

Sensitization of Sn^{2+} on Tb^{3+} luminescence for deep UV excitation in phosphate glasses

Lei Li (李磊), Yang Wang (王洋), Duojin Wang (王多金), Jian Qi (齐健), Fanshu Xia (夏凡舒), Huidan Zeng (曾惠丹), and Guorong Chen (陈国荣)*

Key Laboratory for Ultrafine Materials of Ministry of Education, School of Materials Science and Engineering, East China University of Science and Technology, Shanghai 200237, China

*Corresponding author: grchen@ecust.edu.cn

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Tb^{3+} and Sn^{2+} co-doped strontium phosphate glasses are prepared and their unique photoluminescence (PL) properties for deep UV excitation are investigated. With the co-doped Sn^{2+} ions, Tb^{3+} keeps the original PL behaviors under near UV excitation while its PL action for deep UV excitation is enhanced tremendously. PL emission and excitation spectra demonstrate the sensitization role of Sn^{2+} on the Tb^{3+} emissions for deep UV excitation that is associated with the strong deep UV absorption of Sn^{2+} for greatly enhancing the resonance of the Tb^{3+} excitation with the deep UV light source. The decay curves of Sn^{2+} and Tb^{3+} emissions for both singly doped and co-doped samples are single exponentially well fitted with almost the same emission lifetime (τ) values in the microsecond and millisecond time regimes, respectively, confirming that Sn^{2+} and Tb^{3+} act as an independent activator in the present phosphate glass matrix while an involved energy transfer from Sn^{2+} to Tb^{3+} is radiative. Moreover, Sn^{2+} and Tb^{3+} can be co-excited with deep UV light to emit tunable light from blue to green with the definite CIE chromaticity coordinate for different applications.

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The photoluminescence (PL) spectrum of Tb^{3+} ions is known as being composed of several narrow lines, as is usual for many other trivalent rare-earth (RE) ions due to the well-shielded 4f-4f shell transitions^[1-3]. The most intense emission of Tb^{3+} is at about 542 nm, which corresponds to a transition from the lowest excited state ($^5\text{D}_4$) to the ground state ($^7\text{F}_5$) above the lowest ground state level $^7\text{F}_6$ ^[1,4]. On the other hand, the absorption of Tb^{3+} in the deep UV region is relatively weak compared with the near-UV lines^[5]. In fact, investigations on luminescent materials to be coupled with the deep UV LED chip have great potential because of the rapid development of group III nitride-based UV diodes^[6]. To achieve an enhanced luminescence action with Tb^{3+} for deep UV excitation, it might be of use in an experimental effort by introducing so-called sensitizer ions, which have a strong absorption in this region^[5]. There has been quite a lot of work in this respect about terbium sensitization by doping other REs in inorganic solids. For example, an enhanced energy transfer (ET) mechanism from cerium (Ce^{3+}), gadolinium (Gd^{3+}), or dysprosium (Dy^{3+}) to terbium (Tb^{3+}) has been established in a variety of phosphors or glasses^[7,8]. Meanwhile, sensitization of Tb^{3+} luminescence has also been successfully tried by co-doping ions other than REs in different hosts, such as recently reported work on Cu^+ in borosilicate glass^[9].

In this Letter, we wish to report the experimental observations where Tb^{3+} luminescence for the deep UV excitation is sensitized by co-doping non-RE Sn^{2+} ions in phosphate glasses. As the host in the present work, the phosphate glass possesses the advantage of higher solubility for Tb^{3+} ions, for example, up to 10 mol.%

Tb^{3+} doping without causing concentration quenching of emission^[5], and the wide transmission range from the deep UV to the near-IR region. As a sensitizer, Sn^{2+} exhibits a wide and strong absorption band in the deep UV region due to $\text{S}_0 \rightarrow \text{S}_1$ transitions^[10]. Since the energy level S_1 of Sn^{2+} is energetically close to the higher excited state of Tb^{3+} ($4\text{f}^8 \rightarrow 4\text{f}^75\text{d}^1$), it is especially expected that the resonance of the Tb^{3+} excitation with the deep UV light source could be greatly enhanced via Sn^{2+} ions co-doping. Besides possibly playing a sensitization role for Tb^{3+} luminescence under the deep UV excitation, the Sn^{2+} ion also acts as a co-activator by absorbing UV energy to emit in the blue to green light region^[10]. Thus, emissions from Sn^{2+} and Tb^{3+} ions could be adjusted easily by changing the $\text{Sn}^{2+}/\text{Tb}^{3+}$ concentration ratio to obtain the required composite light with the specific CIE chromaticity coordinates for different applications.

