

A novel blue-emitting phosphor $\text{LiSrPO}_4:\text{Eu}^{2+}$ for white LEDs

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Abstract

A novel blue-emitting phosphor, $\text{LiSrPO}_4:\text{Eu}^{2+}$, was prepared by the solid-state reaction and X-ray powder diffraction (XRD) analysis confirmed the formation of $\text{LiSrPO}_4:\text{Eu}^{2+}$. Photoluminescence (PL) results showed that the phosphor can be efficiently excited by UV-visible light from 250 to 440 nm, and exhibited bright blue emission. The effects of the doped- Eu^{2+} concentration in $\text{LiSrPO}_4:\text{Eu}^{2+}$ on the PL were investigated in detail. The results showed that the relative PL intensity increases with Eu^{2+} -concentration increasing until a maximum intensity is reached, and then it decreases due to concentration quenching and a red-shift appears, which are explained satisfactorily with the luminescent theory. Upon excited with 396 nm light, the present synthesized phosphor has higher emission intensity than that from the commercial blue phosphor, $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$. Bright blue light-emitting diodes were fabricated by the combination of the synthesized $\text{LiSrPO}_4:\text{Eu}^{2+}$ with ~ 397 nm emitting InGaN-based chips.

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Keywords: $\text{LiSrPO}_4:\text{Eu}^{2+}$; Photoluminescence; Blue emission; Concentration quenching; White LEDs

1. Introduction

White light-emitting diodes (LEDs) can offer benefits in terms of high luminous efficiency, energy-saving, maintenance and environmental protection, therefore, they are called the next-generation solid-state light, the replacement of conventional incandescent and fluorescent lamps. Recently, remarkable progress has been made in the development of white LEDs using InGaN chip whose emission bands shift to near-UV range around 400 nm [1–4]. Because UV LED can offer a higher efficient solid-state light [5], more and more attention has been paid to the development of new phosphors, that can be excited in the range of near-UV (370–420 nm) due to the necessity to increase the efficiency of white light emitting solid-state devices [6]. The current phosphor materials for solid-state lighting based on near-UV InGaN-based LEDs are $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$ for blue, $\text{ZnS}:\text{Cu}^+, \text{Al}^{3+}$ for green, and $\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{3+}$ for red [7]. However, there exist a poor

blue emission and the low luminous efficiency in this system due to the suddenly decreasing of excitation intensity of $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$ around 400 nm and the strong re-absorption of the blue light by the red and green phosphors. Therefore, it is necessary to find new blue phosphors that can be effectively excited in the UV range about 400 nm to enhance the luminous efficiency.

To find novel efficient blue-emitting phosphors applied in near-UV LED, LiSrPO_4 was chosen as the host for Eu^{2+} ions doping in this paper in terms of the following consideration. Firstly, the compounds $AB\text{PO}_4$ ($A = \text{Li}^+, \text{Na}^+, \text{K}^+, \text{Rb}^+, \text{Cs}^+$; $B = \text{Sr}^{2+}, \text{Ba}^{2+}$) show excellent thermal and hydrolytic stability and were considered to be efficient luminescent hosts [8–15]. However, to the best of our knowledge, there is no report on the research of $\text{LiSrPO}_4:\text{Eu}^{2+}$ for potential application as a blue phosphor. Then, it is well known that Eu^{2+} exhibits strong broad absorption crossing over 400 nm due to the $5d-4f$ transition in many lattices [16–19], which crosses over the emission wavelength (400 nm) of near-UV InGaN-based LED. Finally, doping Eu^{2+} into different compounds can shift the spectral location of the absorption and emission bands. Hence, it is possible to obtain a blue phosphor with

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broadband absorption around 400 nm that can be efficiently excited with near-UV LED. Eu^{2+} -doped LiSrPO_4 was prepared by the solid-state reaction, and blue LEDs were fabricated by the combination of near-UV InGaN-based LEDs with this phosphor.

