Luminescent and thermal properties of novel orange–red emitting $\text{MgNb}_2\text{O}_6\text{:Sm}^{3+}$ phosphors for displays, photo catalytic and sensor applications

N. Basavaraju¹ · S. C. Prashantha¹ · H. Nagabhushana² · A. Naveen Kumar¹ · M. Chandrasekhar¹ · T. R. Shashi Shekhar¹ · C. R. Ravikumar¹ · M. R. Anil Kumar¹ · B. S. Surendra¹ · H. P. Nagaswarupa³

Received: 6 October 2020 / Accepted: 28 December 2020 / Published online: 10 January 2021

© The Author(s) 2021

Abstract

Novel Sm^{3+} doped columbite-type orthorhombic structured MgNb_2O_6 (MNO) orange-red emitting phosphors were prepared by solution combustion method using ODH as a fuel. The powder phase purity, particle morphology, size, elemental composition, luminescence properties, photocatalytic behaviors and electrochemical studies of prepared samples were studied in detail. Photoluminescence emission spectra of MNO:Sm^{3+} nanophosphors show all the characteristic emissions of Sm^{3+} cations corresponds to the transitions $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{j/2}(j=5,7,9,11)$ when excited at 463 nm energy. Among these the strongest emission peak was at 608 nm which corresponds to $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{7/2}$ transition of Sm^{3+} cations in the host lattice. The luminescence quenching was confirmed by the dipole–dipole interaction among Sm^{3+} ions. As a result of J–O analysis the branching ratio ($\sim 58\% > 50\%$) show that the phosphor was highly suitable for color display devices. Photocatalytic activity of MNO:Sm^{3+} (5 mol%) under UV light shows 99% degradation of AR-88 dye. Electrochemical Impedance Spectroscopy (EIS) confirms the reversibility of the redox reaction, which helps in sensing the presence of paracetamol and alcohol. Thus, MNO:Sm^{3+} phosphors have great potential applications in display, catalytic, photonic, chemical and thermal sensor applications.

Keywords $\text{MgNb}_2\text{O}_6\text{:Sm}^{3+}$ · Photoluminescence · Judd–Ofelt · Photocatalytic · Cyclic voltammogram · Chemical Sensor

1 Introduction

Currently phosphor materials are extensively used in various applications relating to the production of synthetic light for liquid crystal displays, cathode ray tubes, light-emitting diodes, scintillators and many more [1–3]. However, these phosphor oxide materials have more significant and attained high potential interest to researchers due to their enhanced physico-chemical stability. Nowadays, developed oxide phosphors are widely used in the various applications like health and eco-friendly progress [4]. Therefore, the researchers are focusing on the preparation

of various structural oxide materials. Metal niobates (MNb_2O_6 where $\text{M} = \text{Mg, Zn, Ni, Mn Co, etc.}$) are most significant phosphor compounds which exhibit excellent properties [5, 6]. It is impressive to study on the luminescence properties and energy transfer process between metal ion and Nb_2O_6 groups of MNb_2O_6 nanoparticles which have great attention for their wide range of potential applications including solid state lightening [7–9].

The materials doped with rare earth ions known as phosphors, used for white light-emitting diodes (wLEDs) are more potential materials and create high interest to the researchers for their luminescent features [10,

✉ S. C. Prashantha, scphysics@gmail.com; ✉ T. R. Shashi Shekhar, shashishekharr@gmail.com | ¹Department of Science, East West Institute of Technology, VTU, Bengaluru 560091, India. ²Prof. C.N.R. Rao Center for Advanced Materials, Tumkur University, Tumkur 572103, India. ³Department of Studies in Chemistry, Shivagangothri, Davangere University, Davanagere 577 007, India.

11]. Among the rare earth metal ions, Sm^{3+} is generally adapted as a orange red emitting material because of its distinctive $4f-4f$ structure that can be stimulated by NUV or visible (blue) rays efficiently and produce high colour purity [12, 13]. Therefore, $\text{MNO}:\text{Sm}^{3+}$ phosphor plays a vital role in these solid-state lighting applications. In addition, the significant movement has been achieved for the Sm^{3+} doped MNO nanoparticles in the sensor studies. Thus, the sensor activities of prepared material can be used for chemical monitoring applications and is of great use for sustaining human health and also in different detection practices [14, 15]. The Cyclic Voltammetric investigation was carried out for Sm^{3+} doped MNO to illustrate the modified graphite paste electrode which can be used as sensors for the detection of chemical and biochemicals such as Paracetamol and human consumable Alcohol (Red Wine). The nanoparticles with variable energy band gaps are confirmed to be promising candidates for purification of water, toxic waste remediation and undesirable pollutants obtained from various industries [16, 17]. However, it needs to initiate a photocatalyst that potentially response in photocatalytic reactions for eco-friendly progress. In this work, Sm^{3+} doped MNO with single-phase columbite structure by novel synthetic combustion method has been studied for the first time and it is found to be a potential material for multiple applications.

2 Experimental

2.1 Synthesis of the Sm^{3+} doped MNO phosphor

Magnesium niobate doped with Sm^{3+} (1–11 mol%) nanophosphors were synthesized by solution combustion route [15]. The precursors used in the synthesis are Niobium pentoxide (Nb_2O_5) (99.95%, Sisco research laboratories (SLR)), Ammonium nitrate ($\text{NH}_4(\text{NO}_3)_2$), Magnesium nitrate ($\text{Mg}(\text{NO}_3)_2$) (99%, SLR), Samarium oxide (Sm_2O_3) (99.99% Sigma Aldrich Ltd) and Oxalyl dihydrazide ($\text{ODH}-\text{C}_2\text{H}_6\text{N}_4\text{O}_2$) (lab made) as a fuel [18]. Initially the Sm_2O_3 is converted into $\text{Sm}(\text{NO}_3)_2$ by using a small amount of 1:1 HNO_3 and subjected to heating followed by drying. Stoichiometric ratios of nitrates and ODH were well dispersed in doubled distilled water using magnetic stirrer. Finally, the above mixture was subjected to combustion in preheated muffle furnace at $\sim 750 \pm 10^\circ\text{C}$, the entire reaction completed in less than 10 min producing a transparent gel, which boils to yield a white final product. The final product obtained was calcined at 950°C for 6 h to obtain pure single phase. Schematic representations of the steps of synthesis are shown in Fig. 1.

