Vibrationally Induced Photophysical Response of Sr$_2$NaMg$_2$V$_3$O$_{12}$:Eu$^{3+}$ for Dual-Mode Temperature Sensing and Safety Signs

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In the dual-emitting Eu$^{3+}$-activated Sr$_2$NaMg$_2$V$_3$O$_{12}$ garnet, vibrationally induced thermometric response and thermochromic luminescence are investigated for the first time. Based on the diverse thermal quenching of VO$_4^{3-}$ and Eu$^{3+}$ along with the advantage of variation in the fluorescence intensity ratio, a potential phosphor for sensitive dual-mode ratiometric and colorimetric temperature sensors is proposed in which maximum absolute and relative sensitivity of 0.0135 K$^{-1}$ and 1.61% K$^{-1}$ are obtained at 420 K with a temperature resolution $<$0.2 K. Efficient thermochromic luminescence in which color shift from white (300 K) to red (500 K) is observed such that the requirement of larger number of phonons weakens the nonradiative relaxation of Eu$^{3+}$, resulting in slow quenching, substantiated by estimating radiative and nonradiative decay rates by the 4f–4f intensity method. In contrast, a strong vibrational coupling of excited electrons of the VO$_4^{3-}$ complex is identified and verified by means of temperature-dependent Raman and photoluminescence excitation spectra for the first time. Consequently, an increased thermal population of vibrational levels favors rapid thermal quenching of luminescence of VO$_4^{3-}$ via crossover mechanism. Hence dual-centered Sr$_2$NaMg$_2$V$_3$O$_{12}$:Eu is an efficient thermodmetric and thermochromic luminescent material for optical thermometry and safety sign applications in a high-temperature environment.

1. Introduction

Measurement of temperature is an indispensable activity in regular life. Due to the pandemic situation, the popularity of non-contact thermometry is tremendously increased. In short, temperature is one of the basic and most important physical quantities and has profound influence on natural, biological as well as laboratory processes. Thus, the accuracy and consistency in determining temperature using thermometers is a serious concern. Thermometry is generally classified into two-contact and noncontact, based on the interaction of the devices with the objects whose temperature is to be measured. The conventional contact thermometry requires a direct contact of the thermometer with the objects of interest. However, they cannot be used in measurements at microscopic scale, such as for biological samples. Moreover, they suffer from a slow response rate, low resolution, as well as interference of a strong electromagnetic field. On the other hand, noncontact/radiation/optical thermometry involves no direct contact and is also a non-invasive technique that has a fast response rate as well as high spatial resolution and temperature sensitivity. Infrared thermography involves the analysis of infrared radiation emitted by objects of interest. It depends on the surface emissivity of the material and is affected by poor spatial resolution. However, optical temperature sensors based on luminescence are a key solution which offer high detection sensitivity, spatial resolution, and short acquisition time. The basic principle associated with optical thermometers is the temperature-dependent energy-light conversion process taking place in the phosphor material. Accordingly, those phosphor materials which exhibit the respective variation in emission intensity, decay, or rise time and emission color with temperature are termed “thermographic phosphors” (TGP$s$). It is essential that TGP$s$ should not undergo oxidation in high-temperature environments as well as being nonreactive to harsh chemicals, insensitive to electromagnetic fields, etc. There are mainly two methods followed to measure the temperature-dependent luminescence behavior for thermometry applications. The first method is based on the intensity ratio of two luminescence peaks of thermographic phosphors termed “fluorescence intensity ratio” (FIR), whereas the second method is based on the decay time of thermographic phosphors. The FIR has advantages like self-referencing and negligible drift. As the FIR uses the principle of the relative intensity ratio between two emission peaks, the problems due to variations in extrinsic factors can be eliminated. Most of the FIR techniques are based on the thermally coupled levels (TCEL$s$) of rare-earth (RE) ions such as Eu$^{3+}$ ($^5$D$_{0}$, $^5$D$_{1}$), Er$^{3+}$ ($^4$H$_{11/2}$, $^4$S$_{3/2}$), and Tm$^{3+}$ ($^5$F$_{3}$, $^5$G$_{4}$). However, TCEL$s$ have
overlapped emission due to the small energy gap (20 cm$^{-1}$ < $\Delta E$ < 2000 cm$^{-1}$), which significantly reduce the relative sensitivity, thereby limiting the accuracy and signal discrimina-
tibility of the sensor. In addition, RE ions having suitable TCELs are limited in number. All these factors grabbed research attention toward non-TCEL-based thermometry. As a result, strategies such as the intervalence charge transfer state (IVCT), opposite temperature dependence, RE–RE codoped core–shell nanoparticles, and metal–organic frameworks (MOFs) are studied. Recently, the technique of phonon-assisted energy transfer between two different luminescent centers has been found to be a potential candidate for optical thermometry to achieve better relative sensitivity and signal discrimina-
tibility.

