International Journal of Engineering & Technology, 7 (4) (2018) 2917-2921

International Journal of Engineering & Technology

Website: www.sciencepubco.com/index.php/IJET
doi: 10.14419/ijet.v7i4.15760
Research paper

Facile synthesis, structural and luminescence studies of $MgTiO_3:Sm^{3+}$ nanophosphor for display applications

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Abstract

Luminescence properties of combustion prepared $Mg_2TiO_3:Sm^{3+}$ (1-11 mol %) phosphors were studied in the present work. The crystallite size (D) was in the range20- 40 nm as estimated and it was similar to Transmission electron microscopy (TEM) results. The band gap of the materials was in the range 4.45 to 4.87 eV as calculated using Kubelka-Monk function. The PL peaks of Sm^{3+} ions are due to the intra 4-f orbital transitions ($^4G_{5/2}\rightarrow{}^6H_{5/2}$, $^4G_{5/2}\rightarrow{}^6H_{7/2}$, $^4G_{5/2}\rightarrow{}^6H_{9/2}$ and $^4G_{5/2}\rightarrow{}^6H_{11/2}$). Among the samples, 5 mol % doped one shows the highest PL intensity under 413 nm excitation. The CIE chromaticity coordinates showed orange of red emission (CCT ~2036 K), as a result $Mg_2TiO_3:Sm^{3+}$ (1-11 mol %) Nanophosphors were obviously for solid-state lighting and warm white light emissive display applications.

Keywords:*$MgTiO_3:Sm^{3+}$; Nanophosphor; J-O Parameters; Photoluminescence; CIE N CCT;*

1. Introduction

Inorganic luminescent materials doped with Sm^{3+} found its use in counterfeit light creation, white light-emitting diodes (LEDs) with high effectiveness and natural wellbeing [1-3]. Till today, commercial WLEDs have been based on the combination of LED with blue and yellow light. They have poor color render index (CRI), which can be solved by using tricolor (red, green and blue) phosphors energized by a near-ultraviolet (NUV) energy. This leads to the preparation of new efficient phosphors for new generation WLEDs [4-7]. In recent years, ABO_3 perovskite structures [8, 9] have turned out to be very vital materials as host segments in numerous applications [3]. Magnesium titanate ($MgTiO_3$), an excellent host material, can find a place in the perovskite group of mixes with ABO_3 structure and be a member of the ilmenite group (E_g ~ 4 eV) [10].

$MgTiO_3$was prepared using different wet and soft blend techniques including polymerized complex strategy, sol–gel process, co-precipitation method, etc [11]. However, solution combustion synthesis (SCS) method has been developed and successfully used for the low temperature production of pure and doped nanoparticles in the past few years [5]. In the present study, Sm^{3+} doped $MgTiO_3$ phosphor is prepared by SCS.

2. Experimental

2.1. Synthesis of $MgTiO_3:Sm^{3+}$

$MgTiO_3:Sm^{3+}$ phosphors were prepared by solution combustion method [8] using urea as a fuel. Stoichiometric quantities of starting materials were mixed well in a petridish with little amount of distilled water and was put in a muffle furnace (500±10 ^oC). Thereafter, the reaction was initiated finally leaving a white powder.

2.2. Characterization

Shimadzu X-ray diffractometer (operating at 50 kV and 20 mA by means of CuKα (1.541 Å) radiation with a nickel filter) was used for PXRD. JEOL, JEM-2100 (accelerating voltage up to 200 kV, LaB_6 filament) for TEM analysis and Shimadzu UV–Vis spectrophotometer model 2600 for DRS. Photoluminescence studies were carried out using a Hitachi F-4600 fluorescence spectrometer at RT with Xe lamp as a light source.

3. Results and discussions

3.1. Photometric properties

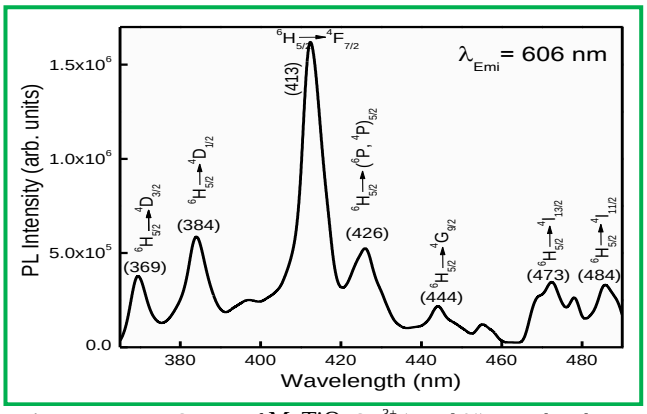

Fig. 1: Excitation Spectra of $MgTiO_3:Sm^{3+}$ (5 mol %) nanophosphors.