2.2 Characterizations

Powder X-ray diffractometer (PXRD) (Shimadzu) (50 kV, 20 mA, CuK_α - $1.541\text{\AA}$ with a nickel filter) was used to get the crystalline nature of the prepared samples. Transmission Electron Microscopy (TEM) analysis was performed on a JEOL, JEM-2100 (200 kV, LaB_6 filament, EDS-1.5 $\text{\AA}$) to obtain the microstructure and lattice parameters. Hitachi SU1510 Scanning Electron Microscopy (SEM) was used to observe the morphology of the samples. Shimadzu UV-Vis spectrophotometer model 2600 (range 200–800 nm) was used for the diffused reflection spectra (DRS) of the samples. Photoluminescence (PL) studies were made using Horiba, (model Fluorolog-3) Spectrofluorimeter with Fluor Essence™ software at RT (Xe-450 W). Photocatalytic studies (PCA) were conducted with lab made photocatalytic setup. Electrochemical Analyzer model-604E (CH-Instruments) with three-electrode system was used for electrochemical impedance studies.

3 Results and discussion

The phase and structural arrangement of the prepared host and Sm-doped MNO samples calcinated at 950°C were investigated by PXRD analysis. All strong and sharp intensity peaks with columbite type orthorhombic phase match well with the JCPDS card number 33-0875 and no impurity parts were observed, representing the same crystal structure even after adding samarium into the host (Fig. 2a) with lattice parameters $a = 5.7\text{\AA}$, $b = 14.19\text{\AA}$, and $c = 5.03\text{\AA}$ [19–21], their average crystallite sizes were calculated by Debye–Scherrer's formula [22]. Significant extent of strains were associated with nanoparticles because they are known to have a number of surface atoms which have unsaturated in co-ordinations. Various structural parameters namely Crystallite size (D), micro strain (ϵ), Stress (σ) and stacking fault (SF) were estimated and all the crystallite values are tabulated in Table 1. Increase in doping concentration influences the expansion of the unit cell volume, resulting in tensile stress and micro strain, hence the peaks of PXRD shifts slightly to the lower angle side (Fig. 2b) [15]. *FULLPROF* program was used to estimate the lattice parameters for MNO nanophosphor. Thomson–Cox–Hasting Pseudo-voigt function [15, 22] was used to fit the several parameters to the data point. The experimental and calculated PXRD pattern obtained by the Rietveld refinement is shown in Fig. 2c. In general, the Rietveld method utilizes the least-squares refinement for obtaining the best

Fig. 1 Schematic representation of the steps involved in combustion process

fit between the experimental data and the calculated pattern based on the simultaneously refined models. The fitting parameters (R_p , R_{wp} and χ^2) indicate a good agreement between the experimental relative intensity (observed PXRD intensities) and stimulated intensity (calculated PXRD intensities) from the model for the orthorhombic MNO phase. Diamond software was utilized for extracting the possible packing diagram (inset of Fig. 2c) and the refined parameters were tabulated in Table 2.

The microstructure, lattice parameters and selected area electron diffraction (SAED) pattern of Sm (5 mol%) doped MNO samples were analyzed by TEM & High Resolution (HR) TEM spectral technique. The microstructures of the samples confirm the consistent distribution of irregular particles, forms agglomeration with average particle size to be around 25 nm [Fig. 3(i)]. The SAED analysis shows and validates the polycrystalline nature with various diffraction peaks [Fig. 3(ii)], the inter planar d-spacing (0.29 nm) for 131 diffraction peaks as measured in HRTEM [Fig. 3(iii)] is very close to that of the theoretical measured value 0.291 nm. EDX (Energy Dispersive X-Ray) Spectra [Fig. 3(iv)]

confirms the Sm doping and purity of the sample [18]. SEM was predominantly utilized to contemplate the composition, porous, voids, agglomerated morphologies of the powders prepared via combustion process and the same was observed at different magnifications (Fig. 3b) in the present case [23].

The bonding nature of metal-metal ions or functional groups of prepared host and Sm doped MNO samples were recorded by FT-IR spectra (Fig. 4). The appearance of broad band around at 3417 cm^{-1} can be represented by O-H stretching and attributed to the presence of water molecule. Whereas the smaller peaks appear at 2338 cm^{-1} was generally allotted to adsorption of CO_2 molecules [24, 25]. The symmetric and asymmetric stretching vibrations of samples were found at 1462 cm^{-1} indicating metal oxygen [Mg-O, Sm-O, Nb-O] vibrations. Also, the presence of peaks in the range $550\text{--}850 \text{ cm}^{-1}$ was indicating to the coordination between metal ions [18].

The conducting nature of prepared series of different moles of Sm-doped MNO are successfully investigated for finding the energy band gap by measuring optical absorbance by means of DRS from 200 to 800 nm

Fig. 2 **a** PXRD patterns of undoped and (1–11 mol%) Sm^{3+} -doped MNO, **b** enlarged portion to show peak shifting, **c** rietveld refinement of MgNb_2O_6 nanophosphor prepared by combustion method (inset: Packing diagram of orthorhombic MgNb_2O_6)

Table 1 Estimated crystallite size and strain values of MNO:Sm³⁺ nanophosphors

Sm3 + (mol%)	$D = \frac{k\lambda}{\beta \cos \theta} \text{ nm}$	$SF = \left[\frac{2\pi^2}{45\sqrt{3}\tan\theta} \right] \epsilon = \frac{\beta \cos \theta}{4}$	$\sigma_{\text{stress}} = \epsilon E$
1	27.62	0.518	1.27×10^{-3}
3	27.56	0.519	1.22×10^{-3}
5	27.80	0.519	1.25×10^{-3}
7	27.21	0.519	1.25×10^{-3}
9	27.60	0.519	1.23×10^{-3}
11	27.11	0.521	1.25×10^{-3}