2. Experimental

2.1. Sample preparation

A series of samples, $\text{LiSr}_{1-x}\text{PO}_4:\text{Eu}^{2+}_x$ ($x = 0.01, 0.03, 0.05, 0.07, 0.09, 0.12$), were prepared by conventional solid-state reaction technique at 1300°C in a weak reductive atmosphere of active carbon. The starting materials, SrCO_3 (analytical grade), Li_2CO_3 (analytical grade), $(\text{NH}_4)_2\text{HPO}_4$ (analytical grade), and Eu_2O_3 (99.99%), were preheated at 120°C and then taken in an agate mortar in stoichiometric molar ratio. After a fully grinding, the reagents were put into corundum crucibles, respectively, and burned in an electric furnace at 1300°C for 3 h. Finally, the samples were gained by a fully grinding in an agate mortar after cooling to room temperature naturally.

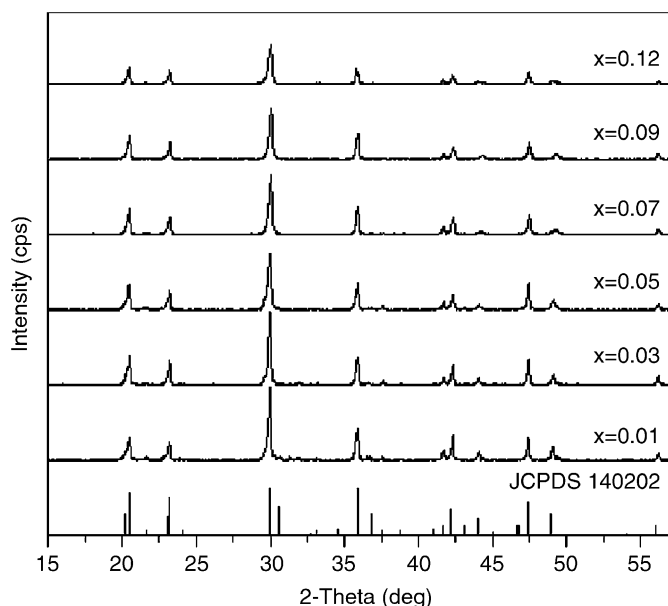


Fig. 1. XRD patterns of $\text{LiSr}_{1-x}\text{PO}_4:\text{Eu}^{2+}_x$ ($x = 0.01, 0.03, 0.05, 0.07, 0.09, 0.12$).

Table 1

The calculated lattice parameters of $\text{LiSr}_{1-x}\text{PO}_4:\text{Eu}^{2+}_x$

x	0	0.01	0.03	0.05	0.07	0.09	0.12
a (Å)	5.004	4.992	4.996	4.994	4.996	4.994	4.993
b (Å)	5.004	4.997	5.004	5.009	5.003	4.995	4.997
c (Å)	8.208	8.219	8.215	8.199	8.162	8.154	8.153
V (Å ³)	178	178	178	178	177	176	176

2.2. Measurements

X-ray diffraction (XRD) studies were carried out on an X-ray diffractometer ($D/\text{max-III}$ A diffractometer, RIGAKU Corporation of Japan. 40 kV and 20 mA, $\text{CuK}\alpha = 1.5406 \text{ \AA}$, Rigaku/ $D\text{max-III}$ A) for crystal phase identification. The XRD patterns were recorded in the range of $15^\circ < 2\theta < 57^\circ$. The excitation and emission spectra of the phosphors were measured at room temperature on a Fluorolog-3-21 spectrometer (JOBIN YVON, America) and a 450 W xenon lamp was used as the excitation source.

3. Results and discussion

The XRD patterns of our samples, $\text{LiSr}_{1-x}\text{PO}_4:\text{Eu}^{2+}_x$ ($x = 0.01-0.12$), are shown in Fig. 1, which indicated that doped Eu^{2+} ions have no obvious influence on the structure of the host and all the peaks can be indexed to the phases of LiSrPO_4 (JCPDS 14-0202) except for little shift. The calculated lattice parameters are shown in Table 1. From the XRD data, we can determine that LiSrPO_4 is hexagonal: $a = b = 5.004 \text{ \AA}$, $c = 8.208 \text{ \AA}$; $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$ when there is no Eu^{2+} doped in this host, which is consistent with the result reported by Stucky et al. [13]. But this structure can only accept trace amount of Eu^{2+} ($< 1\%$). Higher substitution of Eu^{2+} will slightly distort the hexagonal structure and result in the monoclinic structure due to the smaller ionic radius of Eu^{2+} (0.112 nm) than that of Sr^{2+} (0.114 nm) [20].