Various transitions are possible among 4f energy levels of Sm^{3+} with 4f ^{5}configuration.With this idea, we recorded the excitation spectrum of $MgTiO_3:Sm^{3+}$ (5mol %), keeping the emission at ~607 nm (Fig. 1). Peaks between 350 to 500 nm werecredited to f–f change of Sm^{3+} particles. Excitation peaks at ~369, ~ 384 and 413 nm connected to $^6H_{5/2}\rightarrow{}^4D_{3/2}$, $^6H_{5/2}\rightarrow{}^6P_{7/2}$ + $^4K_{13/2}$ and $^6H_{5/2}\rightarrow{}^4F_{7/2}$ transitions respectively [12]. PLE spectra showedthe peak at 413 nm compared to the change of $^6H_{5/2}\rightarrow{}^4F_{7/2,}$ which gave more intense emission, due to resonance transfer of energy [13].

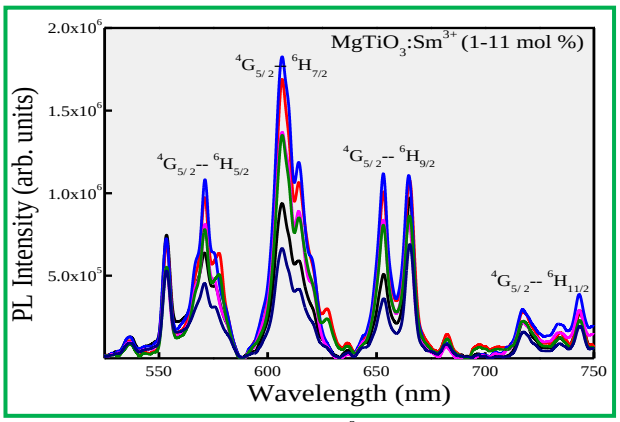

Fig. 2: Emission Spectra of $MgTiO_3:Sm^{3+}$ (1-11 mol %) nanophosphors.

Fig. 2 shows that the emission spectra of Sm^{3+} ions doped $MgTiO_3$ (λ_{exc}-413 nm), the emission peaks were comparable to the change of $^4G_{5/2}\rightarrow{}^6H_{5/2}$ (570 nm) magnetic-dipole (MD) transition, $^4G_{5/2}\rightarrow{}^6H_{7/2}$ (607 nm)incompletely magnetic and somewhat constrained electric-dipole(ED), $^4G_{5/2}\rightarrow{}^6H_{9/2}$ (658 nm) purely ED transition and $^4G_{5/2}\rightarrow{}^6H_{11/2}$ (707 nm) the intra 4-f orbital transitions of Sm^{3+} [14-22] and show in the energy level graph (Fig. 3).

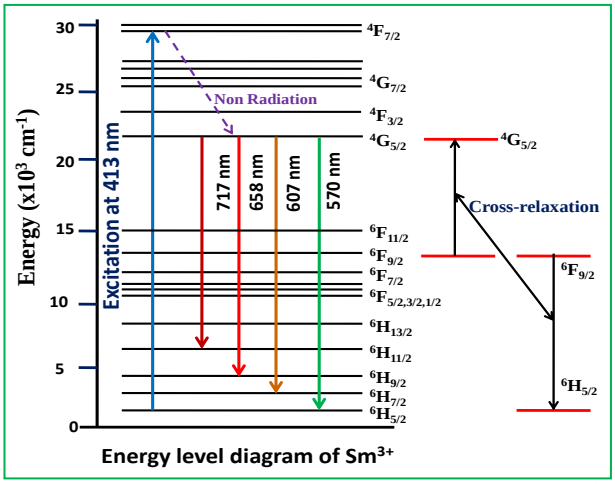

Fig. 3: Energy Level Diagram Indicating Emission Probabilities of Sm^{3+} in $MgTiO_3$ Host.