Table 2 Rietveld refined structural parameters of MNO nanophosphors

Crystal structure	Orthorhombic
Space Group	pb _{cn} (No. 60)
Crystal system	Cubic
Point group	D ¹⁴ _{2h}
Lattice parameters	a = 14.1800 Å, b = 5.7000 Å, c = 5.03300 Å, α = β = γ = 90°
Unit cell volume	407.02 (Å ³)
Cell density (g/cm ³)	4.76
R _{Factors} (%)	
R _p	63.0
R _{wp}	69.7
χ ²	28.3
R _{Bragg}	36.5
GOF	2.2

(Fig. 5) using Kubelka–Munk method and nature of the electronic transitions are as discussed elsewhere [26, 27] and Eg values were found to be in the range 4.0–4.3 eV.

$$F(R)h\nu = A(h\nu - E_g)^n \quad (1)$$

The decrease in Eg for doped samples can be related to the degree of structural order–disorder in the lattice which could affect the distribution of the intermediate energy-level within the band gap. Shallow level donor impurities create energy levels in the band gap near the conduction band edge and shallow acceptor impurities create energy levels near the valence band edge. With an increase in the doping concentration, the density of states of these dopants increased and formed a continuum of states. So, the effective band gap has decreased with an increase in doping concentration. Also, the same may be due to the increase of carrier concentrations or due to the influence of [Sm–O] clusters on the electronic structure of the host materials or the formation

of non-bridging oxygen's (NBO) as per the literature [28–30].

Undoped and Sm³⁺ doped (5 mol%) MNO photocatalyst were successfully used for photo-dye degradation activity under UV light irradiation. Presently, the wide usage of organic dyes in various regions releases toxic pollutants such as dyes containing azo group, phenol derivatives, etc., which are difficult to biodegrade and hence, significantly affects the environmental systems [31]. However, the synthesized host and Sm (5 mol%) doped MNO photocatalysts are potentially practiced for the heterogeneous photodegradation of AR-88 dye measured under UV light irradiation (Fig. 6a, b) and doped sample show high photocatalytic performance (99%) than the host (88%) sample (Fig. 6c). It was reported that the addition of known amount of doping elements into the catalyst resulted in higher surface barrier, narrower space charge layer by increasing the penetration depth of light and makes separation of charge carriers (produced e[−] – h⁺ pairs) effectively. This leads to increase in catalytic activity of the doped sample when compared to the undoped sample [30]. The AR-88 dye gets photosensitized by irradiated photons and furthermore, the presence of O₂ and H₂O molecules captured irradiated light on the surface of the photocatalysts, which creates electron–hole pairs. However, number of active radicals (O^{2−} and OH[•]) are formed by the effect of obtained electron–hole pairs on the surface of the prepared photocatalysts (Scheme 1) [31]. These superoxide and hydroxyl radicals are responding for the ionization of dye molecules and resulting into the less toxic chemicals like H₂O, CO₂, and mineral acids. The schematic representation of degradation mechanism in the present case is as shown in the Fig. 6d [32–34].

Tuning of the light emission by adjusting the compositions of the nanophosphors allow us to investigate the photoluminescence properties of MNO with varied doping concentrations samarium ions, the excitation was studied by monitoring emission at 608 nm (Fig. 7), it has PL excitation maximums at 362, 384, 395, 416, ~440, 463, and ~480 nm because of the transitions ⁶H_{5/2} → ⁴D_{3/2,5/2}, ⁴D_{1/2}, ⁴F_{7/2}, ⁴M_{19/2}, ⁴G_{9/2}, ⁴I_{13/2}, and ⁴I_{11/2} respectively which are the excitations from f–f shell transition of Sm³⁺ ions [12]. Among these the transition due to ⁶H_{5/2} → ⁴F_{7/2} is intense one at 395 nm which imply that the interaction between O^{2−} and Sm³⁺ was stronger [13, 15]. The PL intensity of ⁴G_{5/2}–⁶H_{7/2} (608 nm) transition was stronger under 463 nm excitation when compared to 395 nm (Fig. 8), even though the excitation intensity was stronger for the later one, this may be due strong energy transfer between the host and lanthanide ions or due to resonance transfer of energy [22]. Hence, visible energy (463 nm) was used to excite the samples in the present case. It shows that the present phosphor can be effectively excited by radiations

Fig. 3 **a** TEM (i), SAED pattern (ii), HRTEM (iii), EDX (iv) of (5 mol%) MNO:Sm^{3+} NPs. **b** SEM images of MNO:Sm^{3+} (5 mol%) NPs at various magnifications

of wavelength in the visible region saves lot of energy compared to the materials pumped by UV or NUV energies; therefore MNO can be used for the fabrication of white LEDs. The broad excitation peaks attributed to the characteristic intrinsic $4f-4f$ transitions of Sm^{3+} , indicating that the energy transfer from Mg–O or Nb–O charge

transfer (CT) bands of the $\text{MgO}_6/\text{NbO}_6$ octahedral group to Sm^{3+} ions was very efficient, also which can be attributed to the e_g and t_{2g} field splitting 5d bands of samarium ions.

Emission of MNO:Sm^{3+} (1–11%) at RT under 463 nm pumping (Fig. 9) show all the characteristic emission at 564, 608, 656 and 718 nm, assigned to transitions

$^4G_{5/2} \rightarrow ^6H_{5/2}$, $^6H_{7/2}$, $^6H_{9/2}$ and $^6H_{11/2}$ respectively [13, 15, 35] since photo excited carriers transfer energy to Sm^{3+} ions from the host lattice, resulting in the $^4G_{5/2} \rightarrow ^6H_{J/2}$ transitions and all the transitions were reflected in energy level diagram (Fig. 10). In MNO, Mg^{2+} occupies the sites (M1 & M2) i.e., inversion symmetry (CI) and mirror symmetry (CS), two non equivalent octahedral sites. The emission at 608 nm was hyper sensitive in nature when dopant ions occupies CS site results in characteristic orange red emission which was partly magnetic and partly electric dipole transition with shoulder peaks may be due to $(2J+1)$

splitting, the transition at 656 nm was due to purely electric dipole (ED) sensitive to the crystal field [36, 37], no emission peak positions shifted while doping concentrations were relatively varied, suggesting that the nature of Sm^{3+} activators remained unchanged, whereas the intensity reaches maximum at 5 mol% and falls afterwards (inset of Fig. 9) due to concentration quenching [18].

