Synthesis and luminescence properties of novel NaSCN: xCe³⁺ phosphor

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ABSTRACT
The blue-emitting novel phosphor NaSCN: xCe³⁺(x = 0.005, 0.01, 0.02) is reported here for the first time. The synthesis method is simple, time saving, and cost effective. X-ray power diffraction (XRD) analysis confirmed the formation of said phosphor, and SEM images were recorded for the surface morphology. Photoluminescence emission (PL) and excitation (PLE) measurements were also recorded. Variations in emission intensity with the Ce³⁺ concentration were observed and recorded leading to determination of the critical concentration. The concentration quenching observed in this phosphor is due to mainly electric multipole interaction. The CIE1931 color co-ordinates and the critical distance were determined.

1. Introduction
Luminescent materials, also known as phosphors, have several applications ranging from fluorescent lamps, PL-LCD and plasma displays to conversion materials in solar cells and wavelength conversion phosphors in white LEDs. The search for new phosphors for various applications is widely recognized. Researchers in this field are exploring new hosts and dopants along with simplification of synthesis methods that can lead to cost reductions [1–6]. The rare earth lanthanide ion Ce³⁺ is a well-known dopant ion with the simplest of electronic configurations. It has a 4f⁵5d°ground state and 4f⁵5d¹ excited state and therefore shows typical 4f-5d transitions. The 4f-5d transitions permit parity and hence show a large absorption cross-section and appear as intense bands in the spectra. Thus, phosphors doped with Ce³⁺ absorb excitation energy efficiently. It is reported, further that in nitride and sulfide [7,8] hosts, the Ce³⁺ activator shows excitation and emission at longer wavelengths. In thiocyanate compounds both sulfur and nitrogen atoms are present. In 2004 Michel Fleck [9] reported more than 80 inorganic thiocyanate hosts. Eu²⁺ luminescence in some of these hosts such as strontium thiocyanate (Sr (SCN)₂) [10], barium thiocyanate (Ba (SCN)₂) [11] and in Ca (SCN)₂ · 2H₂O [12] was reported by C. Wickleder et al. The green-emitting CsSCN: Eu²⁺ phosphor was reported by Bertha Abdu Danja et al [13]. But there are no studies on Ce³⁺ luminescence in these hosts. Thus, we chose to study Ce³⁺ luminescence in these hosts. In an earlier paper we reported Ce³⁺ luminescence in a potassium thiocyanate host [14] for the first time. As per expectations, excitation as well as emission wavelengths were observed on the longer side. That prompted us to investigate Ce³⁺ luminescence in other thiocyanate hosts. In this paper we report a Ce³⁺ luminescence in NaSCN host. To the best of our knowledge, we are reporting it for the first time. The simple, time-saving and economical synthesis method has been adopted.

2. Experimental
Phosphor samples of NaSCN: xCe³⁺ doped with different molar concentrations of Ce³⁺ (x = 0.005, 0.01, 0.02) were prepared by re-crystallization through an aqueous solution at 353 K. NaSCN (AR grade) and cerium chloride (hydrated) from Indian rare earths (99.9% purity) were weighed in stoichiometric proportions and dissolved in a minimum amount of water. The water was then boiled off and the solution was evaporated to dryness. The resulting mass was dried at room temperature for one hour and then crushed to a fine powder with an agate mortar. An outline of this method is shown in the flow-chart (Figure 1). The compound formed is hygroscopic and captures moisture if left in open air. Hence, the samples were stored in air-tight bottles. No change in the PL properties was observed in the phosphor samples thus stored for several months.

The XRD pattern was recorded using a Rigaku miniflex automatic diffractometer with Cu Kα radiation (λ = 1.540598Å) operated at a scan speed of 4.000°/min. The XRD data was collected in a 2θ range from 10° to 80°. The photoluminescence (PL) emission and photoluminescence excitation spectra (PLE) were recorded at room temperature with the help of a Hitachi-F7000 florescence spectrophotometer. The spectral resolution of both the excitation and emission spectra, and the width of the monochromator slits as well the measurement conditions such as the...
PMT detector sensitivity and scan speed were maintained with no change for all the samples.