It was observed that at 5 mol percentage PL intensity was more and thereafter, concentration quenching happened [23] and non-radiative transitions increased because normal collaboration, separate between Sm ions diminished thereby diminishing the PL intensity (Fig 4). As Blasse [24] suggested, the critical energy transfer distance (R_c) was calculated to know non-radiative energy transfer process, which was found to be 3.2 Å (<5 Å) [22], showing that the exchange interaction was responsible between samarium ion in this host.

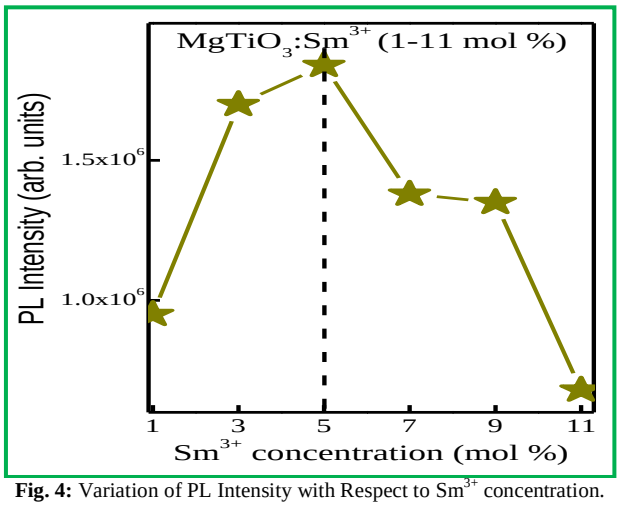

Fig. 4: Variation of PL Intensity with Respect to Sm^{3+} concentration.

The possible defect mechanism for non radiative energy transfer was proposed as,

$$(1-x)MgTiO_3 + 0.5xSm_2O_3 = xSm'_{Mg} + 0.5xV''_O + (1-x)Mg^x_{Mg} + (2-0.5x)O^x_o \quad (1)$$

where'Sm'_{Mg}' means 'Sm' occupying the Mg^{2+} site, 'V''_O' was the 'O^{2-}' vacancy, 'Mg^x_{Mg}' represents the rest Mg atoms and 'O^x_o' (oxygen in $MgTiO_3$) [25].Also, Dexter theory was used to find the value Q [26], $\left\{\frac{I}{X} = k\left[1+\beta(x)^{\frac{Q}{3}}\right]^{-1}\right\}$, Q = 6, 8 and 10 for (d-d), (d-q), (q-q) collaborations separately [27]. By assuming $\beta(X)^{Q/3}>>1$, it show $\left\{\log\left(\frac{I}{X}\right) = k' - \frac{Q}{3}\log x\right\}$, using the plot of log I/x v/slog x (Fig. 5), Q=3.09 (close to 3), indicates that exchange collaboration is in charge of concentration quenching.

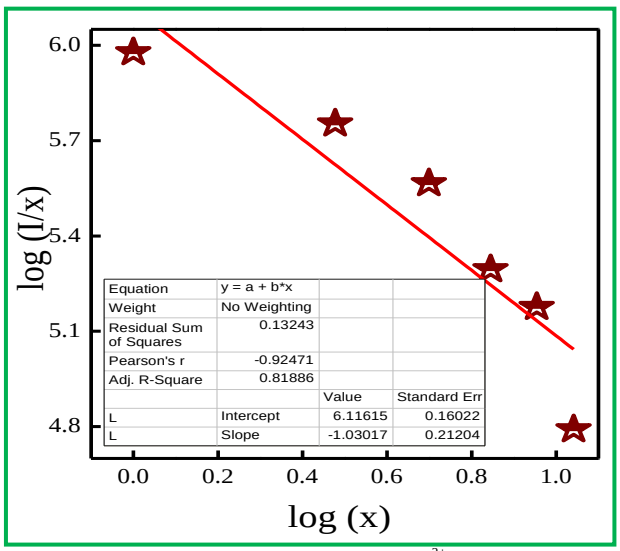

Fig. 5: Relation between Log(X) and Log (I/X) Sm^{3+} (1- 11 mol %) doped $MgTiO_3$.