The octahedral sites $MgNb_2O_6$ are occupied by dopants in the host matrix, charge imbalance will be compensated by oxygen vacancies, if the dopants are excess then they will be appear on the surfaces or grain boundaries to yield optimum strain relief in their oxide form. The defect reaction can be represented in the following way,

Fig. 4 FTIR spectra of MNO:Sm³⁺ (1,5,9 mol%) NPs

Fig. 5 Wood and Tauc's plot to find band gap and the variation of band gap with Sm³⁺ concentration (inset: DRS of MNO:Sm³⁺)

where ' Sm'_{Mg} ' means ' Sm ' occupying the site normally occupied by a ' Mg^{2+} ', ' V''_O ' is the ' O^{2-} ' vacancy, ' Mg^x_{Mg} ' represents the rest Mg^{2+} in the lattice and ' O^x_O ' is the oxygen in the lattice of $MgNb_2O_6$ structure [38, 39].

According to Blasse, the critical distance (R_c) between two Sm^{3+} activators can be calculated as [12, 40]:

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

where C ; the critical dopant concentration = 0.05, N ; the number of Mg ion in the unit cell = 8, and V ; the volume of the unit cell = 407.02 Å³. R_c was found to be 12.46 Å, which is larger than 5 Å, for the present phosphor confirms that the non-radiative energy transfer is due to multipole–multipole interaction and is the main reason for quenching, in order to know the type of interaction like dipole–dipole (Q-6), dipole–quadrupole (Q-8) or quadrupole–quadrupole (Q-10), we have to utilize Dexter's theory and Van-Uitert equation [41] and by plotting $\log(X)$ V/s $\log(1/X)$ (Fig. 11):

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

where ' x '; activator concentration, ' k ' and ' β ' are the constants for the given host, and the value of Q was identified to be around 6, hence dipole–dipole (d–d) interaction was responsible for concentration quenching in the present case.

The quantum efficiency (QE) of the optimized MNO:Sm³⁺ (5 mol%) was calculated by the method described by De Mello [42] and Palsson [43]

$$QE = \frac{\text{Number of photons emitted}}{\text{Number of photons absorbed}} = \frac{E_c - E_a}{L_a - L_c} \quad (5)$$

Fig. 6 **a** Absorption spectra of the AR-88 dye with MNO as catalysts, **b** MNO: Sm^{3+} NPs catalysts under UV light irradiation, **c** Percentage degradation and **d** schematic of dye degradation mechanism

Scheme 1 The formation of active radicals ($\text{O}_2^{\cdot-}$ and $\text{OH}^\cdot$) from Sm-doped MgNb_2O_6 photocatalysts

where E_C : the integrated luminescence of the phosphor caused by direct excitation, E_a : the integrated luminescence from the empty integrating sphere (blank, without sample), L_a : the integrated excitation profile from the empty integrating sphere, L_C : the integrated excitation profile when the sample is directly excited by the incident beam. The QE for the MNO: Sm^{3+} (5 mol%) nanophosphor

Fig. 7 Excitation spectra of MNO: Sm^{3+} (1, 5 mol%) NPs

Fig. 8 Emission spectra of MNO:Sm³⁺ (5 mol%) compare with different excitation energies

Fig. 9 Emission spectra of MNO:Sm³⁺, inset (Variation of PL intensity with Sm³⁺ concentration)

was estimated to be ~68% by integrated emission counts from the 500–750 nm.

The J-O parameters Ω_λ were estimated in detail [44–46] to study the site symmetry and luminescence behavior of the Sm³⁺ ions in MNO host crystal to understand site symmetry and luminescence behavior using emission data, the adopted procedure is similar to our earlier work [18]. Spontaneous emission probability (A_R), the experimental intensity of $^4G_{5/2}$ to $^6H_{7/2}$ transitions Ω_λ ($\lambda = 2, 4$ and 6), Total radiative rate (A_T), Non-radiative rates (A_{NR}), luminescence quantum efficiency (η), fluorescence branching ratio (β), radiative lifetime (τ_{rad}) were estimated.

Fig. 10 Energy level diagram of Sm³⁺ showing all possible transitions in MNO host lattice

Fig. 11 Relation between $\log(x)$ and $\log(I/x)$ in MNO:Sm³⁺ NPs

$$A_R(\Psi J \rightarrow \Psi' J') = \frac{64\pi^4 \nu^3}{3h(2J+1)} \left[\frac{n(n^2+2)^2}{9} D_{ED} + n^3 D_{MD} \right] \quad (6)$$

$$D_{MD} = \frac{e^2 h^2}{16\pi^2 m^2 c^2} |\Psi J L + 2S\Psi' J'|^2 \quad (7)$$

$$D_{ED} = e^2 \sum_{\lambda=2,4,6} \Omega_\lambda |\Psi J U^{(\lambda)} \Psi' J'|^2 \quad (8)$$

$$\Omega_{\lambda} = \frac{D_{MD} v_1^3}{e^2 v_{\lambda}^3} \frac{9n^3}{n(n^2 + 2)^2 |\Psi J U^{(\lambda)} \Psi' J'|^2} \frac{\int I_{\lambda}(\nu) d\nu}{\int I_1(\nu) d\nu} \quad (9)$$

$$A_T(\psi J) = \sum_{\psi' J'} A_R(\psi' J', \psi J) \quad (10)$$

$$A_{NR} = \frac{1}{\tau} - A_R \quad (11)$$

$$\eta = \frac{A_R}{(A_R + A_{NR})} = \frac{A_R}{A_T} \quad (12)$$

$$\beta(\psi J) = \frac{A(\psi' J', \psi J)}{A_T(\psi J)} \quad (13)$$

$$\tau_{rad}(\psi' J') = \frac{1}{A_R(\psi J)} \quad (14)$$

$$n = xn_b + (1 - x)n_m \quad (15)$$

All the calculated J-O parameters are tabulated in Table 3 and all the obtained values uphold this system a promising material for displays [46–48].