For the tunability of any physical property, the proper choice of host material plays a prominent role. In the current case, the host material should have a large bandgap, low phonon energy, etc. In addition, proper energy absorption as well as energy transfer should take place between luminescent centers. Among luminescent centers, (VO$_4$)$^{3-}$ complexes are known for their strong absorption in the near-ultraviolet (NUV) region and self-activated broad emission band due to $^7T_{2g} \rightarrow ^5T_{1g}$ transitions, whereas RE possess low absorbance due to narrow excitation due to the $4f$–$4f$ forbidden transition. Consequently, phonon-assisted energy transfer from the (VO$_4$)$^{3-}$ complex to RE ions can be used in vanadate materials and if these complexes are introduced into a host structure that is flexible and adjustable by cation-site substitution, then the tunability of emission properties and therefore design of phosphors can be easily achieved. Among the phosphor family, garnet structures have a unique position due to their unparalleled interrelating structural and luminescence properties. Garnets have general stoichiometry $A_3[\text{B}_2(C)_2]O_{12}$, where $A$, $B$, and $C$ correspond to dodecahedral, octahedral, and tetrahedral sites, respectively, with space group $Ia3d$ (230, $O_h^{10}$). They are highly stable. Even though they have a simple cubic structure, their polyhedral network is highly intricate and hence cationic substitutions offer new avenues for tailored luminescence and sensing properties. Combining these, RE-doped vanadate garnets are a perfect choice for non-TCEL applications and are expected to obtain high-performance sensors. Among the RE ions investigated for the FIR, Eu$^{3+}$ is special owing to the characteristic sharp orange red emission of $^5D_{0,2} \rightarrow ^7F_{J}$ ($J = 0$ to 6) transitions. In addition, the hypersensitive $^5D_0 \rightarrow ^7F_2$ transition stands out due to the strong interconnection with crystal symmetry. Moreover, optical thermometry studies on Eu$^{3+}$-doped vanadate garnets are still limited. To fill this void and to understand the potentiality of vanadate garnets in the field of thermometry and thermochromic luminescence applications, we selected Sr$_2$NaMg$_2$V$_3$O$_{12}$ as the host material and Eu$^{3+}$ as an activator due to its better luminescence properties.

In this work, Eu$^{3+}$-doped Sr$_2$NaMg$_2$V$_3$O$_{12}$ phosphor material is synthesized via a conventional solid state reaction route. The crystal structure is examined by X-ray diffraction (XRD) and the room temperature photoluminescence properties for varied concentrations are investigated. Moreover, the temperature-dependent photoluminescence intensity and emission color are systematically studied, in which distinct thermal responses of the (VO$_4$)$^{3-}$ group and Eu$^{3+}$ ions are observed. The possible mechanisms involved in the diverse thermal quenching assisted by phonon vibrations of the present system are also discussed. Thermometric performances are evaluated by determining temperature sensitivities, repeatability, and temperature resolution. Thermochromic luminescence is studied by evaluating the transit of CIE coordinates with increase in temperature.

2. Results and Discussion

2.1. XRD Patterns and Crystal Structure

The crystal structure and phase purity of the samples were analyzed using XRD patterns. Figure 1a shows the XRD patterns of Sr$_2$NaMg$_2$V$_3$O$_{12}$ (SNMV):xEu ($x = 0, 0.03, 0.05, 0.08, 0.10, and 0.14$) indexed with the cubic $Ia3d$ (230, $O_h^{10}$) space group and it is evident that the introduction of Eu$^{3+}$ does not change the crystallinity or phase purity of the samples. The samples of various concentrations are phase-pure and isosstructural with that of Sr$_2$NaMg$_2$V$_3$O$_{12}$, ICDD file No. 00-024-1131. The general stoichiometry of the garnet structure is $A_3[\text{B}_2(C)_2]O_{12}$, in which cations occupy special sites in such a manner that A-site cations occupy dodecahedral site having eightfold oxygen coordination with $D_3$ symmetry, B-site cations occupy sixfold octahedral sites with $C_3$ symmetry, and C cations occupy a tetrahedral site having $S_4$ point symmetry. In Sr$_2$NaMg$_2$V$_3$O$_{12}$, the Sr$^{2+}$ and Na$^+$ ions are in the A site with 2/3 and 1/3 occupancy with Wyckoff position 24c to form SrO$_8$/NaO$_8$ dodecahedra, whereas Mg$^{2+}$ ions occupy the B site with 16a position, forming MgO$_6$ octahedra and V$^{5+}$ in the C site with 24d position to form VO$_4$ tetrahedra. On the other side, oxygen atoms occupy general sites with Wyckoff symbol 96h. On the basis of charge and similar ionic radii for dodecahedral coordination, the Eu$^{3+}$ ion (1.066 Å, CN = 8) prefers the position of (SrNa)$_3$ ions according to Pires and Davlos. The acceptable radius percentage difference “$D_r$” between doped and matrix ions should not exceed 30% and it can be calculated as

$$D_r = 100% \times \frac{R_m(C_N) - R_d(C_N)}{R_m(C_N)}$$

where $R_m(C_N)$ and $R_d(C_N)$ are the radii of the substituted matrix and dopant ions, respectively. The calculated $D_r$ value for Sr$_2$NaMg$_2$V$_3$O$_{12}$:Eu between the host cation and Eu$^{3+}$ is tabulated in Table S1, Supporting Information, and the theoretical calculation is given in the Supporting Information.

It is evident that $D_r$ values corresponding to the Sr$^{2+}$/Na$^+$ site do not exceed 30% such that Eu$^{3+}$ can substitute (SrNa)$^{3+}$ sites. To investigate the crystal structure of the studied SNMV: Eu samples, Rietveld refinements were performed. The Sr$_2$NaMg$_2$V$_3$O$_{12}$ garnet was considered as the initial structural model. Figure 1b shows the Rietveld refinement profile of the Sr$_{1.84}$Na$_{1.08}$Eu$_{0.08}$Mg$_2$V$_3$O$_{12}$ phosphor and Figure 1c shows the simulated crystal structure using the generated cif (crystallographic information file) obtained from refinement. The corresponding refined unit cell parameters, refinement parameters, atomic positions, and occupancy are listed in Table 1. The
reliability parameters ($R_{wp} = 4.17\%$, $R_p = 3.13\%$, and Goodness of fit (GoF) = 1.66) suggest that Eu$^{3+}$ occupies the dodecahedral site.

The atomic position of the O atoms in the garnet structure deduced theoretically also matches with the refined atomic positions of the oxygen atom, indicating that the obtained refinement is in agreement with the theory, and the description is given in the Supporting Information.[37] Moreover, the decrease in the lattice parameter with increase in Eu$^{3+}$ concentration as tabulated in Table S2, Supporting Information, points out the unit cell compression.