The nominal composition of the host glass used for the present work is $30\text{SrO}-70\text{P}_2\text{O}_5$ ^[10], while dopants (Tb^{3+} , Sn^{2+}) are introduced in two groups with the concentrations (mol. %) given in Table 1. Samples in the first group contain the varied Sn^{2+} concentration from 0 to 2.0

Table 1. Extra Tb, SnO Doping Concentrations (mol.%)

Samples	G1	G2	G3	G4	G5	G6	G7	G8	G9	G10
Tb^{3+}	0.2	0.0	0.2	0.2	0.2	0.2	0.4	0.6	0.8	0.8
Sn^{2+}	0.0	2.0	2.0	1.5	1.0	0.5	2.0	2.0	2.0	1.0

(G1, G3-G6) while fixing the Tb^{3+} concentration constant at 0.2, whereas those in the second group keep the same concentration of Sn^{2+} at 2.0 but increased the Tb^{3+} from 0 to 0.8 (G2, G6-G9). The sample G10 was additionally prepared in order to demonstrate the effect of the varied Tb^{3+}/Sn^{2+} concentration ratio on the CIE chromaticity coordinates of emission.

Glass samples were prepared using the melt-quenching method. The starting materials are chemical purity compounds including $NH_4H_2PO_4$, $SrCO_3$, and SnO , as well as elemental Tb . The as-prepared glass batches according to Table 1 were mixed thoroughly and uniformly, and then poured into Al_2O_3 crucibles for melting in an electric furnace at $1250^\circ C$ for 2–3 h. The melts were quenched in air, and all as-prepared glasses were then annealed at $450^\circ C$ for 2–3 h and finally cut into rectangular shapes with 2 mm thickness and polished to mirror smoothness and ready for optical measurements.

All glass samples are transparent in the UV and visible regions as characterized by their absorption spectra (omitted herein). PL emission and excitation spectra were collected by a high-resolution spectrofluorometer (Fluorolog-3, Horiba Jobin Yvon Inc., Edison, NJ) using a 450 W Xe lamp as the excitation source. The PL decay lifetime was measured by FLSP920 (Edinburgh Instruments, Livingston, UK) using an nF900 μs pulsed Xe lamp as the source with a pulse width of 2–3 μs . All measurements were carried out at room temperature.

Figure 1 presents PL excitation (PLE) spectra of Tb^{3+} , Sn^{2+} singly doped (G1, G2) and co-doped (G3) samples for emissions of Tb^{3+} and/or Sn^{2+} ions. As shown in Fig. 1(a), several narrow excitation lines are observed in G1 for the Tb^{3+} 542 nm emission, with corresponding energy levels given in the figure for clear illustrations of the electronic transition characters of Tb^{3+} ions [1,4,5,11]. For the Sn^{2+} 421 nm emission in G2, a broad and strong excitation band appears in the deep UV region peaking at around 270 nm due to the $S_0 \rightarrow S_1$ transition of Sn^{2+} , which agrees well with the results of the previous work [10]. For the case of G3, by monitoring the Tb^{3+} emission at 542 nm where

Sn^{2+} has a small but sizable emission, there remain the narrow excitation lines of Tb^{3+} . However, the intensity ratio of the deep UV to the near-UV excitation increases obviously due to the superimposed excitation of Sn^{2+} and Tb^{3+} in this region. PLE spectra are monitored at 488 nm where Sn^{2+} and Tb^{3+} emissions are more largely overlapped. It is interesting to note from Fig. 1(b) that, relative to G1, G3 shows a tremendously enhanced deep UV excitation peaking at 270 and 282 nm, respectively. In particular, the 270 nm excitation band well resembles that for the Sn^{2+} emission of G2 in shape, implying convincingly the role of Sn^{2+} as a sensitizer for enhancing the deep UV excitation of Tb^{3+} in the present phosphate glass.