The luminescence decay curve of MNO:Sm³⁺ (5 mol%) phosphors (Fig. 12) due to possible interactions between Sm³⁺ ions was well fitted by triple exponential and the average decay time (τ_r) was estimated to be 7.68 ms [46].

$$I = \left[A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_2}\right) + A_3 \exp\left(-\frac{t}{\tau_3}\right) \right] \quad (16)$$

$$\tau_r = \frac{(A_1 \tau_1^2 + A_2 \tau_2^2 + A_3 \tau_3^2)}{(A_1 \tau_1 + A_2 \tau_2 + A_3 \tau_3)} \quad (17)$$

Inset of Fig. 12 shows the decay curve at different temperatures, decrease in decay time with increase of temperature was due to the forbidden nature of the f–f

Fig. 12 Luminescence decay curves of MNO:Sm³⁺ (5 mol%) NPs. (Inset: luminescence decay time at different temperatures)

transition or self-absorption rate among dopants. Also, it was affected by the existence of defects, which could shorten the decay time by capture electrons, hence the values are in millisecond and were reasonably good to meet the purpose of the w-LEDs [12], a probable candidate for temperature sensor and the decay time quenching can be estimated as discussed elsewhere and the value of E_{CTS} and b were found to be 2650 cm⁻¹ and 1.7×10^6 s⁻¹ respectively [24, 46]:

$$\tau_d = \left[\tau_0^{-1} + b \exp\left(\frac{-E_{CTS}}{kT}\right) \right]^{-1} \quad (18)$$

These properties of the present material confirms good to be used as a temperature sensor operated in the temperature interval of between 50 and 400 °C where the decay time is decreasing. When temperature increases, the pathways of non-radiative transition will enhance which decrease the decay times. The emission intensities of MgNb₂O₆:Sm³⁺ (1–11 mol %) where

Table 3 Judd-Ofelt intensity parameters of MNO:Sm³⁺ nanophosphors (λ_{exi} = 463 nm)

Sm ³⁺ mol%	J-O intensity parameters ($\times 10^{-22}$ cm ²)		Transitions	A_R (s ⁻¹)	A_{NR} (s ⁻¹)	A_T (s ⁻¹)	τ_{rad} (ms)	η (%)	β (%)
	Ω_2	Ω_4							
1	0.6745	0.9765	$^4G_{5/2} \rightarrow ^6H_{5/2}$	92.13	28.97	119.3	12.37	78.01	58.26
3	0.6489	0.9111	$^4G_{5/2} \rightarrow ^6H_{7/2}$	93.45	28.05	118.6	12.55	79.96	58.24
5	0.6350	0.9669	$^4G_{5/2} \rightarrow ^6H_{9/2}$	93.47	27.63	117.2	12.73	80.09	58.23
7	0.6263	0.9698		94.52	26.71	116.4	12.64	78.76	58.27
9	0.6211	0.9945		92.58	26.52	118.7	12.25	79.50	58.25

Fig. 13 CIE diagram of MNO:Sm³⁺ (1–11 mol%) NPs for excitation wavelength of 463 nm

Fig. 14 CCT diagram of MNO:Sm³⁺ (1–11 mol%) NPs

characterized by using Commission International de l'Eclairage (CIE) chromaticity coordinates spectra shown in Fig. 13. The method estimate CIE chromaticity coordinates (x, y) and correlated colour temperature (CCT) coordinates (u', v') as discussed elsewhere [15, 48–51]. Besides, the average CCT of nanophosphor was (Fig. 14) found to be 1772 K (warm white light). The color purity of the nano phosphor can be estimated as:

$$\text{Color purity} = \frac{\sqrt{(x - x_{ee})^2 + (y - y_{ee})^2}}{\sqrt{(x_d - x_{ee})^2 + (y_d - y_{ee})^2}} \quad (19)$$

where, (x_{ee}, y_{ee}) and (x_d, y_d) are the coordinates of standard white point and dominate wavelength point respectively, considering pure white point at $x = 0.3127$ and $y = 0.3290$ (D65) [18] and it was found to be 99.2%, which was very close to 98.88% in our previous work on MNO:Eu³⁺ [18]. These values indicate that present phosphor was highly useful for the production of artificial white light, wLEDs and solid state display applications with near-UV or blue light chips [12].

Figure 15a shows the CV curve of MNO:Sm³⁺ (5 mol%) electrode at different scan rates in 1 M KOH using home-made carbon paste electrode [52]. The presence of redox peaks in the anodic and cathodic scan show the noteworthy contributions in the electrochemical process of pseudo-capacitance. The peak potentials were 0.296 V at 10 mVs⁻¹ and 0.401 V at 50 mVs⁻¹ respectively, which confirms reversibility of redox reaction is more [53]. Figure 15b shows the Nyquist plot and equivalent circuit (inset of Fig. 15b) of the MNO:Sm³⁺ (5 mol%) electrode. With the support on the frequency, the Nyquist plot has basically

Fig. 15 **a** Cyclic voltammogram (different scan rate), **b** Nyquist plot of MgNb₂O₆:Sm³⁺ (5 mol%) electrode

Table 4 The EIS circuit fitted parameters of $\text{MNO}:\text{Sm}^{3+}$ (5 mol%) nanomaterial

Type of Nyquist response	R_{ct} (V)	C_{dl} (F)	R_s (V)	R_1 (V)	Q_1 (rad/S)	Q_2 (F)
Without Sensor	164	0.0000543	0.876	6754	4.79×10^{-9} 0.7196	9.36×10^{-4} 0.5817
Paracetamol sensor	141	0.000178	0.675	4352	9.12×10^{-7} 0.6582	2.15×10^{-3} 0.6651
Alcohol sensor	42	0.000986	0.345	3467	3.67×10^{-6} 0.5687	1.32×10^{-3} 0.7806