Fig. 2 is the photoluminescence spectra of the obtained $\text{LiSr}_{0.95}\text{PO}_4:\text{Eu}^{2+}_{0.05}$ phosphor. A broad excitation band ranged 250–440 nm appears (Fig. 2a), which means this phosphor can be well excited by the near-UV about 400 nm. Since the host LiSrPO_4 hardly shows any absorption between 250 and 440 nm, the excitation band is originated from the $4f-5d$ transition of the doped Eu^{2+} ions. There are no observed differences for the emission band shape and position under different excitation wavelengths ($\lambda_{\text{ex}} = 304, 356, 396 \text{ nm}$) except for luminescent intensity and the emission spectrum was symmetric, which implies that Eu^{2+} ions just occupy one kind site in the LiSrPO_4 lattice and give rise to a single emission center. The emission spectrum peaked at 450 nm with the full-width half-maximum (FWHM) of 43 nm is attributed to the $4f^65d^1-4f^7$ transition of the Eu^{2+} ion.

The effect of doped-Eu concentration on the emission of $\text{LiSrPO}_4:\text{Eu}^{2+}$ phosphors was also investigated. The emission spectra of $\text{LiSrPO}_4:\text{Eu}^{2+}$ phosphors prepared at

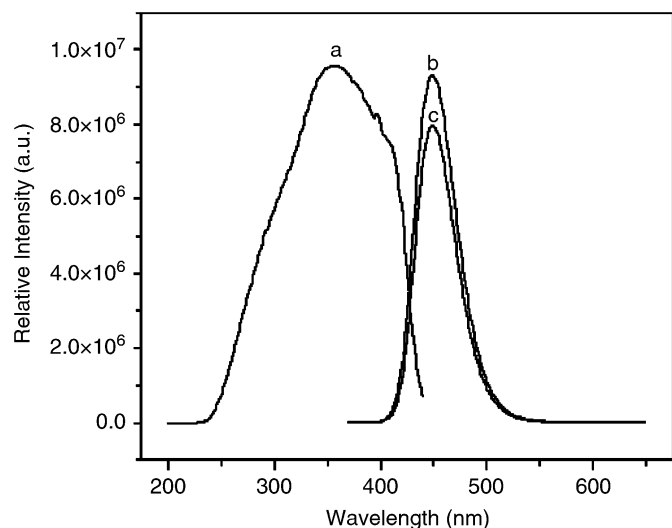


Fig. 2. PL spectra of $\text{LiSr}_{0.95}\text{PO}_4:\text{Eu}_{0.05}^{2+}$: (a) excitation spectrum ($\lambda_{\text{em}} = 450 \text{ nm}$), (b,c) emission spectra ($\lambda_{\text{ex}} = 356 \text{ nm}$, 396 nm , respectively).

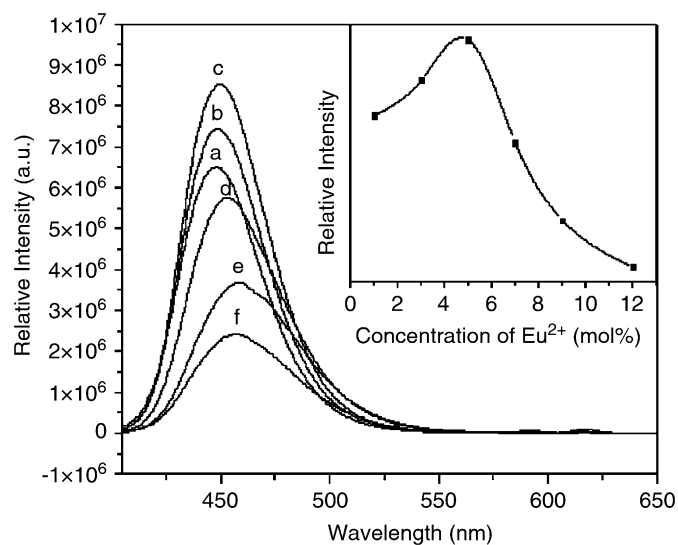


Fig. 3. The emission spectra of $\text{LiSr}_{1-x}\text{PO}_4:\text{Eu}^{2+}_x$ with varying Eu^{2+} concentrations (a: $x = 0.01$, b: $x = 0.03$, c: $x = 0.05$, d: $x = 0.07$, e: $x = 0.09$, f: $x = 0.12$) ($\lambda_{\text{ex}} = 396 \text{ nm}$).