For characterizing PL spectra of samples G1-G3, we choose 375 and 282 nm as the near and deep UV excitation sources, respectively, where 282 nm (instead of 270 nm) was used for the purpose of avoiding frequency doubling in the Tb^{3+} main emission region (542 nm). It follows from Fig. 2(a) that with $\lambda_{exc} = 375$ nm G2 is not excited, while G1 and G3 show the same PL spectra characteristic for Tb^{3+} electronic transition behaviors [11,12]. This demonstrates that Sn^{2+} co-doping exerts no negative effect on Tb^{3+} emissions for near-UV excitation. On the other hand, with $\lambda_{exc} = 282$ nm [Fig. 2(b)], Tb^{3+} emission bands in G3 are all superimposed onto the Sn^{2+} emission band. To identify variations of the Tb^{3+} emission intensity between G3 and G1, GAUSSIAN fitting was made on the PL spectrum of G3, and the fitted curve after subtracting the Sn^{2+} emission is shown in the inset of Fig. 2(b) where the PL spectrum of G1 is presented for comparison. It is clear that, relative to G1, the Tb^{3+} emission intensity of G3 increases in general, especially at 542 nm, evidencing the role of Sn^{2+} as a sensitizer for Tb^{3+} emission under deep UV excitation. To describe the possible ET process from Sn^{2+} to Tb^{3+} , the simplified diagrams of energy levels for Tb^{3+} and Sn^{2+} are jointly presented in Fig. 2(c). It is seen that there most likely exists an ET channel to Tb^{3+} from Sn^{2+} due to the quasi-resonance in energy of the $Sn^{2+}:T_1$ level with the Tb^{3+} center: 5D_4 level. That is, an excitation of Sn^{2+} ions from the ground state S_0 to the excited state S_1

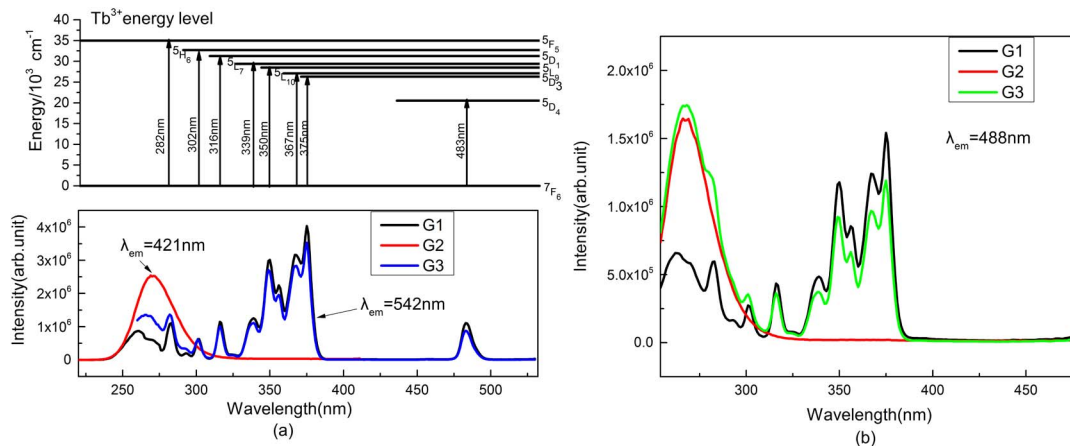


Fig. 1. PLE spectra of G1-G3 monitored, respectively, at (a) 421/542 nm and at (b) 488 nm.

