



Synthesis and luminescence properties of Eu^{3+} - substituted $\text{CsK}_2\text{La}(\text{VO}_4)_2$ a Glaserite-type orthovanadates

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Abstract

A new rare-earth free self-activated and Eu^{3+} activated Glaserite-type orthovanadate phosphor $\text{CsK}_2\text{La}(\text{VO}_4)_2$ was synthesized via the high temperature solid-state reaction route. The powder X-ray diffraction (XRD) reveals that the synthesized compounds crystallize in glaserite structure i.e., monoclinic structure with a space group of $\text{P2}_1/\text{m}$. The self-activated luminescence of the host lattice and europium doped luminescence behaviours have been studied in detail by photoluminescence (PL) excitation and emission spectra. The broad-band green emission was found from the as-prepared $\text{CsK}_2\text{La}(\text{VO}_4)_2$ compound, originating from the VO_4^{3-} emission. Orange-red emission was observed for $x\text{Eu}^{3+}$ doped $\text{CsK}_2\text{La}_{(1-x)}[\text{VO}_4]_2$ compound. The presence of the elements of the synthesized compound is confirmed by FESEM with EDX spectra. The optical studies reveals that the self-activated $\text{CsK}_2\text{La}(\text{VO}_4)_2$ and Eu^{3+} doped phosphors show great potential for the application in the near-UV excited white LEDs.

Keywords: A. Greenish phosphor, B. self-activated phosphor, C. Eu^{3+} luminescence, D. white LEDs

1. INTRODUCTION

In recent years, rare earth luminescent materials have considerable practical applications in various optoelectronic devices involving the artificial production of light such as Field emission displays (FEDs), Plasma display panels (PDPs), Cathode-ray tubes (CRTs), X-ray detectors and tricolour white light emitting diodes (w-LEDs) [1]. Solid state light emitting diodes have attracted much attention for their potential applications and have become interesting field due to their superior properties and excellent characteristics such as high luminescence efficiency, long operation lifetime, greater reliability, toxicity-free, energy-saving, mercury-free and environment friendliness [2].

Recently, vanadate-based phosphors have drawn more attention due to the self-activated emitting properties of $[\text{VO}_4]^{3-}$ group, the sensitization from $[\text{VO}_4]^{3-}$ to rare earth ions as well as their long wavelength excitation, better chromaticity and the excellent chemical stabilities [3].

The vanadate group $[\text{VO}_4]^{3-}$, where the central metal ion V is coordinated by four oxygen ligands in a tetrahedral (Td) symmetry, is known to be an efficient luminescent centre. It has broad and intense charge transfer (CT) absorption bands in the near-UV region. The excitation wavelength matches well with the emission of AlGaIn-based near UV LED chips and some of the vanadates can produce intense broadband CT emission spectra from 400nm to more than 700 nm, related to the local structure. When excited by UV or near UV light, these vanadates or rare earth ions-doped materials have the capability to convert UV or near UV photons into visible light [4].

Among all rare earth ions, Eu^{3+} is renowned as a red-emitting activator in commercial phosphors because of the line like red emission. The emission lines are originated from the $^5\text{D}_0 \rightarrow ^7\text{F}_J$ ($J = 1, 2, 3, 4, 5$ and 6) electronic transitions. Eu^{3+} has a simple electronic energy level and its transitions are hypersensitive transitions [5]. Recently, rare earth activated vanadates, especially Eu^{3+} doped orthovanadate have been investigated intensely, because of their high efficiency, long lifetimes and environment friendly characteristics. For example, Eu^{3+} doped REVO_4 is known as an

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excellent phosphor with bright red emission [6]. Europium doped glaserite type orthovanadates have also been focussed to develop novel red emitting phosphors for the white LEDs e.g., Eu^{3+} doped $\text{Ca}_9\text{La}(\text{VO}_4)_7$ [7], Eu^{3+} activated $\text{Ca}_3\text{La}(\text{VO}_4)_3$ [8], Eu^{3+} doped triple orthovanadates $\text{NaAla}(\text{VO}_4)_2$ ($A = \text{Ca}, \text{Sr}, \text{Ba}$) [9], $\text{Ca}_9\text{Eu}_{1-x}\text{Ln}_x(\text{VO}_4)_7$ ($\text{Ln} = \text{Y}, \text{La}, \text{Gd}, \text{Lu}$) [10]. Recently $\text{CsK}_2\text{Gd}(\text{VO}_4)_2$ doped with Eu^{3+} crystalizing in hexagonal glaserite structure also been explored [11].