various concentrations of Eu ($x = 0.01$ – 0.12) excited by 396 nm light and the dependence of PL intensity of $\text{LiSr}_{1-x}\text{PO}_4:\text{Eu}^{2+}_x$ on doped-Eu concentration are shown in Fig. 3. The PL intensity increases with Eu-concentration increasing until a maximum intensity is reached, and then it decreases due to concentration quenching. The critical quenching concentration of Eu (χ_c) is defined as the concentration at which the emission intensity begins to decrease and the critical distance is defined as the average distance between the nearest Eu ions in which energy transfer occurs. From Fig. 3, we can see that χ_c of Eu in $\text{LiSrPO}_4:\text{Eu}^{2+}$ phosphors is about 5 mol\% . No emission peaks of Eu^{3+} are observed in the spectra when the doped-

Eu concentration is less than 7 mol\% , which proves that Eu^{3+} ions in the matrix crystals have been reduced to Eu^{2+} completely. However, when the doped-Eu concentration is more than 7 mol\% , weak Eu^{3+} peaks at 592 nm (${}^5D_0 \rightarrow {}^7F_1$) and 617 nm (${}^5D_0 \rightarrow {}^7F_2$) appear, revealing that there is a trace of Eu^{3+} remains in the host and Eu^{3+} ions cannot be reduced to Eu^{2+} completely at high doped-Eu concentration. In addition, as illustrated in Fig. 3, the emission peak of the phosphors shifts to longer wavelength with Eu-content increasing. This type of luminescence behavior may be due to some changes in the crystal field around Eu^{2+} which results from the slight distortion of the crystal structure.

While discussing the mechanism of energy transfer in phosphors, Blasse [21] has pointed out that if the activator is introduced solely on Z ion sites, then there is on the average one activator ion per $V/\chi_c N$, where χ_c is the critical concentration, N is the number of Z ions in the unit cell, and V is the volume of the unit cell. The critical transfer distance (R_c) is approximately equal to twice the radius of a sphere with this volume:

$$R_c \approx 2 \left(\frac{3V}{4\pi\chi_c N} \right)^{1/3}. \quad (1)$$

By taking the appropriate values of V, N and χ_c , the critical transfer distance of center Eu^{2+} in $\text{LiSrPO}_4:\text{Eu}^{2+}$ phosphor is found to be 15.04 \AA .

Non-radiative energy transfer between different Eu^{2+} ions may occur by exchange interaction, radiation re-absorption, or multipole–multipole interaction. Generally speaking, the mechanism of exchange interaction plays the role in energy transfer both when the overlapping of the wave functions of the sensitizer and activator is enough to exchange electronics and when the activator and sensitizer occupy adjacent lattice sites. Eu^{2+} is an isolated emission center in $\text{LiSrPO}_4:\text{Eu}^{2+}$ phosphor and typical critical distance is then about 5 \AA [22], which is far less than that of the sated calculation result of Eu^{2+} -doped in LiSrPO_4 . This indicates that the mechanism of exchange interaction plays little role in energy transfer between Eu^{2+} ions in $\text{LiSrPO}_4:\text{Eu}^{2+}$ phosphor. The mechanism of radiation re-absorption comes into effect only when there is a broad overlap of the fluorescent spectra of the sensitizer and activator, and in view of the emission and excitation spectra of $\text{LiSrPO}_4:\text{Eu}^{2+}$ phosphor is unlikely to be occurring in this case. Because the fluorescent mechanism of Eu^{2+} in $\text{LiSrPO}_4:\text{Eu}^{2+}$ phosphor is the $5d$ – $4f$ allowed electric-dipole transition, the process of energy transfer should be controlled by electric multipole–multipole interaction according to Dexter's theory [22]. If the energy transfer occurs between the same sorts of activators, the intensity of multipolar interaction can be determined from the change of the emission intensity from the emitting level, which has the multipolar interaction. The emission intensity (I) per activator ion follows the equation [23–25]:

$$I/\chi = K[1 + \beta(\chi)^{Q/3}]^{-1}, \quad (2)$$

where x is the activator concentration; $Q = 6, 8$ or 10 for dipole–dipole, dipole–quadrupole or quadrupole–quadrupole interaction, respectively; and K and β are constants for the same excitation condition for a given host crystal.