Fig. 16 Cyclic voltammogram of $\text{MgNb}_2\text{O}_6:\text{Sm}^{3+}$ (5 mol%) NP detection of **a** Paracetamol and **b** Alcohol (concentration range 1–8 mM)

two regions: (i) a semicircle-high frequency region and (ii) a straight line-low frequency region. The impedance data obtained by fitting the equivalent circuit are presented in Table 4. In the given circuits, solution resistance (R_s), charge transfer resistance (R_{ct}) and the double-layer capacitance (C) were calculated by intercepting the semicircle on the real axis and electrode–electrolyte interface in high-frequency region, whereas the Warburg element (W) was calculated by straight line in the low-frequency region. Q_1 : constant phase element which was parallel to R_{ct} and Q_2 : the low frequency capacitance parallel to the leakage resistance (R_l) [54–56]. Figure 16a, b show the cyclic voltammograms of $\text{MgNb}_2\text{O}_6:\text{Sm}^{3+}$ (5 mol%) NP used for detection of paracetamol/acetaminophen (Dolo 650 mg, Micro Labs) and alcohol (Sula red Wine, Cabernet Shiraz, Vineyards) respectively. Anodic oxidation peak and cathodic reduction peak in cyclic voltammogram for $\text{MNO}:\text{Sm}^{3+}$ (5 mol%), paracetamol sensor and alcohol sensor are at (–0.10 V, –0.41 V) and (–0.168 V, –0.41 V) respectively. A drastic variation of oxidation and reduction peak positions confirms that, $\text{MNO}:\text{Sm}^{3+}$ (5 mol%) was an effective material for chemical sensor applications in alkaline medium for quantities of 1–8 mM concentrations (Fig. 17).

Fig. 17 Nyquist plot of $\text{MgNb}_2\text{O}_6:\text{Sm}^{3+}$ (5 mol%) electrode (without, with paracetamol and alcohol sensor)

4 Conclusions

Single phase columbite type orthorhombic structured $\text{MNO}:\text{Sm}^{3+}$ (1–11 mol%) nanophosphors were prepared in

the present work, TEM results uphold the nano and polycrystalline nature of the samples, having energy gap in the range of 4 eV as confirmed by DRS. Better photocatalytic activity of 99% degradation for AR-88 dye under UV light irradiation was observed in this work. All the characteristic transitions were observed with average decay time (τ_r) of 7.68 ms, it was found to decrease with increase in temperature indicating the thermal sensing property of this material. CIE n CCT coordinates confirms orange red emission and ~ 1772 K respectively. Electrochemical studies show high reversible electrode reaction, high charge transfer resistance and exhibit high sensitivity for detection of paracetamol and alcohol. All the above results validate that; the present material can be a good candidate for solid state display, photocatalytic, thermal and chemical sensor applications.

Compliance with ethical standards

Conflict of interest We wish to confirm that there are no known conflicts of interest associated with this publication and there has been no significant financial support for this work that could have influenced its outcome.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit <http://creativecommons.org/licenses/by/4.0/>.

References

- Ashwini S, Prashantha SC, Ramachandra N, Nagabhushana H, Jnaneshwara DM, Narasimhamurthy KN (2019) Bi₂O₃:Dy³⁺ nanophosphors: its white light emission and photocatalytic activity. *SN Appl Sci* 1:1028
- Xia Z, Miao S, Chen M, Molokeev MS, Liu Q (2015) Structure, crystallographic sites, and tunable luminescence properties of Eu²⁺ and Ce³⁺/Li⁺-activated Ca_{1.65}Sr_{0.35}SiO₄ Phosphors. *Inorg Chem* 54:7684–7691
- Girish KM, Prashantha SC, Ramachandra N, Nagabhushana H, Anantharaju KS (2019) Effect of Bi³⁺ and Li⁺ co-doping on the luminescence properties of Zn₂TiO₄:Eu³⁺ nanophosphor for display applications. *SN Appl Sci* 1:926
- Zanga Z, Zenga X, Wanga M, Hua W, Liub C, Tang X (2017) Tunable photoluminescence of water-soluble AgInZnS-graphene oxide (GO) nanocomposites and their application in vivo bioimaging. *Sens Actuators B Chem* 252:1179–1186
- Zhang YC, Yue ZX, Gui ZL, Li LT (2003) Effects of CaF₂ addition on the microstructure and microwave dielectric properties of ZnNb₂O₆ ceramics. *Ceram Inter* 29:555–559
- Ngamjarurojana A, Khamman O, Yimnirun R, Ananta S (2006) Effect of calcination conditions on phase formation and particle size of zinc niobate powders synthesized by solid-state reaction. *Mater Lett* 60:2867–2872
- Narendran N, Gu Y, Freyssinier-Nova JP, Zhu Y (2005) Extracting phosphor-scattered photons to improve white LED efficiency. *Phys Stat Sol (Wiley)* 6:202
- Wang Y, Sun Y, Zhang J, Ci Z, Zhang Z, Wang L (2008) New red Y_{0.85}Bi_{0.1}Eu_{0.05}V_{1-y}M_yO₄ (M = Nb, P) phosphors for light-emitting diodes. *Phys B Cond Matt* 403:2071–2075
- Janga HS, Ima WB, Leeb DC, Jeona DY, Kimc SS (2007) Enhancement of red spectral emission intensity of Y₃Al₅O₁₂:Ce³⁺ phosphor via Pr co-doping and Tb substitution for the application to white LEDs. *J Lumin* 126:371–377
- Rajua GSR, Junga HC, Parka JY, Moona BK, Balakrishnaiah R, Jeonga JH, Kim JH (2010) The influence of sintering temperature on the photoluminescence properties of oxyapatite Eu³⁺:Ca₂Gd₈Si₆O₂₆ nanophosphors. *Sens Actuators B Chem* 146:395–402
- Naik R, Prashantha SC, Nagabhushana H, Sharma SC, Nagabhushana BM, Nagaswarupa HP, Premkumar HB (2014) Low temperature synthesis and photoluminescence properties of red emitting Mg₂SiO₄:Eu³⁺ nanophosphor for near UV light emitting diodes. *Sens Actuators B Chem* 195:140–149
- Zhang L, Che J, Ma Y, Wang J, Kang R, Deng B, Yu R, Geng H (2020) Luminescent and thermal properties of novel orange-red emitting Ca₂MgTeO₆:Sm³⁺ phosphors for white LEDs. *J Lumin* 225:117374
- Dabre K, Dhoble S (2014) Synthesis and photoluminescence properties of Eu³⁺, Sm³⁺ and Pr³⁺ doped Ca₂ZnWO₆ phosphors for phosphor converted LED. *J Lumin* 150:55–58
- Zhang J, Zhang W, Yang Z, Yub Z, Zhang X, Chang TC, Javey A (2014) Vertically aligned tungsten oxide nanorod film with enhanced performance in photoluminescence humidity sensing. *Sens Actuators B Chem* 202:708–713
- Girish KM, Prashantha SC, Ramachandra N, Nagabhushana H (2017) Zn₂TiO₄: A novel host lattice for Sm³⁺ doped reddish orange light emitting photoluminescent material for thermal and fingerprint sensor. *Opt Mater* 73:197–205
- Poornima Parvathi V, Parimaladevi R, Sathe Vasant, Mahalingam Umadevi (2019) Graphene boosted silver nanoparticles as surface enhanced Raman spectroscopic sensors and photocatalysts for removal of standard and industrial dye contaminants. *Sens Actuators B Chem* 281:679–688
- Surendra BS (2018) Green engineered synthesis of Ag-doped CuFe₂O₄: characterization, cyclic voltammetry and photocatalytic studies. *J Sci Adv Mater Device* 3(1):44–50
- Basavaraju N, Prashantha SC, Nagabhushana H, Chandrasekhar M, NaveenKumar A, ShashiShekhar TR, Ashwini S, Anantharaju KS (2020) A benign approach for novel synthesis of Eu³⁺ doped MgNb₂O₆: its photoluminescence and photocatalytic studies. *Ceram Int*. <https://doi.org/10.1016/j.ceramint.2020.07.242>
- Sarkar K, Mukherjee S (2016) Synthesis, characterization and property evaluation of single phase MgNb₂O₆ by chemical route. *J Aust Ceram Soc* 52(2):32–40
- Sia JY, Songa SY, Liua N, Caib GM, Sub LM (2018) Synthesis and photoluminescence of host-sensitized MgNb₂O₆ based phosphors. *J Lumin* 198:10–18
- Fang TH, Hsiao YJ, Chang YS, Ji LW, Kang SH (2008) Luminescent and structural properties of MgNb₂O₆ nanocrystals. *Curr Opin Soli State Mater Sci* 12:51–54
- Jisha PK, Naik R, Prashantha SC, Nagaswarupa HP, Nagabhushana H, Basavaraj RB, Sharma SC, Prasad Daruka (2016) Structural