Further, the optical bandgap of SNMV:xEu ($x = 0.03, 0.05, 0.08, 0.10, \text{and} 0.14$) Eu is measured using diffuse reflectance spectra and is calculated using the Kubelka–Munk function.[38] The samples possess a wide and direct bandgap of 3 eV, making them suitable for incorporating activator ions so that the excited and ground state of

![Figure 1](image-url)

**Table 1.** Rietveld refinement and crystallographic data of Sr$_2$NaMg$_2$V$_3$O$_{12}$:0.08Eu.

| Atom  | Site | x     | y     | z     | Occupancy | $B_{eq}$ (Å$^2$) |
|-------|------|-------|-------|-------|-----------|-----------------|
| Sr$^{2+}$ | 24c  | 0.375 | 0.5   | 0.25  | 0.667     | 0.009(6)        |
| Na$^+$  | 24c  | 0.375 | 0.5   | 0.25  | 0.333     | 0.009(6)        |
| Mg$^{2+}$ | 16a  | 0.50  | 0.50  | 0     | 1         | 0.008(9)        |
| V$^{5+}$ | 24d  | 0.625 | 0.50  | 0.25  | 1         | 0.005(9)        |
| O$^{2-}$ | 96h  | 0.040 | 0.0478| 0.066 | 1         | 0.009(7)        |
Activators will be located between the conduction and valence band, which is essential for phosphor applications. The intense optical absorption in the UV region is due to the characteristic ligand-to-metal charge transfer transition taking place from V$^5+$ to O$^2-$ of the VO$_4$ tetrahedra. The DRS spectrum is shown in Figure S1, Supporting Information.

### 2.2. Photoluminescence Spectra of Sr$_2$NaMg$_2$V$_3$O$_{12}$:xEu$^{3+}$

The self-activated photoluminescence behavior of the host Sr$_2$NaMg$_2$V$_3$O$_{12}$ is characterized by photoluminescence (PL) and PL excitation (PLE) spectra, as shown in Figure S2, Supporting Information. To resolve the energy-level positions corresponding to the self-activated (VO$_4$)$_3$/C$^0$ emission and excitation, both spectra are deconvoluted using a Gaussian function. The excitation bands Ex$_1$ and Ex$_2$ at 292 nm (FWHM = 73 nm) and 336 nm (FWHM = 42 nm) correspond to $^1$A$_1$ → $^3$T$_2$ and $^1$A$_1$ → $^3$T$_1$ transitions due to the charge transfer (CT) transition from the 2p orbital of the O$^2-$ ion to the 3d orbital of the V$^5+$ ion, whereas the broad emission band is due to $^3$T$_2$ → $^1$A$_1$ and $^3$T$_1$ → $^1$A$_1$ transitions, which falls in 472 nm (FWHM = 86.11 nm) and 525 nm (FWHM = 118 nm), as shown in the Figure S2, Supporting Information. Further, the luminescence properties of Eu$^{3+}$-doped Sr$_2$NaMg$_2$V$_3$O$_{12}$ samples were investigated for various concentrations of Eu$^{3+}$. The PL emission spectra of SNMV:xEu is shown in Figure 2a. The PLE spectra of SNMV:0.08Eu monitored at 495 nm in the range of 250–450 nm shows the characteristic charge transfer transition of (VO$_4$)$_3^-$ (Figure S3a, Supporting Information). In addition, the excitation spectra (Figure S3b, Supporting Information) obtained by monitoring the dominant Eu$^{3+}$ emission band at 609 nm shows the presence of additional bands located 394, 465, and 534 nm apart from the broad excitation band of the (VO$_4$)$_3^-$ complex. These are due to the inter-4f orbital transitions of the Eu$^{3+}$ ion in the 4f$^6$ configuration—$^7$F$_{0}$→$^5$D$_{0}$, $^7$F$_{0}$→$^5$D$_{2}$, and $^7$F$_{0}$→$^5$D$_{1}$, respectively. The variation in the PL intensity of both (VO$_4$)$_3^-$ and Eu$^{3+}$ emission with Eu$^{3+}$ concentration is shown in Figure 2b. Furthermore, time-resolved emission spectra (TRES) of SNMV:0.08Eu under 345 nm excitation is collected at different delay times (t$_d$), as shown in Figure 2c. It is obvious from the spectra that only VO$_4^-$ emission is observed at initial delay times. In addition, with increase in t$_d$, VO$_4^-$ emission decreases and vanishes when t$_d$ ≥ 200 μs, whereas Eu$^{3+}$ emission appears. This observation further elucidates the existence of energy transfer from the (VO$_4$)$_3^-$ group to Eu$^{3+}$. The energy-level diagram showing the energy transfer from (VO$_4$)$_3^-$ to Eu$^{3+}$ is displayed in Figure 2d. As shown, the (VO$_4$)$_3^-$ complex absorbs the incident radiation and hence electrons are excited to the $^1$T$_1$ energy level from the ground state $^1$A$_1$. Following this, through nonradiative transition, a part of the excited electrons transit to triplet states $^3$T$_{1,2}$ and a subsequent characteristic broad emission takes place.
place when it gives off energy and occupies the ground state $^1A_1$. On the other side, the energy acquired by the other part of the excited electrons transfers energy to Eu$^{3+}$, which results in the population of the $^7D_0$ level and subsequent radiative transitions from the $^7D_0$ level to $^7F_J$ ground levels ($J = 0, 1, \ldots, 6$) take place. On further analysis of the concentration-dependent PLE and PL spectra, it is seen that with increase in Eu$^{3+}$ concentration, the intensity of the (VO$_4$)$^{3-}$ emission decreases monotonously, whereas the sharp red emission of Eu$^{3+}$ increases due to the energy transfer from the (VO$_4$)$^{3-}$ group to Eu$^{3+}$. The increase in Eu$^{3+}$ emission intensity continues up to 0.08 mol concentration and decreases further due to the concentration quenching effect. The concentration quenching occurs due to the nonradiative energy transfer taking place between Eu$^{3+}$ ions, which can be due to electric multipolar interaction or due to exchange interaction. The type of interaction responsible for quenching in the SNMV:Eu system is estimated using the Blasse expression for critical distance, in which the critical distance is taken as the average least distance between neighboring activator ions at the critical concentration[49] and the estimated critical distance is 18.1 Å. Since the critical distance is greater than 4 Å, electric multipolar interaction occurs between Eu$^{3+}$ ions. Accordingly, the type of interaction involved in the concentration quenching is electric multipolar in origin and the type of polar interaction can be estimated using Van Uitert’s model given by[40]