Since the critical concentration of Eu^{2+} has been determined as 5 mol%, the dependence of the emission intensity of the $\text{LiSrPO}_4:\text{Eu}^{2+}$ phosphor excited at 396 nm on the doped- Eu^{2+} concentration which is not less than the critical concentration (5 mol%) is determined (see Fig. 4). It can be seen from Fig. 4 that the dependence of $\log(I/\chi_{\text{Eu}^{2+}}^2)$ on $\log(\chi_{\text{Eu}^{2+}})$ is linear and the slope is -2.59 . The value of Q can be calculated as 7.77, which is approximately equal to 8, by using Eq. (2). This indicates that the dipole–quadrupole interaction is the major mechanism for concentration quenching of the central Eu^{2+} emission in $\text{LiSrPO}_4:\text{Eu}^{2+}$.

Additionally, the emission spectra of the present synthesized $\text{LiSrPO}_4:\text{Eu}^{2+}$ phosphor and commercial BAM ($\text{BaMgAl}_{11}\text{O}_{17}:\text{Eu}^{2+}$) blue-emitting phosphor have been presented in Fig. 5 for comparison. As expected, the present synthesized phosphor exhibits stronger relative emission intensity than that of BAM upon 396 nm UV light excitation.

In order to investigate the luminescent properties of our phosphor in UV LED, a blue LED was fabricated by combination of a near-UV InGaN chip and the prepared $\text{LiSrPO}_4:\text{Eu}^{2+}$ phosphor. The emission spectrum is shown in Fig. 6. A broad emitting band peaked at 450 nm appears excited by the near-UV InGaN chip while the 397 nm emitting peak from the chip itself partly remains. Bright blue light from the LED is observed by naked eyes and its CIE chromaticity coordinates are calculated as $(x = 0.160, y = 0.062)$, which are close to the NTSC standard values for blue $(x = 0.150, y = 0.060)$. It is advantageous to obtain a white LED by combining this phosphor with

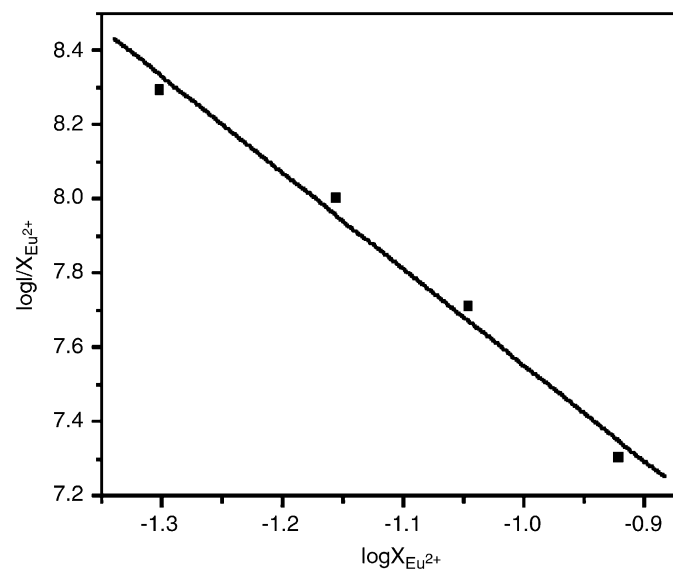


Fig. 4. The curve of $\log I/\chi_{\text{Eu}^{2+}}^2$ vs. $\log \chi_{\text{Eu}^{2+}}$ in $\text{LiSr}_{1-x}\text{PO}_4:\text{Eu}^{2+}_x$ phosphor ($\lambda_{\text{ex}} = 396$ nm).