The present work is in quest for a new vanadate host for (RE) Eu^{3+} ions. Here we selected $\text{CsK}_2\text{La}(\text{VO}_4)_2$, because to the best of our knowledge, the photoluminescence properties of neither undoped nor doped glaserite orthovanadate have been reported. The prototype of this compound is the sulphate $\text{K}_3\text{Na}(\text{SO}_4)_2$. The host lattice $\text{CsK}_2\text{La}(\text{VO}_4)_2$ has been derived from the general formula $\text{XY}_2[\text{M}(\text{TO}_4)_2]$ in accordance with the specificity and occupancy of the cationic positions of X, Y, M and T as 12, 10, 6 and 4 coordination respectively, with a condition $X \neq Y \neq M \neq T$. It comes under the category of orthovanadates with glaserite (aphthitalite)-like structure [12]. In order to explore the optical properties, we systemically studied the luminescence behaviour of the host lattice and rare earth doped phosphor material has been carried out. This investigation was carried out to study emissions not only from the dopant Eu^{3+} but also from the host $[\text{VO}_4]^{3-}$.

2. EXPERIMENTAL

2.1 Materials

The high-purity (99.99%) oxides and carbonates were used as precursors in the form of a mixture of reagent grade NH_4VO_3 , Cs_2CO_3 , K_2CO_3 , La_2O_3 and Eu_2O_3 .

2.2 Synthesis

The host lattice glaserite orthovanadate $\text{CsK}_2\text{La}(\text{VO}_4)_2$ and Eu^{3+} doped glaserite orthovanadate was synthesized by conventional high temperature solid-state reaction route. The corresponding precursors were weighed

according to the stoichiometric ratio. Each mixture of starting materials was ground for an hour, loaded into a high purity silica crucible, and then sintered using furnace. First, the stoichiometric mixture was slowly heated up to 350°C for a duration of 7 hours and was kept at this temperature for 5 hours. The obtained powder was mixed again and then heated up to 700°C for 5 hours. The sample was then thoroughly mixed and heated again at a temperature of $780 - 800^\circ\text{C}$ for 10 hours and cooled down to room temperature to obtain white powder. The obtained synthesized powder was characterized for its structural and optical properties.

2.3 Characterization Methods

The Phase purity was checked by powder X-ray diffraction (XRD) analysis collected on a X'Pert PRO PANalytical diffractometer (45kV, 30mA) and with Bragg-Brentano geometry using $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). The Photoluminescence - PL and PLE spectra were recorded on a Fluoromax-4 Spectrofluorometer [Horiba Scientific] equipped with a 150 W Xe lamp as the excitation source. The Surface Morphology and Elemental analysis was made with FESEM with EDAX instrument by High Resolution Imaging through CARL ZEISS SUPRA – Oxford Instrument. All the measurements were observed at room temperature. The CIE chromaticity coordinates were calculated using MATLAB software and CIE calculator – a software based system was employed.

3. RESULTS AND DISCUSSIONS

3.1. Phase Formation

The crystallinity of the synthesized phosphor materials was checked by X-ray diffraction (XRD). The XRD pattern of the undoped $\text{CsK}_2\text{La}[\text{VO}_4]_2$ and Eu^{3+} doped phosphor material is shown in figure - 1. The reflections for undoped host lattice and Eu^{3+} doped phosphor materials were identical and all the peaks shown in the graph were indexed well to

the patterns and were in good agreement with the powder diffraction file 2 (PDF 2) card no. 89-6536 [$\text{CsK}_2\text{La}(\text{VO}_4)_2$] in the International Centre for Diffraction Data (ICDD) database. The synthesized compound crystallize in monoclinic structure with space group of $P2_1/m$. The unit cell parameters are $a = 10.094(6) \text{ \AA}$, $b = 5.991(3) \text{ \AA}$, $c = 7.858(6) \text{ \AA}$ and $V = 475.19 \text{ \AA}^3$ and the interfacial angles $\alpha = \gamma = 90^\circ$ and $\beta = 90.76^\circ(8)$.