$$I = \frac{k}{x} \left(1 + \beta(x)^{\theta/3}\right)^{-1} \quad (2)$$

where $x$ is the activator ion concentration, $k$ and $\beta$ are constants for a particular system, $I$ is the luminescence intensity, and $\theta$ represents the type of polar interaction, which causes nonradiative loss. For values of $\theta = 3, 6, 8$, and 10 the interaction types are of exchange, electric dipole–dipole (D–D), electric dipole–quadrupole (D–Q), and electric quadrupole–quadrupole (Q–Q) interactions. The slope of the linear fit (Figure S4, Supporting Information) of the aforementioned equation is $-\theta/3$ and therefore, the estimated $\theta$ for SNMV:Eu is close to 6, which implies that the interaction is of electric dipole in origin. Generally, RE activated vanadate garnets have comparatively higher critical distance, which results in the type of polar interaction responsible for quenching in the SNMV:Eu system is due to the higher polyhedron distortion factor, $d_{60}/d_{41}$. The polyhedron distortion factor is the ratio of the O–O bond distance shared between two adjacent dodecahedra to that of a dodecahedron and an adjacent tetrahedron. Figure 1c shows the $d_{60}$ and $d_{41}$ bond distances associated with the dodecahedra. The calculated value of $d_{60}/d_{41}$ for Sr$_2$NaMg$_2$V$_3$O$_{12}:0.08$Eu$^{3+}$ is 0.82, which favors distortion-assisted electric dipole transition.

### 2.3. Coloric Properties

In addition, the increase in the concentration of Eu$^{3+}$ has profound influence on the emission color of the phosphor Sr$_2$NaMg$_2$V$_3$O$_{12}:\chi$Eu$^{3+}$ ($\chi = 0.03, 0.05, 0.08, 0.10$, and 0.14), which is illustrated through the chromaticity diagram shown in Figure 3. A significant tunability from blue-green to red emission is obtained in which emission from the optimum concentration, 0.08 mol, very close to the achromatic point with CIE coordinates (0.353, 0.335) is obtained. Table S3, Supporting Information, shows the corresponding CIE coordinates of samples having various concentrations of Eu$^{3+}$. The room temperature internal quantum yield of the material is 47% and is comparatively higher among the reported vanadate garnets. This might be due to the lowering of symmetry surrounding the VO$_4$ tetrahedra, which contributes to the relaxation of parity-forbidden $d$-$d$ transition of V$^{5+}$ ions.[31] A comparison of the internal quantum yield of various vanadate garnets is made and tabulated in Table S4, Supporting Information.

Further, the decay time of the sample was estimated by monitoring (VO$_4$)$^{3-}$ as well as $^5D_0\rightarrow^7F_2$ emission of Eu$^{3+}$ at 495 and 609 nm, respectively, in which (VO$_4$)$^{3-}$ emission has a short decay time of 8 µs, whereas Eu$^{3+}$ has a more delayed decay time of 1085 µs. The decay curves are shown in Figure S5, Supporting Information.
Sr$_2$NaMg$_2$V$_3$O$_{12}$ was analyzed and the corresponding spectra for the (VO$_4$)$_3$ quenching. In addition, the response to temperature is different, a decrease in intensity with an increase in temperature due to thermal quenching.

Figure 4c.

This is noted for Eu$^{3+}$ where an equation given by

$$I_T = \frac{I_0}{1 + Ae^{-\Delta E/KT}}$$

(4)

where $I_0$ and $I_T$ are the intensity at room temperature and that at temperature $T$, $A$ is the constant, $k = 8.617 \times 10^{-5}$ eV K$^{-1}$ is the Boltzmann constant, and $\Delta E$ is the activation energy. From the Arrhenius plot of $1/KT$ versus $\ln(I_0/I_T - 1)$, as shown in Figure 4b, the activation energy $\Delta E$ corresponding to the thermal quenching of Eu$^{3+}$ is estimated as 0.36 eV.

Furthermore, it is seen that the emission band shows a decrease in intensity with an increase in temperature due to thermal quenching. In addition, the response to temperature is different for the (VO$_4$)$_3^{3-}$ and Eu$^{3+}$ bands. The (VO$_4$)$_3^{3-}$ band undergoes a sharp decline in intensity, whereas a slow reduction in intensity is noted for Eu$^{3+}$ bands, as indicated in the histogram shown in Figure 4c.

2.4. Thermographic Properties

To discover the response of photoluminescence with temperature, the temperature-dependent PL emission spectra in the range 100–500 K of the optimum concentration 0.08 mol of Sr$_2$NaMg$_2$V$_3$O$_{12}$ was analyzed and the corresponding spectra are shown in Figure 4a. It is found that the temperature-dependent PL emission intensity agrees with the Arrhenius equation given by

$$I_T = \frac{I_0}{1 + Ae^{-\Delta E/KT}}$$

where $I_0$ and $I_T$ are the intensity at room temperature and that at temperature $T$, $A$ is the constant, $k = 8.617 \times 10^{-5}$ eV K$^{-1}$ is the Boltzmann constant, and $\Delta E$ is the activation energy. From the Arrhenius plot of $1/KT$ versus $\ln(I_0/I_T - 1)$, as shown in Figure 4b, the activation energy $\Delta E$ corresponding to the thermal quenching of Eu$^{3+}$ is estimated as 0.36 eV.