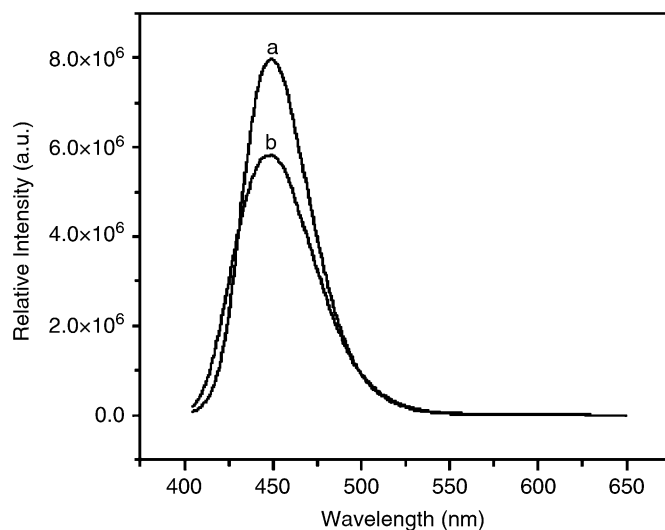


Fig. 5. The emission spectra of the present synthesized $\text{LiSrPO}_4:\text{Eu}^{2+}$ phosphor (a) and the commercial BAM phosphor (b) ($\lambda_{\text{ex}} = 396$ nm).

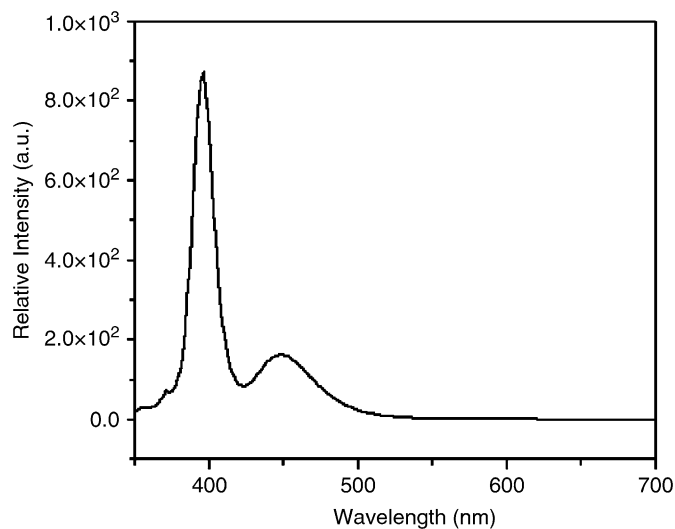


Fig. 6. The EL spectrum of the blue LED-based $\text{LiSrPO}_4:\text{Eu}^{2+}$.

appropriate green and red phosphors. In views of application, each proper mono-color LED phosphor must meet the following necessary conditions. Firstly, the phosphor must efficiently absorb the ~ 400 nm excitation light emitted from the InGaN chip. Then the phosphor exhibits higher luminescent intensity under ~ 400 nm light excitation. Finally, the chromaticity coordinates of the phosphor are close to the NTSC standard values. Since $\text{LiSrPO}_4:\text{Eu}^{2+}$ meets all these conditions, it is considered to be a potential candidate for the blue component of a three-band white LED.

4. Conclusions

A novel blue-emitting phosphor of $\text{LiSrPO}_4:\text{Eu}^{2+}$ was prepared by conventional solid-state reaction at 1300°C in CO atmosphere. The photoluminescence spectra show that

this phosphor can be excited efficiently by UV-visible light from 250 to 440 nm and emits intensely blue light with broadband peaked at about 450 nm. Based on the experimental results and the theoretical calculation, it is identified that the dipole–quadrupole interaction plays the major role in the mechanism of concentration quenching of Eu^{2+} in $\text{LiSrPO}_4:\text{Eu}^{2+}$ phosphor. A blue light-emitting LED was fabricated by combination of a near-UV InGaN chip and the prepared $\text{LiSrPO}_4:\text{Eu}^{2+}$ phosphor. Compared with the commercial blue-emitting phosphor BAM, the present synthesized phosphor has higher emission intensity.

Acknowledgments

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