Radiant imaging color calculator software was used to obtain the Commission International de l’Eclairage (CIE) color coordinates.

3. Results and discussion

3.1. XRD analysis

It was observed that the powder XRD pattern of as-synthesized phosphor NaSCN: xCe³⁺ prepared by re-crystallization through an aqueous solution (Figure 2) is in good agreement with JCPDS card No. 74–0946. NaSCN is orthorhombic with the Pnma group and the reported lattice constants are a = 13.38 Å, b = 4.09 Å, and c = 5.66Å with Z = 4. The thiocyanate group is linear and the Na⁺ ion is surrounded octahedrally by three S and three N atoms in a fac arrangement [15]. The recorded SEM images show a surface morphology of as-synthesized phosphor. It was observed that the particles were irregular in shape with particle sizes ranging from 5–10 μm (Figure 3).

The acceptable percentage difference in ionic radii between doped and substituted ions must not exceed 30% [16]. The calculations of the radius percentage difference (Dr) between the doped ions (Ce³⁺) and the possible substituted ion (Na⁺) in NaSCN: xCe³⁺ are summarised in Table 1. The values are based on the following formula:

![Figure 1](image1.png)

**Figure 1.** Powder XRD pattern of NaSCN: xCe³⁺ prepared by re-crystallization through aqueous solution.

![Figure 2](image2.png)

**Figure 2.** Flow chart for the synthesis of NaSCN: xCe³⁺ phosphor.

![Figure 3](image3.png)

**Figure 3.** SEM images of as-synthesized NaSCN: xCe³⁺.
where,  
\[ CN = \text{co-ordination number}, \quad Rm(CN) = \text{Radius of host cations and} \quad Rd(CN) = \text{Radius of dopant.} \]

The Ce\(^{3+}\) ionic radius (r = 1.01 Å, CN = 6) is closest to that of Na\(^+\) (r = 1.02 Å, CN = 6), indicating that Ce\(^{3+}\) ions substitute Na\(^+\) ions in the NaSCN host \[17\]. In the sodium thiocyanate host, Na\(^+\) is six co-ordinated with three sulfur atoms and three nitrogen atoms (Figure 4). With this co-ordination a large red shift is observed. Hence, emissions in the visible range of the spectrum are expected.

### 3.2. Photoluminescence

It is well known that for the phosphors, the activator rare earth ions as well the host matrix play important roles in deciding the excitation as well as the emission band. Due to the exposure of the "d" orbital to the crystal coordination environment, the 4f→5d transition of RE ions is strongly affected by the crystal field. The Ce\(^{3+}\) ion has the simplest electronic configuration with a 4f\(^1\) 5d\(^0\) ground state and a 4f\(^0\)5d\(^1\) excited state and therefore shows typical 4f-5d transitions. The positions of the 5d levels are influenced much more by crystal field interactions than the 4f levels. This is because of the strong interaction of the 5d-electron with neighbouring anion ligands in the compound.

Figure 5 shows the photoluminescence excitation and emission spectra of NaSCN: xCe\(^{3+}\) (for x = 0.01). The excitation spectrum monitored at 452 nm emissions, exhibits a broad excitation band peaking at 346 nm. It was observed that the emission spectrum is also broad, peaking at 452 nm, corresponding to the d→f transition of Ce\(^{3+}\) ions.

The emission spectra of NaSCN: xCe\(^{3+}\) doped with different Ce\(^{3+}\)concentrations for an excitation wavelength of 350 nm were recorded (Figure 6). All of the emission spectra exhibit a similar profile with different relative intensities. The emission intensity increases initially with increases in the Ce\(^{3+}\) concentration until reaching the maximum at x = 0.01, and then decreases due to internal concentration quenching.