The color coordination (CIE) and relevant color temperature (CCT) of the samples were calculated for$MgTiO_3:Sm^{3+}$ (1-11 mol %) phosphors and is shown in Fig. 6. It was observed that orange red emission by the present phosphor and CCT (Fig. 7) [28], [29] was found to be 2036 K (<5000 K).

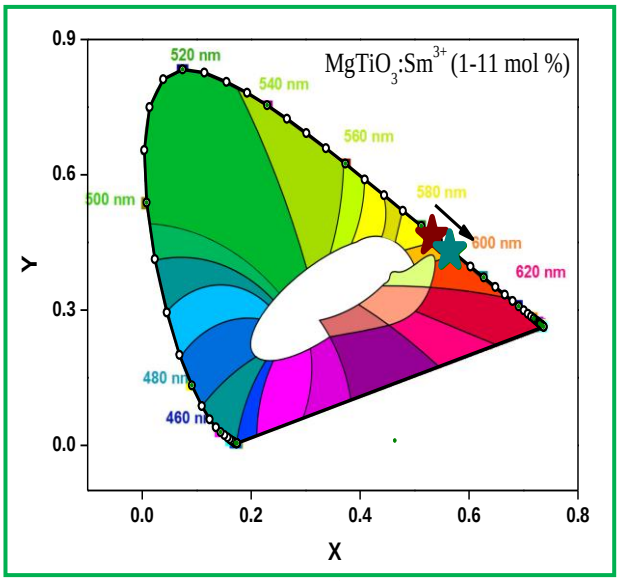

Fig. 6: CIE Diagram of $MgTiO_3:Sm^{3+}$ (1-11 mol %) nanophosphor.

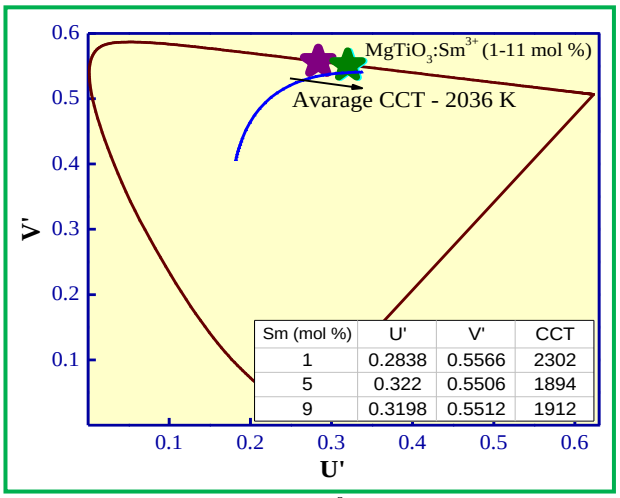

Fig. 7:CCT Diagram of $MgTiO_3:Sm^{3+}$ (1-11 mol %) nanophosphor.

3.2. Judd-OFELT analysis of $MgTiO_3:Sm^{3+}$ (1-11 mol %) nanophosphors

The Judd-Ofelt (J-O) hypothesis was utilized to contemplate the spectral performance, and all the J-O parameters (Ω λ (λ = 2, 4 and 6)) could beevaluatedfrom the PL emanation data [30-32]. The spontaneous emission probability of 4G5/2→6H5/2 is given by [33].

$$A_{5/2-5/2} = \frac{64\pi^4\nu_{5/2}^3 n^3 S_{md}}{3h(2J+1)} \quad (2)$$

The ED transition (A5/2J) of 4G5/2 → 6HJ (J = 7/2 and 9/2) is given by

$$A_{5/2\,J} = \frac{64\pi^4\nu_J^3}{3h(2J+1)} e^2 \frac{n(n^2+2)^2}{9} \sum_{\lambda=2,4,6} \Omega_\lambda \left|\langle {}^4G_{5/2} \| U^\lambda \| {}^6H_J \rangle\right|^2 S_{md} \quad (3)$$

The MD line strength and n ; refractive index is given by [34-35].