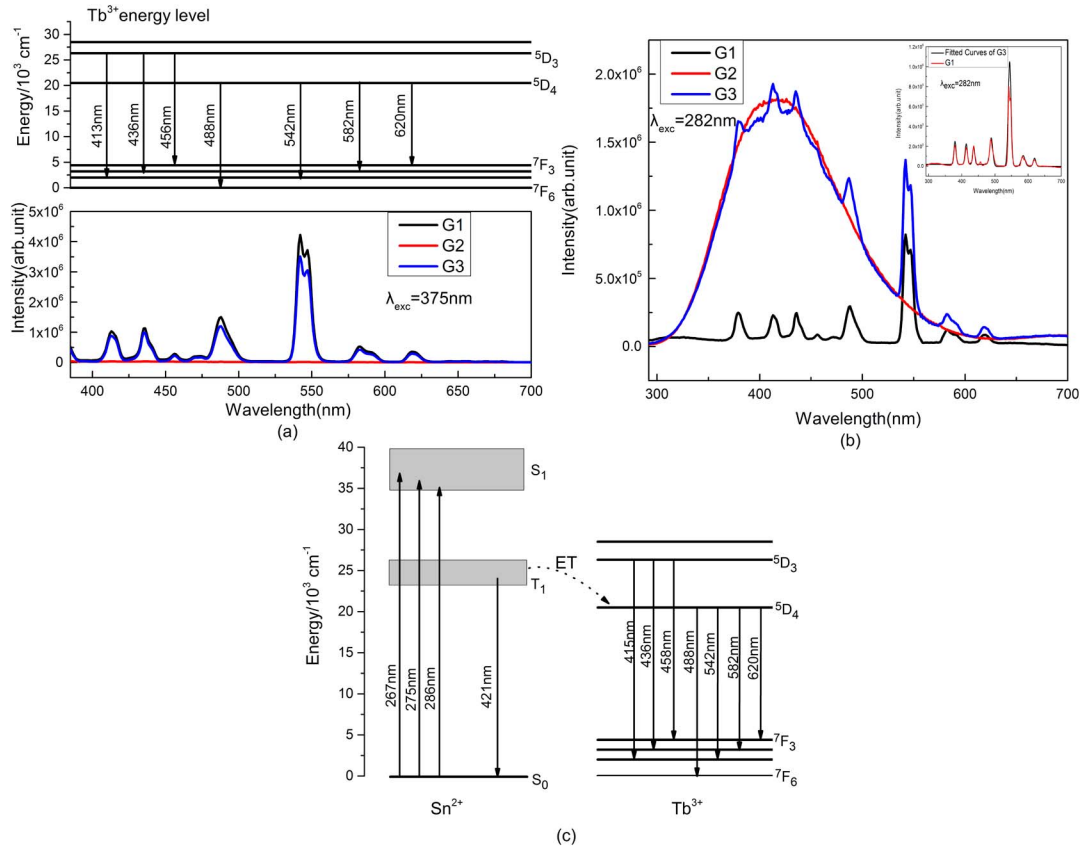


Fig. 2. (a, b) PL spectra and (c) simplified energy level diagrams of Sn^{2+} and Tb^{3+} .

produces the emission of Sn^{2+} ions at 421 nm. It then results in population of Tb^{3+} excited state $5D_4$ from the ground state $7F_6$ due to cross relaxation, yielding the enhanced emission at 602 nm.

It is also observed from Fig. 2(b) that the broad Sn^{2+} emission appearing in G3 is almost the same as that in G2, suggesting that the depression of the entire emission spectrum of the sensitizer did not occur. It thus means that the radiative ET from Sn^{2+} to Tb^{3+} is involved under the deep UV excitation of the present $\text{Tb}^{3+}/\text{Sn}^{2+}$

co-doped phosphate glass^[5]. To confirm this conclusion, the decay rate of the Sn^{2+} emission in G3 was measured and the result is compared with that of G2 in Fig. 3(a). It is seen from Fig. 3 that the PL decay curves of both G2 and G3 for the Sn^{2+} emission are single exponentially fitted well, indicating that Sn^{2+} also acts as an independent activator for blue emission. The Sn^{2+} emission lifetime (τ) is calculated from the fitting equation $I = A \exp(-t/\tau)$, where I is the luminescence intensity, A is the constant, and t is the time, and the result does not show an obvious