- refinement, band-gap analysis and optical properties of GdAlO₃ nanophosphors influenced by Dy³⁺ ion concentrations for white light emitting device applications. *Mater Res Express* 3:045007
23. Shetty M, Murthy M, Shastri M, Sindhusree M, Nagaswarupa HP, Prasanna D Shivaramu, Rangappa Dinesh (2019) Hydrothermally synthesized Bi₂MoO₆/Reduced Graphene Oxide composite as anodes for lithium-ion batteries. *Ceram Int* 45(18):24965–24970
 24. Santos LPS, Camargo ER, Fabbro MT, Longo E, Leite ER (2007) Wet-chemical synthesis of magnesium niobate nanoparticles powders. *Ceram Int* 33:1205–1209
 25. Hong YS, Park HB, Kim SJ (1998) Preparation of Pb(Mg_{1/3}Nb_{2/3})O₃ powder using a citrate-gel derived columbite MgNb₂O₆ precursor and its dielectric properties. *J Euro Ceram Soc* 18:613–619
 26. Yadava RS, Dhoble SJ, Raia SB (2018) Enhanced photoluminescence in Tm³⁺, Yb³⁺, Mg²⁺ tri-doped ZnWO₄ phosphor: three photon upconversion, laser induced optical heating and temperature sensing. *Sens Actuators B Chem* 273:1425–1434
 27. Naik R, Prashantha SC, Nagabhushana H, Sharma SC, Nagaswarupa HP, Anantharaju KS, Jnaneshwara DM, Girish KM (2016) Tunable white light emissive Mg₂SiO₄:Dy³⁺ nanophosphor: its photoluminescence, Judd Ofelt and photocatalytic studies. *Dyes Pigment* 127:25–36
 28. Shivakumara C, Saraf R, Halappa P (2016) White luminescence in Dy³⁺ doped BiOC_l phosphors and their Judd–Ofelt analysis. *Dyes Pigment* 126:154–164
 29. Aguielera RC, Han Z, Cai Y, Kimerling LC, Michel J (2013) Direct band gap narrowing in highly doped Ge. *Appl Phys Lett* 102:152106
 30. Vidya YS, Gurushantha K, Nagabhushana H, Sharma SC, Anantharaju KS, Shivakumara C, Suresh D, Nagaswarupa HP, Prashantha SC, Anilkumar MR (2015) Phase transformation of ZrO₂:Tb³⁺ nanophosphor: color tunable photoluminescence and photocatalytic activities. *J Alloy Compd* 622:86–96
 31. Zaldo C, Martin MJ, Coyat C, Polgar K, Peter A, Paitz J (1995) Optical properties of MgNb₂O₆ single crystals: a comparison with LiNbO₃. *Phys Cond Matter* 7:2249–2257
 32. Renuka L, Anantharaju KS, Vidya YS, Nagaswarupa HP, Prashantha SC, Sharmac SC, Nagabhushana H, Darshan GP (2017) A simple combustion method for the synthesis of multi-functional ZrO₂/CuO nanocomposites: excellent performance as Sunlight photocatalysts and enhanced latent finger print detection. *Appl Catal B Environ* 210:97–115
 33. Surendra BS, Veerabhadrswamy M, Anantharaju KS, Nagaswarupa HP, Prashantha SC (2018) Green and chemical engineered CuFe₂O₄: characterization, cyclic voltammetry, photocatalytic and photoluminescent investigation for multifunctional applications. *J Nano Chem* 8:45–59
 34. Gurushantha K, Anantharaju KS, Nagabhushana H, Sharmac SC, Vidya YS, Shivakumara C, Nagaswarupa HP, Prashantha SC, Anil Kumar MR (2015) Facile green fabrication of iron-doped cubic ZrO₂ nanoparticles by *Phyllanthus acidus*: structural, photocatalytic and photoluminescent properties. *J Mole Catal A Chem* 397:36–47
 35. Ashwini S, Prashantha SC, Naik R, Naik YV, Nagabhushana H, Narasimhamurthy KN (2019) Photoluminescence and photocatalytic properties of novel Bi₂O₃:Sm³⁺ nanophosphor. *J Sci Adv Mater Device* 4(4):531–537
 36. Unal Fatma, Kaya Faruk, Kazmanli Kursat (2019) Effects of dopant rate and calcination parameters on photoluminescence emission of Y₂O₃:Eu³⁺ phosphors: a statistical approach. *Ceram Int* 45:17818–17825
 37. Naik R, Prashantha SC, Nagabhushana H, Sharma SC, Nagaswarupa HP, Anantharaju KS, Nagabhushana BM, Premkumar HB, Girish KM (2015) A single phase, red emissive Mg₂SiO₄:Sm³⁺ nanophosphor prepared via rapid propellant combustion route. *Spectrochim Acta Part A Mol Biomol* 140:516–523