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2.4.1. Temperature-Sensing Properties of Sr$_2$NaMg$_2$V$_3$O$_{12}$.08Eu$^{3+}$

The diverse thermal response, in which the emission intensity of (VO$_4$)$_3^{3-}$ falls rapidly, whereas Eu$^{3+}$ show a slow decrease in intensity can be explicitly noted in the present system. This kind of inconsistency in the intensity of these optical centers can be exploited for optical thermometry applications based on the FIR technique. Since they possess two diverse thermal responses, the intensity ratios of (VO$_4$)$_3^{3-}$ and Eu$^{3+}$ emission definitely have strong dependence on temperature and therefore can be applied for sensing purposes.

The FIR expression of Eu$^{3+}$ ions to the (VO$_4$)$_3^{3-}$ group can be defined as

$$FIR = \frac{I_{Eu^{3+}}}{I_{(VO_4)^{3-}}} = \frac{I_{0,Eu^{3+}}}{I_{0,(VO_4)^{3-}}} \frac{(1 + A_{VO_4^{3-}} \exp(\frac{-\Delta E_{VO_4^{3-}}}{KT}))}{(1 + A_{Eu^{3+}} \exp(\frac{-\Delta E_{Eu^{3+}}}{KT}))}$$

(5)

Based on this, the ratio of integrated intensities of Eu$^{3+}$ and VO$_4^{3-}$ emission is calculated. Here, the integrated wavelength range of VO$_4^{3-}$ emission is 400–575 nm with maxima at 495 nm and for Eu$^{3+}$ it is 600–613 nm with maxima at 609 nm, respectively. Further, the FIR plot is fitted by the equation given by

$$FIR = \frac{2.17}{1 + 2801e^{-2674/\gamma}}$$

(6)

To understand the temperature-sensitizing properties of the phosphors as possible temperature sensors, thermometric parameters were calculated and compared with reported phosphors. The absolute and relative sensor sensitivities, $S_a$ and $S_r$, as per the literature can be calculated using the following expressions.

$$S_a = \frac{d(FIR)}{dT}$$

(7)

$$S_r = 100\% \frac{1}{FIR} \frac{d(FIR)}{dT}$$

(8)

The relative and absolute sensitivities of Sr$_2$NaMg$_2$V$_3$O$_{12}$.08Eu$^{3+}$ are determined using the TeSen calculator developed by Kaczmarek et al.

Based on the aforementioned expression, the plot of temperature versus relative sensitivity was obtained and it is shown in Figure 5a.b. It is obvious that the relative sensitivity $S_r$ increases rapidly with rise in temperature from 200 K onward and the maximum value is 1.61% at 420 K. The absolute sensitivity at 420 K is 0.0135 K$^{-1}$.

A comparison of the relative and absolute sensitivities of the phosphors investigated for ratiometric thermometry based on the downshift process is tabulated in Table 2, in which the current system has reasonably good sensitivity. Furthermore, SNMV:Eu was tested through a three-cycle measurement, as shown in Figure 5c, and exhibited a high repeatability for the data collected between 300 and 500 K in consecutive heating–cooling cycles. As temperature sensitivity is low in the range 100–300 K, the repeatability is shown only for the 300–500 K range.

Furthermore, the temperature resolution or temperature uncertainty $\delta T$, defined by the smallest temperature that can be detected in a given measurement, is calculated using the equation given by

$$\delta T = \sqrt{\frac{2 \delta I}{S_r I}}$$

(9)

where $\delta I$ represents the ratio of noise fluctuation to the maximum PL intensity and $S_r$ is the relative sensitivity. In other words,
the temperature resolution gives the accuracy of the measurement that can be obtained from a given thermometer. The values of $\delta I$ at each temperature from 300 to 500 K are tabulated in Table S5, Supporting Information. Figure 5d shows a graph of $\delta T$ versus $T$ (K). It is found that the temperature resolution is less than 0.2 K, which is comparable to the reported fluorescent thermometers.\[50,51,53\]

Furthermore, significant redshift of the charge transfer band (CTB) is observed by studying temperature-dependent PLE spectra, as shown in Figure 6a. The excitation maxima of the $V^{5+}$--$O^{2-}$ CTB shifts from 335 (100 K) to 361 nm at 500 K, with a redshift of 26 nm. Along with this, broadening of the CTB is also noted. Also the decrease in the intensity of PLE bands with increase in temperature is in accordance with the thermal quenching phenomena. Apart from the FIR method, the redshift of the CTB with respect to the increase in temperature provides an additional degree of freedom for the temperature readout and thus multimode sensing can be achieved. Consequently, the maximum peak position versus temperature plot as shown in Figure 6b is fitted with the linear relationship given by $\lambda = 0.0623 T + 329$, where $\lambda$ is the maximum peak position and $T$ is the temperature. The relative sensitivity $S_r$ is given by $S_r = \frac{\lambda}{\Delta T} \times 100\%$, as given in Figure 6c, whereas the slope $\frac{\lambda}{\Delta T}$ represents the absolute sensitivity.\[54,55\] Hence, the values of $S_a$ and $S_r$ are determined to be 0.0623 K$^{-1}$ and 0.018% K$^{-1}$ at 300 K, respectively. However, the relative and absolute sensitivities for the temperature readout using the FIR method offer more sensitivity than the spectral shift method. Thus, the current material Sr$_2$NaMg$_2$V$_3$O$_{12}$:0.08 Eu$^{3+}$ shows good temperature-sensing properties and is one of the potential candidates for thermometry applications.

