4} \quad (7)$$

Note that A_6 is neglected as its intensity is very low and because the transition ${}^5D_0 \rightarrow {}^7F_6$ lies outside the visible range. The radiative lifetime is the inverse of the total radiative transition probability:

$$\tau_R = (A_1 + A_2 + A_4)^{-1} \quad (8)$$

The intrinsic quantum yield can then be calculated from the ratio of the observed and radiative lifetimes:

$$\eta = \frac{\tau}{\tau_{rad}} \quad (9)$$

A complete Judd–Ofelt analysis was performed on all concentrations and the results are summarized in Table 5. The Ω_2 parameter, which is related to the degree of symmetry and covalency of the Eu^{3+} ion, is unchanged with the Eu^{3+} concentration, while the Ω_4 and Ω_6 parameters related to the long-range effects and rigidity of the matrix [34] see a small decrease with rising concentration. According to the branching ratio and the radiative transition probability, the hypersensitive ${}^5D_0 \rightarrow {}^7F_2$ transition is dominant in the emission spectrum. The concentration has no significant impact on the rather long radiative lifetime of ${}^5D_0$ emissions, as confirmed by experimental data given previously in Figure 5e.

Table 5. Judd–Ofelt analysis of $\text{NaY}_9\text{Si}_6\text{O}_{26}$ doped with various concentrations of Eu^{3+} .

C [%]	$\Omega_2 \cdot 10^{20}$ [cm ²]	$\Omega_4 \cdot 10^{20}$ [cm ²]	$\Omega_6 \cdot 10^{20}$ [cm ²]	A_1 [s ^{−1}]	A_2 [s ^{−1}]	A_4 [s ^{−1}]	β_1 [%]	β_2 [%]	β_4 [%]	τ_R [ms]	τ [ms]	η [%]
1	6.5	6.51	1.31	35.5	139.4	68.1	14.6	57.4	28	4.1	3.4	83
5	6.66	6.45	0.69	35.5	142.7	67.4	14.5	58.1	27.4	4.1	3.4	83
7	6.22	6.37	0.632	35.5	133.2	66.6	15.1	56.6	28.3	4.3	3.4	79
10	6.57	6.05	0.494	35.5	140.6	63.2	14.8	58.7	26.4	4.2	3.2	76

4. Conclusions

This study gives a comprehensive insight into Eu^{3+} -doped $\text{NaY}_9\text{Si}_6\text{O}_{26}$ oxyapatite phosphor—its synthesis, structural, morphological, electronic, and optical properties. It is shown that with hydrothermal synthesis, it is possible to obtain single-phase hexagonal $\text{NaY}_9\text{Si}_6\text{O}_{26}$ oxyapatite nanophosphors. Differential thermal analysis shows that, in the $\text{NaY}_9\text{Si}_6\text{O}_{26}$ host material, amorphous-to-crystalline transformation is somewhat lower compared to simple orthosilicates (Y_2SiO_5 and $\text{Y}_2\text{Si}_2\text{O}_7$) and comparable to similar, apatite-type silicates (i.e., $\text{La}_{10}\text{Si}_6\text{O}_{27}$). Photoluminescent measurements show typical orange-red emission of trivalent Eu^{3+} showing that 7 mol% Eu^{3+} is the optimal doping concentration in the $\text{NaY}_9\text{Si}_6\text{O}_{26}$ host lattice. However, lifetime measurements show that the Eu^{3+} concentration has no significant impact on the rather long radiative lifetime of ${}^5D_0$

emission. The findings presented here can be used to further develop alkaline metal/rare earth orthosilicate phosphors that meet specific needs in technology and industry.

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