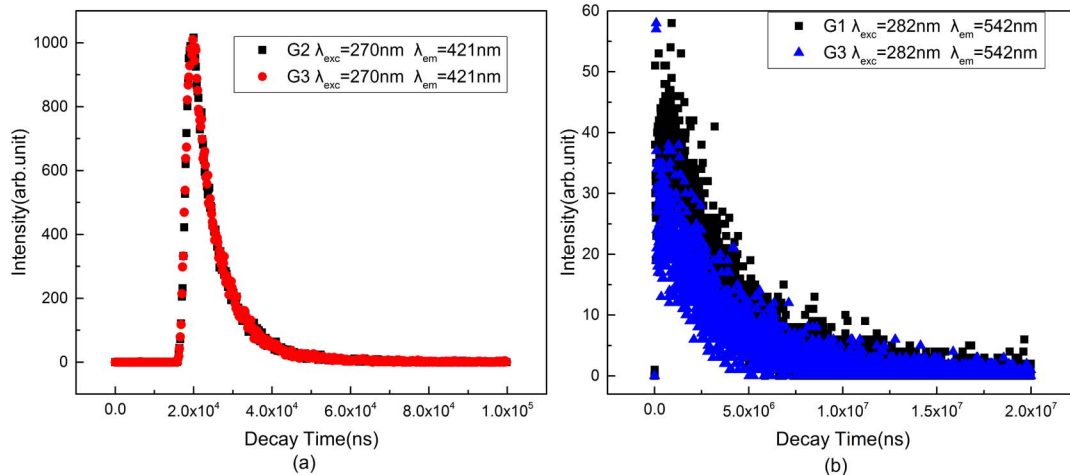


Fig. 3. Decay curves of G1-G3.

Table 2. Equivalent Decay Times of Sn^{2+} (421 nm) and Tb^{3+} (542 nm) Emissions for Samples G1-G9

Sample Code	PL Decay Rate Measurements		
	λ_{exc} (nm)	λ_{em} (nm)	τ
G1	375	542	2.89 ms
	282		2.88 ms
G2	270	421	6.34 μs
G3	375	542	2.99 ms
	2823		2.94 ms
	270	421	6.32 μs
G4	282	542	3.05 ms
G5			2.96 ms
G6			3.01 ms
G7	270	421	6.32 μs
G8			6.39 μs
G9			6.33 μs

difference in the τ value between G3 (6.32 μs) and G2 (6.34 μs), supporting the suggested radiative transfer mechanism.

To verify the origin of the sensitized green emission in G3, the decay curves for the 542 nm emission were measured on G1 and G3 as well, and the results are compared in Fig. 3(b). Similar to Fig. 3(a), the green emission decay curves of G1 and G3 follow a single exponential decay function, with the emission lifetime calculated, respectively, as 2.88 ms (G1) and 2.94 ms (G3). This is typical for the forbidden f-f transitions of Tb^{3+} , which is clearly reminiscent of the green emission in G3 originating independently from Tb^{3+} , although sensitized by Sn^{2+} . The PL lifetimes of all samples are summarized in Table 2, where τ values of the green (542 nm) and blue (421 nm) emissions in singly doped (G1-G2) and co-doped (G3-G9) samples are all reasonably fluctuated in the millisecond (ms) and microsecond (μs) time regimes, respectively, identical to the foregoing discussions.

Figure 4(a) presents additional PL spectra of samples G4-G6 for the 282 nm excitation where the Tb^{3+} emission at 542 nm is enhanced regularly with increased Sn^{2+} doping. It demonstrates consistently the close tie of the Tb^{3+} emission with the presence of Sn^{2+} . Meanwhile, the intensity ratio of green to blue emissions increases gradually with the decreased Sn^{2+} , or, on the other hand, with the increased Tb^{3+} [Fig. 4(b)]. As examples, PL spectra of several typical samples (G1-G3, G9-G10) are characterized by the CIE chromaticity diagram in Fig. 4(c) together