2.4.2. Thermochromic Luminescence of Sr$_2$NaMg$_2$V$_3$O$_{12}$:0.08Eu$^{3+}$

As described, the PL emission intensities of the Sr$_2$NaMg$_2$V$_3$O$_{12}$: Eu$^{3+}$ material show a distinct response to the temperature and it was anticipated that this variation can result in a change of the emission color with temperature. As a proof of concept, the temperature response of SNMV:0.08Eu was studied using the CIE diagram, as shown in Figure 7. It is evident that a drastic change of emission color from white to orange to deep red is obtained for a short temperature range of 300–500 K. A corresponding shift of the CIE coordinates from (0.353, 0.335) to (0.611, 0.360) is obtained. The variation of CIE coordinates with temperature is tabulated in Table S6, Supporting Information. This temperature-dependent colorific behavior implies that they have a potential application as a safety sign in a high-temperature environment. In comparison, with the CIE coordinates of other reported inorganic phosphors for safety sign application listed in Table 3, it is obvious that Sr$_2$NaMg$_2$V$_3$O$_{12}$:0.08Eu$^{3+}$ displays...
a superior colorific shift than the materials reported till date and therefore is a promising candidate for safety sign applications in high-temperature environments. Although colorific shift from white to red has been reported earlier, the CIE coordinates of the current system are wider than those of the reported systems and can be utilized for colorimetric temperature sensing.

2.5. The Phenomenon of Diverse Thermal Quenching

The unprecedented colorific shift from white to deep red is due to the increased thermal quenching of the (VO$_4$)$_3^-$ complex, which provides a dominant blue-green luminescence at room temperature and the slow quenching of red emission of Eu$^{3+}$. To investigate the possible reasons for rapid thermal quenching of (VO$_4$)$_3^-$, we analyzed the temperature-dependent decay time monitoring both 495 and 609 nm, respectively. The decay curves monitored at 495 and 609 nm were fitted with biexponential and single exponential functions, respectively. As shown in Figure 8a, the decay time corresponding to 495 nm decreases rapidly from 8 to 2.8 μs, whereas the decay time corresponding to Eu$^{3+}$ remains constant, around 1 ms, for the temperature range of 300–500 K, which implies that the probability of nonradiative transition is more in (VO$_4$)$_3^-$ emission. At the same time, the almost constant decay time of Eu$^{3+}$ implies that a pronounced

Table 2. Temperature sensitivity comparison of reported phosphors based on downshift process.

| Compounds                  | Temperature [K] | $\lambda_{ex}$ [nm] | $S_r$ [%] | $S_a$ [K$^{-1}$] | Ref.       |
|----------------------------|-----------------|---------------------|----------|------------------|------------|
| CaBaZn$_2$Ga$_2$O$_7$:Bi$^{3+}$ | 298–473 K       | 340                 | 1.453    | 0.154            | [76]       |
| Y$_3$Al$_2$O$_7$:Dy$^{3+}$/Cr$^{3+}$ | 293–573 K      | 365 nm              | 2.32     | 0.0011           | [47]       |
| Y$_2$MgTiO$_4$:Mn$^{4+}$            | 10–513 K        | 335 nm              | 0.14     | –                | [77]       |
| Ba$_3$(VO$_4$)$_2$:Sm$^{3+}$        | 303–463 K       | 352 nm              | 2.24     | 0.039            | [27]       |
| LuAG: Eu$^{3+}$/Mn$^{4+}$            | 303–358 K       | 393 nm              | 0.7      | 0.07             | [78]       |
| LiCa$_3$Zn$_2$V$_3$O$_7$:Sm$^{3+}$ | 303–463 K       | 352 nm              | 1.8      | 0.25             | [56]       |
| NaYF$_4$:Ce$^{3+}$/Tb$^{3+}$/Eu$^{3+}$ | 303–563 K     | 248 nm              | 1.17     | 0.012            | [79]       |
| CaSc$_2$O$_4$:Pr$^{3+}$             | 275–490 K       | 289 nm              | 2.49     | –                | [50]       |
| BaYF$_3$:Dy$^{3+}$                 | 293–773 K       | 355 nm              | 1.8      | 2 <0.001         | [80]       |
| Y$_2$Al$_2$O$_2$:Dy$^{3+}$         | 573–973 K       | 355 nm              | 0.3      | –                | [81]       |
| CaEu$_2$(VO$_4$)$_3$:Eu$^{3+}$      | 300–500 K       | 395 nm              | 1.4      | –                | [82]       |
| NaEuF$_3$:Eu$^{3+}$                | 298–523 K       | 394 nm              | 0.43     | –                | [83]       |
| YF$_3$:Pr$^{3+}$                   | 293–421 K       | 457 nm              | 1.24     | –                | [84]       |
| Na$_2$Sr$_2$P$_2$O$_7$:Eu$^{2+}$/Mn$^{2+}$ | 293–473 K   | 340 nm              | 1.536    | –                | [85]       |
| Ca$_4$NaMg$_2$V$_3$O$_7$:Sm$^{3+}$ | 303–503 K       | 335 nm              | 1.889    | 0.01649          | [86]       |
| Ca$_4$NaMg$_2$V$_3$O$_7$:Eu$^{3+}$  | 303–503 K       | 335 nm              | 1.686    | 0.0156           | [86]       |
| Sr$_2$NaMg$_2$V$_3$O$_7$:Eu$^{3+}$  | 300–500 K       | 345 nm              | 1.61     | 0.0135           | This work  |

Figure 5. a,b) The plots of FIR and relative sensitivity, $S_r$ versus $T$, of Sr$_2$NaMg$_2$V$_3$O$_7$:0.08Eu$^{3+}$. c) Temperature cycling of FIR for SNMV:Eu between 300 and 500 K. d) The temperature resolution in the measuring range 300–500 K.