$$n = xn_b + (1-x)n_m (4)$$

Where n_b ; refractive indexof the bulk, x ; optical filling factor and xcan be controlled by utilizing the connection

$$x = \frac{n_s - n_m}{n_b - n_m} (5)$$

Wheren$_s$ the R.I of the sample. J-O parameters can be controlled by utilizing the connection

$$\frac{\int I_J dv}{\int I_{5/2} dv} = \frac{A_{5/2J}}{A_{5/2\,5/2}} = \frac{e^2\nu_J^3(n^2+2)^2}{S_{md}\nu_{5/2}^3 9n^2} \Omega_\lambda \left|\langle {}^4G_{5/2} \| U^\lambda \| {}^6H_J \rangle\right|^2 \quad (6)$$

In all the nanophosphorsthe trend Ω2> Ω4 wasrather expected [36].
The add up to radiative progress (AR) was controlled by

$$A_R = \sum_J A_{5/2J} = A_{5/2\,-5/2} \frac{\nu_{5/2-5/2}}{I_{5/2\,-5/2}} \sum_{J=5/2}^{9/2} \frac{I_{5/2J}}{\nu_{5/2J}} \quad (7)$$

A5/2-5/2: Einstein's coefficient. I5/2J: integrated area of the emission spectrum.

The radiative lifetime (τrad) is determined by

$$\tau_{rad} = \frac{1}{\sum_J A_{5/2J}} = \frac{1}{A_R} (8)$$

The luminescence quantum efficiency (η) was measured and found to be ~ 72 %.

$$\eta = \frac{A_R}{A_R + A_{NR}} = \frac{A_R}{A_T} (9)$$

The branching ratio ($\beta_{5/2}$ J) was expressed as [48]

$$\beta_{5/2\,J} = \frac{A_{5/2\,J}}{\sum A_{5/2\,J}} \quad (10)$$

All the J-O intensity parameters are tabulated in Table 1, showing that the present phosphor can be a potential candidate for warm WLED and solid state displays.

Table 1: Judd-OfeltParameters of $MgTiO_3:Sm^{3+}$ Nanophosphors (λ_{exi} = 413 nm)

Sm^{3+} Mol %	J–O Intensity Parameters($\times10^{-22}$ Cm^2)		Transitions	$A_R(S^{-1})$	$A_{NR}(S^{-1})$	$A_T(S^{-1})$	τ_{Rad} (Ms)	H (%)	B (%)
	Ω_2	Ω_4							
1	0.9660	0.6393	$^4G_{5/2} \rightarrow {}^6H_{5/2}$	93.11	27.79	120.9	10.73	77.01	56.27
3	1.0111	0.5389		94.75	20.85	115.6	10.55	81.96	56.22
5	0.9879	0.6170	$^4G_{5/2} \rightarrow {}^6H_{7/2}$	96.40	22.60	119.0	10.37	81.00	56.24
7	0.9896	0.6236		95.59	22.81	118.4	10.46	80.73	56.24
9	0.9947	0.6332	$^4G_{5/2} \rightarrow {}^6H_{9/2}$	95.18	23.02	118.2	10.50	80.50	56.23

3.3. Crystallite size and band gap analysis

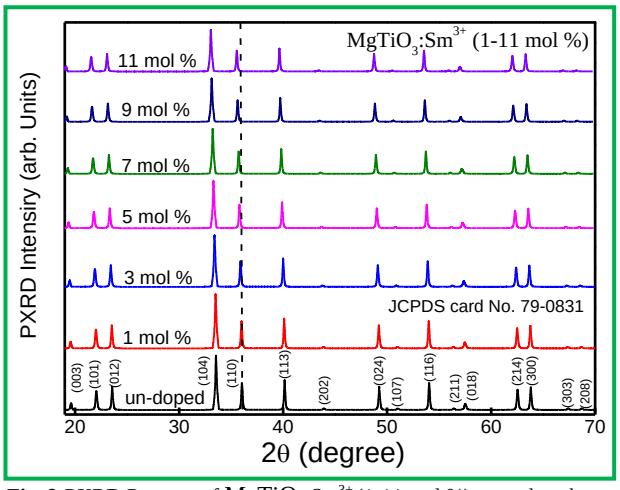

Fig. 8:PXRD Patterns of $MgTiO_3:Sm^{3+}$ (1-11 mol %) nanophosphors.

PXRD examples of Sm^{3+} (1-11 mol %) doped $MgTiO_3$ are shown in Fig. 8 and theymatch well with the JCPDS card No. 2-901, with rhombohedral structure (space group R-3) [37]. The 'a' and 'V' for (104) plane were found to be 2.891 Å and 355.911 x 10^{-30} m^3 respectively. 20-40 nm was the value of 'D' by Scherrer's method [38], the peaks moved towards less angle side because the doping of cations led to change of 'V' bringing about stress and small scale strain [39].