 38. Jisha PK, Naik R, Prashantha SC, Nagabhushana H, Sharma SC, Nagaswarupa HP, Anantharaju KS, Daruka Prasad B, Premkumar HB (2015) Facile combustion synthesized orthorhombic GdAlO₃:Eu³⁺ nanophosphors: Structural and photoluminescence properties for WLEDs. *J Lumin* 163:47–54
 39. Shi S, Hossu M, Hall R, Chen W (2012) Solution combustion synthesis, photoluminescence and X-ray luminescence of Eu-doped nanoceria CeO₂:Eu. *J Mater Chem* 22:23461–23467
 40. Blasse G (1968) Energy transfer in oxidic phosphors. *Phys Lett A* 28:444–445
 41. Uitert LGV (1967) Characterization of energy transfer interactions between rare earth ions. *J Electrochem Soc* 114:1048–1053
 42. De Mello JC, Wittmann HF, Friend RH (1997) An improved experimental determination of external photoluminescence quantum efficiency. *Adv Mater* 9:230–232
 43. Palsson LO, Monkman AP (2002) Measurements of solid-state photoluminescence quantum yields of films using a fluorimeter. *Adv Mater* 14:757–758
 44. Judd BR (1962) Optical absorption intensities of rare-earth ions. *Phys Rev* 127:750
 45. Ofelt GS (1962) Intensities of crystal spectra of rare earth ions. *J Chem Phys* 37:511
 46. Manohar T, Prashantha SC, Naik R, Nagabhushana H, Nagaswarupa HP, Anantharaju KS, Girish KM, Premkumar HB (2017) A benign approach for tailoring the photometric properties and Judd-Ofelt analysis of LaAlO₃:Sm³⁺ nanophosphors for thermal sensor and WLED applications. *Sens Actuators B Chem* 243:1057–1066
 47. Lalla EA, Konstantinidis M, De Souza I, Daly MG, Martin IR, Lavin V, Rodriguez-Mendoza UR (2020) Judd-Ofelt parameters of RE³⁺-doped fluorotellurite glass (RE³⁺ = Pr³⁺, Nd³⁺, Sm³⁺, Tb³⁺, Dy³⁺, Ho³⁺, Er³⁺, and Tm³⁺). *J Alloys Compd* 845:156028
 48. Vijaya Prakash G (2000) Absorption spectral studies of rare earth ions (Pr³⁺, Nd³⁺, Sm³⁺, Dy³⁺, Ho³⁺ and Er³⁺) doped in NASICON type phosphate glass, Na₄AlZnP₃O₁₂. *Mater Lett* 46(1):15–20
 49. Rakov N, Vieira SA, Silva QPS, Maciel GS (2015) Facile fabrication of Eu³⁺-doped lanthanum oxyfluoride powders by combustion processes and temperature analysis of its fluorescence for thermal sensor application. *Sens Actuators B Chem* 209:407–412
 50. Srihari T, Jayasankar CK (2017) Fluorescence properties and white light generation from Dy³⁺-doped niobium phosphate glasses. *Opt Mater* 69:87–95
 51. Judd DB (1936) Estimation of chromaticity differences and nearest color temperatures on the Standard 1931 I.C.I. Colorimetric coordinate system. *J Opt Soc Am* 26:421–4261
 52. Bhatt AS, Ranjitha R, Santosh MS, Ravikumar CR, Prashantha SC, Maphanga RR, Lenze Silva GFB (2020) Optical and electrochemical applications of Li-doped NiO nanostructures synthesized via facile microwave technique. *Materials* 13:2961
 53. Ravikumar CR, Anil Kumar MR, Nagaswarupa HP, Prashantha SC, Bhatt Aarti S, Santosh MS, Kuznetsov Denis (2018) CuO embedded β-Ni(OH)₂ nanocomposite as advanced electrode materials for supercapacitors. *J Alloys Compd* 736:332–339
 54. Ravikumar CR, Kotteeswaran P, Bheema Raju V, Murugan A, Santosh MS, Nagaswarupa HP, Prashantha SC, Anil Kumar MR, Shivakumar MS (2017) Influence of zinc additive and pH on the electrochemical activities of β-nickel hydroxide materials and its applications in secondary batteries. *J Energy Storage* 9:12–24
 55. Er E, Erk N (2020) A novel electrochemical sensing platform based on mono-dispersed gold nanorods modified graphene for the sensitive determination of topotecan. *Sens Actuators B Chem* 320:128320

56. Kaur I, Sharma M, Kaur S, Kaur A (2020) Ultra-sensitive electro-chemical sensors based on self-assembled chelating dithiol on gold electrode for trace level detection of copper (II) ions. *Sens Actuators B Chem* 312:127935

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.