The unpreceotected colorific shift from white to deep red is due to the increased thermal quenching of the (VO$_4$)$_3^-$ complex, which provides a dominant blue-green luminescence at room temperature and the slow quenching of red emission of Eu$^{3+}$. To investigate the possible reasons for rapid thermal quenching of (VO$_4$)$_3^-$, we analyzed the temperature-dependent decay time monitoring both 495 and 609 nm, respectively. The decay curves monitored at 495 and 609 nm were fitted with biexponential and single exponential functions, respectively. As shown in Figure 8a, the decay time corresponding to 495 nm decreases rapidly from 8 to 2.8 μs, whereas the decay time corresponding to Eu$^{3+}$ remains constant, around 1 ms, for the temperature range of 300–500 K, which implies that the probability of nonradiative transition is more in (VO$_4$)$_3^-$ emission. At the same time, the almost constant decay time of Eu$^{3+}$ implies that a pronounced
The increase of the nonradiative decay rate is not favored in Eu³⁺ emission. To provide a more detailed analysis, the radiative and nonradiative decay rates at various temperatures were calculated using 4f–4f intensity theory. The total radiative decay rate ($A_R$) is estimated by taking the sum of radiative rates $A_{0j}$ for each $^5D_0$–$^7F_J$ transition given by

$$A_R = \sum A_{0j} = A_{01} \frac{\nu_{01}}{I_{01}} \sum_{J=2,4} \frac{I_{0j}}{\nu_{0j}}$$  \hspace{1cm} (10)$$

where $\nu_{01}$ and $\nu_{0j}$ are frequencies and $I_{01}$ and $I_{0j}$ are the integrated intensities of the $^5D_0$–$^7F_1$ and $^5D_0$–$^7F_J$ transitions and $A_{01}$ is the Einstein coefficient between the $^5D_0$ and $^7F_J$ levels. Using the observed lifetime $\tau_{obs}$ of the $^5D_0$ level, the nonradiative decay rate, $A_{NR}$, is calculated by

$$A_{NR} = \frac{1}{\tau_{obs}} - A_R$$ \hspace{1cm} (11)$$

The luminescence quantum efficiency of the $^5D_0$ level, $\eta$, is obtained by

$$\eta = \frac{A_R}{A_R + A_{NR}}$$ \hspace{1cm} (12)$$

Table 4 lists the radiative and nonradiative decay rates and the quantum efficiencies for Sr₂NaMg₂V₃O₁₂:0.08Eu³⁺ for the temperature range of 100–500 K. The estimated quantum efficiency is lower than the measured quantum efficiency. This is because
only photons involved in the $^5D_0$ level of the Eu$^{3+}$ emission alone are considered in the theoretical studies. Analyzing the table, one can see that the quantum efficiency of the $^5D_0$ level is independent of temperature. At the same time, the radiative decay rate does not show a decreasing trend at higher temperature. Unlike VO$_4^{3-}$, it is now evident that Eu$^{3+}$ is quite resistant to the fast thermal quenching. Or, in other words, the VO$_4^{3-}$ center undergoes nonradiative decay faster than that of Eu$^{3+}$ emission.

In addition, the relative dominance of radiative transition in Eu$^{3+}$ can be explained by means of the higher number of phonons (p) required to bridge the energy gap between the lowest excited $^5D_0$ and highest ground $^7F_6$ states given by $p = \Delta E/h\omega$, where $\Delta E$ is the energy difference between the $^5D_0$ and $^7F_6$ states and $h\omega$ corresponds to the maximum phonon energy of all the lattice vibrations. For the SNMV:Eu system, the maximum phonon energy is 844 cm$^{-1}$, associated with the symmetric stretching vibration mode of VO$_4$ tetrahedra (Figure S6a, Supporting Information) and the energy gap between $^5D_0$ and $^7F_6$ is 12 500 cm$^{-1}$. Consequently, the approximate value of $p$ is about 15, which indicates that more phonons are required for the nonradiative relaxation of excited electrons to the ground state of Eu$^{3+}$. It is commonly accepted that the process is radiative if the number of phonon is greater than 7. Thus, radiative transition is dominant among Eu$^{3+}$ levels and a schematic representation of the model is shown in Figure 9. These points strengthen the fact of good resistance of Eu$^{3+}$ to rapid thermal quenching.

In contrast, VO$_4^{3-}$, which exhibits rapid thermal quenching, was analyzed in connection with lattice dynamics. For any material under high temperature, we have to consider the perturbation in the harmonic potential, which leads to variation in the vibrational properties. As a result, the population of different vibrational level changes, which in turn alters the lattice parameters, leading to the origin of anharmonicity in the lattice potential. This means, at higher temperatures, the population density of phonons will increase and thus electron–phonon interaction will be a dominant process. The changes in the frequency of phonon modes, line widths with temperature can provide basic information on the lattice dynamics and therefore the temperature-dependent Raman spectra of SNMV:Eu was
analyzed in detail. The detailed analysis of Raman bands observed at room temperature, along with the group theoretical predictions, is given in the Supporting Information (Figure S6b, c, Supporting Information). To understand how the various modes of vibration respond to the temperature rise, the temperature-dependent Raman spectra of SNMV:Eu were analyzed in detail. Figure 10a shows the temperature evolution of the Raman bands. The band assignments of each phonon mode and the type of motion of the associated polyhedra are shown in Table S7, Supporting Information.

It is obvious from the spectra that the phonon modes undergo rapid thermal response. Moreover, it is noted that the bending vibration of the O–V–O bond ($\nu_2$) corresponding to 338 cm$^{-1}$ is higher compared to the stretching vibration at 844 cm$^{-1}$. A significant broadening of the bending mode is noted at elevated temperatures, as shown in Figure 10b. It is reported that the increased broadening is due to the enhanced structural distortion at elevated temperatures.\[^{71}\] Also, the temperature-induced frequency shift of Raman modes was observed, as shown in Figure S7, Supporting Information. The redshift of the phonon modes as well as line width in progression with temperature is shown in Figure 10c. The phenomenon of redshift of phonon bands at high temperatures might be due to the lattice distortion or volume expansion of the unit cell.\[^{72,73}\] Moreover, the softening of the phonon modes with temperature is interrelated with the lifetime of strongly interacting optical phonons. Because thermal interaction, which is larger at higher temperature, reduces the mean free path of phonons, the lifetime also decreases, which in turn leads to the increased line width.\[^{74}\]

The relaxation time for the present system SMMV:Eu was calculated using the equation given by\[^{74}\]

$$\tau = \frac{1}{\pi c \Gamma} \quad (13)$$

Figure 9. Schematic model showing thermal quenching of Eu$^{3+}$.  
Figure 10. a) Temperature-dependent Raman spectra. b) Plot showing the broadening of the bending vibration of VO$_4$ tetrahedra with temperature. c) Temperature dependence of the Raman band frequency showing the redshift and the increase in line width.
where $\Gamma$ is the line width and $\tau$ is the lifetime of the phonons and $c$ is the velocity of light. For SMMV:Eu, $\Gamma$ is 338 cm$^{-1}$ (corresponding to the dominant phonon band) and the calculated lifetime of phonons is 0.63 and 0.23 ps at 300 and 500 K, respectively.