Fig. 9 illustrates the TEM, high resolution TEM (HRTEM) and SAED patterns of undoped samples, showing that irregular shaped and well dispersed particles, with lattice fringes (HRTEM), show the crystallinity of the sample [40].

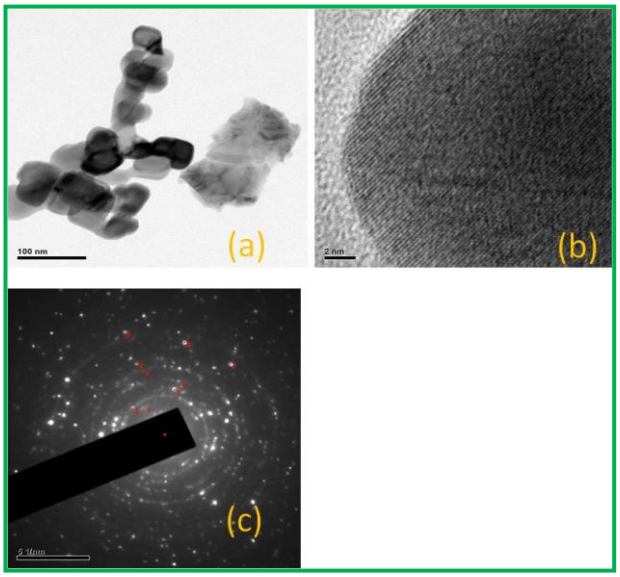

Fig. 9: A) TEM Image, B) HRTEM and C) SAED of $MgTiO_3$.

The bandgap of the samples (DRS-Fig. 10) were calculated using Kubelka- Munk function F(R), $F(R) = (1-R)^2/2R$. The bandgap of $MgTiO_3:Sm^{3+}$ NPs increased from 4.45 to 4.87 eV, may be due to the influence of [Sm-O] clusters or due to non bridging oxygen's (NBO) [39, 41]. A number of transitions were possible between 4f levels of Sm^{3+} since; $4f^5$ configuration had complex energy levels.

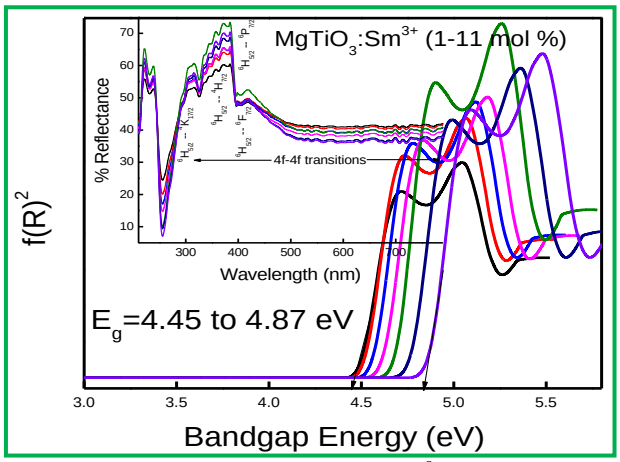

Fig. 10: Energy Band Gap Spectra of $MgTiO_3:Sm^{3+}$ (1-11 mol %) nanophosphors
(Inset: DRS Patterns of $MgTiO_3:Sm^{3+}$ (1-11 mol %) nanophosphors).

4. Conclusions

The normal crystallite was observed to be between20-40 nm for Sm^{3+} doped $MgTiO_3$ phosphors. The emission spectra were attributed to $^4G_{5/2}$–^6H_J (J = 5/2, 7/2, 9/2, 11/2) transitions of Sm^{3+} ion; the most exceptional emanation of Sm^{3+} was recorded for the change $^4G_{5/2}\rightarrow{}^6H_{7/2}$. The J-O intensity parameters show $\Omega_2>\Omega_4$ tendency, high covalence of metal-ligand bond of the Sm^{3+} sites in the host lattice. Further, the emission properties of the $MgTiO_3:Sm^{3+}$ show that it is a promising material in red region for WLEDs and optical display applications.

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