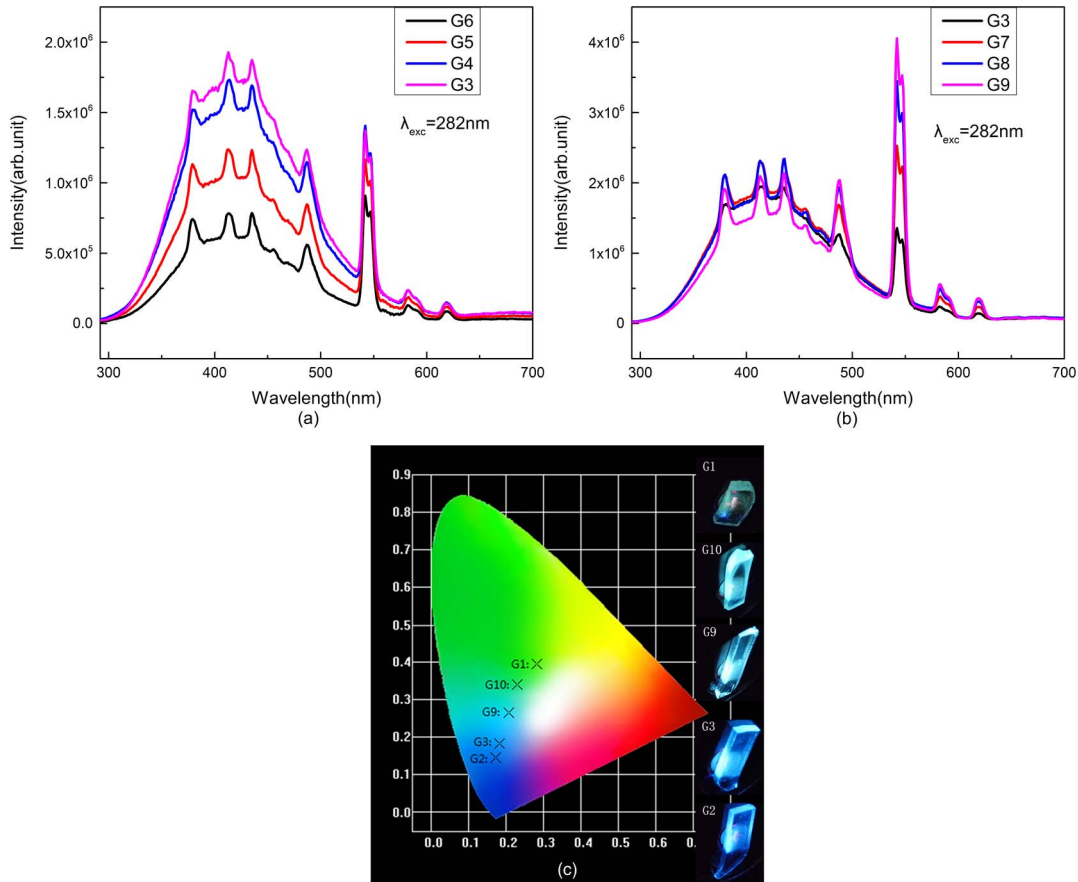


Fig. 4. PL spectra of (a) G3-G6 and (b) G3, G7-G9, and (c) a CIE chromaticity diagram for G1-G3 and G9-G10 together with photos of luminescent samples.

Table 3. CIE Chromaticity Coordinates of Emissions for Samples G1-G10

Sample Codes	CIE Chromaticity Coordinates	
	λ_{exc} (nm)	Coordinates
G1	375, 282	(0.261,0.443), (0.283, 0.395)
G2	270, 282	(0.180,0.173), (0.172, 0.144)
G3	282	(0.183, 0.182)
G4	282	(0.187, 0.191)
G5	282	(0.191, 0.202)
G6	282	(0.196, 0.217)
G7	282	(0.192, 0.215)
G8	282	(0.200, 0.241)
G9	282	(0.207, 0.265)
G10	282	(0.230, 0.339)

with the luminescent photos of the samples. CIE chromaticity coordinates of emissions for all samples are given in Table 3. It is seen that PL spectra can be tuned from blue to green by adjusting the $\text{Tb}^{3+}/\text{Sn}^{2+}$ concentration ratio, thus achieving the tunable composite emission with different chromaticity coordinates of emission for the deep UV excitation.

Benefited energy harvest of Tb^{3+} ions under deep UV excitation is realized by co-doping Sn^{2+} ions in Tb^{3+} doped 30 SrO -70 P_2O_5 phosphate glass. PL, PLE, and decay lifetime data consistently present evidence of terbium sensitization in the presence of Sn^{2+} ions via the radiative ET from Sn^{2+} to Tb^{3+} . The mechanism involved is associated with the strong deep UV absorption of Sn^{2+} , which greatly enhances the resonance of the Tb^{3+} excitation with the deep UV light source. The tunable luminescence

from blue to green is achieved in the co-doped phosphate glass by adjusting the $\text{Tb}^{3+}/\text{Sn}^{2+}$ concentration ratio. Our work indicates potential applications of $\text{Tb}^{3+}/\text{Sn}^{2+}$ co-doped phosphate glasses as converting phosphors pumped by deep and near-UV LED chips.

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