The concentration quenching mechanism is generally associated with energy transfer. The non-radiative energy transfer process from one Ce\(^{3+}\) ion to another Ce\(^{3+}\) ion can be described by three different methods: (1) exchange interaction, (2) radiation reabsorption, and (3) multipolar interaction. When discussing the mechanism of energy transfer in phosphors, Blasse \[18\] suggested that if the activator is introduced solely on one crystallographic site, the critical energy transfer distance \(R_C\) is approximately equal to twice the radius of a sphere with the same volume. In order to discuss the mechanism of energy transfer between the activators in the NaSCN host further, the critical energy transfer distance \(R_C\) can be calculated by the following equation:

\[
R_C \approx 2 \left( \frac{3V}{4\pi\chi_cN} \right)^{\frac{1}{3}}
\]

where,  
\[ \chi_c \] is the critical concentration, N is the number of cation sites in the unit cell, and V is the volume of the unit cell. In this case, therefore, V = 300.43Å, N = 4 and

![Figure 4](#)  
Co-ordination of Na\(^+\) ions in NaSCN crystal.

![Figure 5](#)  
(a) PLE and (b) PL curves of Na\(_{1-x}\)SCN: xCe\(^{3+}\) (for x = 0.01).
the critical doping concentration of Ce$^{3+}$ in the NaSCN host is found to be 0.01. Thus, the $R_C$ of Ce$^{3+}$ in the NaSCN: xCe$^{3+}$ phosphor is 24.30 Å. An exchange interaction typically occurs with a large direct or indirect overlap between the donor and acceptor, which is responsible for the energy transfer of forbidden transitions and shorter critical distances of less than 5 Å [19,20]. It is well known that the 4f $\rightarrow$ 5d transition of Ce$^{3+}$ is allowed and hence, the mechanism of the exchange interaction plays no role in NaSCN: xCe$^{3+}$ phosphors. The mechanism of radiation re-absorption is the primary method only if the fluorescence spectra of the excitation and emission have an obvious overlap. Thus, the small spectral overlap of <1% observed for the NaSCN: xCe$^{3+}$ phosphor indicates that the radiation re-absorption can be ignored in this case. As a result, the process of energy transfer of Ce$^{3+}$ ions in NaSCN must be due to an electric multipole interaction.

Figure 7 shows the dependence of the peak intensity of the emission centered at 452 nm on the Ce$^{3+}$ doping concentration (x) in NaSCN: xCe$^{3+}$. The maximum intensity of the emission is observed for x = 0.01 doping concentration of Ce$^{3+}$.

Figure 8 shows CIE 1931 color coordinates of (0.14, 0.11) for NaSCN: 0.01Ce$^{3+}$. The NaSCN: xCe$^{3+}$ phosphor shows a hygroscopic nature. Packed in air-tight
bottles however, the phosphor powder remains intact. A comparison of the as-synthesized Ce$^{3+}$ doped blue-emitting thiocyanate host phosphors with respect to different parameters is tabulated in Table 2.

4. Conclusion

A blue-emitting Ce$^{3+}$-doped sodium thiocyanate phosphor is reported here for the first time. The phosphor is prepared using a simple, time-saving, economical method of re-crystallization through an aqueous solution at a temperature of 353 K. The XRD pattern of NaSCN: xCe$^{3+}$ prepared by this method is in good agreement with JCPDS card No. 74–0946.

Photoluminescence measurements showed that the NaSCN: xCe$^{3+}$ phosphor exhibits emissions at 452 nm corresponding to the d–f transitions of Ce$^{3+}$ ions. Ce$^{3+}$ ions occupy the Na$^+$ sites and form one emission center at 452 nm. PL spectra at various doping concentrations of Ce$^{3+}$ show maximum emission intensity at x = 0.01, after which concentration quenching is observed. The phosphor NaSCN:0.01 Ce$^{3+}$ shows the CIE 1931 color coordinates to be (0.14, 0.11).

Disclose statement

No potential conflict of interest was reported by the authors.

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