Furthermore, the temperature dependence of PLE spectra monitored under 495 nm was analyzed, as shown in Figure 6a, in which redshift of the excitation maxima is noted. This can be attributed to the relative positions of the transitions from the ground state $^1A_1$.[54,75] That means, in the low-temperature regime the absorption takes place from the first vibrational level $v_1$ of ground state $^1A_1$, whereas at larger temperatures, higher vibrational levels are populated and therefore transitions from levels $v_{2-1}$ are favored, denoted by $\text{Ex}^\ast$ in Figure 11.[54,75]

Consequently, rise in temperature favors a shorter energy for the optical absorption and hence the redshift. Simultaneously an increased thermal population of higher vibrational levels increases the probability for the excited electrons in $^3T$ states to go back to the ground state $^1A_1$ nonradiatively via the cross-over, as shown in the configuration coordinate diagram. As a result, rapid thermal quenching of VO$_4^{3-}$ via nonradiative transitions occurs at higher temperatures. As a matter of fact, the rapid and slow thermal quenching of VO$_4^{3-}$ and Eu$^{3+}$ respectively culminates in the fast colorific shift from white to deep-red region in the temperature range 300–500 K, making SNMV:Eu a potential candidate for safety sign application in high-temperature environments. The resistance of Eu$^{3+}$ to fast thermal quenching was discussed based on the temperature-dependent Raman and PLE spectra and decay curve analysis. The resistance of Eu$^{3+}$ to fast thermal quenching was studied by analyzing the effect of temperature on the radiative and nonradiative decay rates of $^5D_0$ and the effective number of phonons required to bridge the energy gap between $^5D_0$ and $^7F_0$ states. An increased thermal population of vibrational levels which favored rapid quenching of VO$_4^{3-}$ emission through the cross-over mechanism was confirmed. Thus, the findings of this research demonstrate that SNMV:Eu is an efficient thermometric and thermochromic luminescent material for developing sensors based on optical thermometry and safety sign applications. In a nutshell, this work proposes an efficient strategy of vibrational coupling for achieving rapid colorific shift by incorporating Eu$^{3+}$ in self-activated single-phase phosphors based on vanadate garnets, which would promote research in designing temperature-sensitive sensors.

4. Experimental Section

Polycrystalline samples of Sr$_2$NaMg$_2$V$_3$O$_{12}$:Eu$^{3+}$ (SNMV:Eu$^{3+}$, $x = 0$, 0.03, 0.05, 0.08, 0.10, and 0.14) phosphors were synthesized via a conventional solid-state reaction route. SrCO$_3$, Na$_2$CO$_3$, MgO, NH$_4$VO$_3$ (Sigma Aldrich, >99%), and Eu$_2$O$_3$ (Alfa Aesar, 99.9%) were the starting materials used. Due to its hygroscopic nature, MgO was preheated at 900 °C for 2 h. Stoichiometric amounts of these materials were accurately weighed and mixed together in acetone medium using ceria-stabilized zirconia balls for 18 h. The obtained slurries were dried and ground thoroughly and calcined at 900°C for 4 h. The calcined powders were reground for further characterization.

The phase compositions of the samples were studied using a Bruker D8 Advance X-ray diffractometer (40 kV, 40 mA) equipped with a Cu Kα source ($\lambda = 1.5406 \text{ Å}$), nickel filter, and a Lynx eye-position-sensitive detector. The Rietveld refinement of XRD patterns was performed using Topas 4.2 software, in which the Chebyshev polynomial was used to fit the background signal. The crystal structure was simulated using the CrystalMaker software. The room temperature and temperature-dependent Raman scattering spectra were recorded using a LABRAM HR-800 Raman Spectrometer with a 785 nm high-power single-frequency-diode laser (90 mW) using a Linkam stage in the temperature range of 100–700 K. The diffuse reflectance spectra (DRS) were obtained in the range 190–900 nm using a JASCO-V-750 UV–Vis Spectrophotometer. The room temperature PL emission and PLE spectra were recorded using a 450 W xenon lamp equipped FLS 1000 spectrophotometer of Edinburgh Instruments and temperature-dependent PL spectra were collected using a cryostat in the temperature range.
range of 80–500 K designed by Oxford Instruments, and decay time measurements and time-resolved emission spectra were obtained using a pulsed xenon lamp of 10 and 100 Hz frequency attached to the same device. Quantum yield was measured using the Quantafluor integrating sphere setup of a Fluorolog-3 spectrophotometer with a 450 W xenon lamp. Regarding the calculation of $\delta I$/I, the PL baseline from 720 to 745 nm was taken to estimate the noise fluctuation. Further, from the linear fit, the maximum noise fluctuation ($\delta I$) of the temperature-dependent PL spectra was estimated. Combining the maximum intensity ($I$) at 609 nm, $\delta I$/I was calculated. The radiative and nonradiative decay rates and quantum efficiency of Eu$^{3+}$ were calculated using Judd–Ofelt intensity parameters $\Omega_k$ ($k = 2, 4, 6$) and LUMPAC 1.4.1 software.[82]

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

Keywords

garnets, thermal quenching, thermochromic luminescence, thermometric response, vibrational levels

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