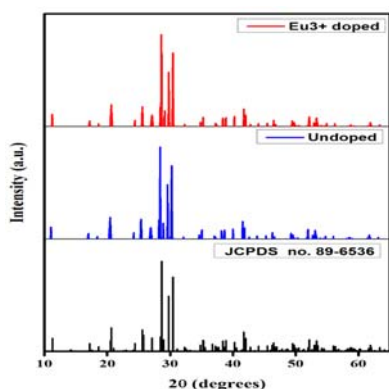


Figure-1. Powder XRD pattern of undoped $\text{CsK}_2\text{La}(\text{VO}_4)_2$ and $x\text{Eu}^{3+}$ doped $\text{CsK}_2\text{La}_{(1-x)}[\text{VO}_4]_2$ (with $x = 0.6$) with PDF standard card no. 89-6536.

No other phase was detected, indicating that the obtained samples are single phase and Eu^{3+} ions have been successfully incorporated in the host lattice by replacing La^{3+} ions due to their similar ionic radii and charge. The radius of Eu^{3+} ion is 0.947 \AA and for La^{3+} ion is 1.032 \AA [13]. Due to this similarity in the ionic radii between these two rare earth ions, even when La^{3+} in the host lattice is replaced by Eu^{3+} , the crystal structure does not change dramatically. Hence, one can conclude that the XRD patterns of undoped and Eu^{3+} doped phosphor material have unique crystal structure.

3.2 ELEMENTAL ANALYSIS

To confirm the presence of elements in the synthesized compound and also to find its weight percentage, EDX was done. The EDX spectrum of the host lattice $\text{CsK}_2\text{La}(\text{VO}_4)_2$ is shown in figure- 2(a).

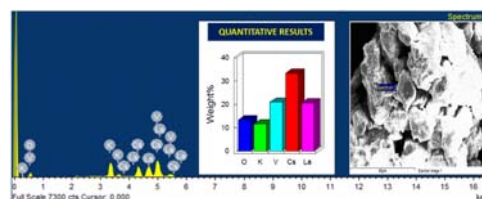


Figure-2 (a) EDX spectra of undoped Glaserite orthovanadate $\text{CsK}_2\text{La}(\text{VO}_4)_2$.

The spectrum and the quantitative results evidently confirmed the existence of the elements like Cs (Cesium), K (Potassium), La (Lanthanum), V (Vanadium) and O (Oxygen) which is an anticipated result. The EDX spectrum of Eu^{3+} doped $\text{CsK}_2\text{La}(\text{VO}_4)_2$ is shown in figure-2(b), from this spectrum the presence of elements due to host Cs (Cesium), K (Potassium), La (Lanthanum), V (Vanadium) and O (Oxygen) and the dopant Eu^{3+} (Europium) was confirmed.

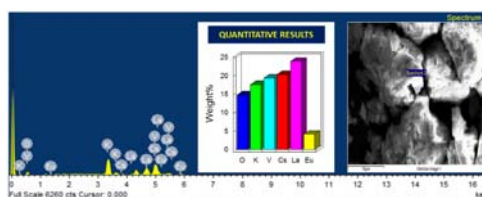


Figure-2 (a) EDX spectra of Eu^{3+} doped $\text{CsK}_2\text{La}_{(1-x)}[\text{VO}_4]_2$ (with $x = 0.6$).

This infers that the dopant Eu^{3+} is successfully incorporated into the host $\text{CsK}_2\text{La}(\text{VO}_4)_2$. The quantitative result reveals a very less weight percentage of Eu^{3+} when compared with other elements in the host material which is highly predictable, since the dopant ratio is very small in comparison with the other elements in the host.

3.3 LUMINESCENCE PROPERTIES

3.3.1 PL of rare earth free self-activated phosphor

The PL and PLE spectra of undoped $\text{CsK}_2\text{La}(\text{VO}_4)_2$ are shown in Figure-3. The undoped sample shows broad excitation spectrum band lying between the range 250 and 400 nm with two peaks at 272 nm ($\text{Ex}_1: {}^1\text{A}_1 \rightarrow {}^1\text{T}_2$) and 361 nm ($\text{Ex}_2: {}^1\text{A}_1 \rightarrow {}^1\text{T}_1$) ascribed to

(CT) charge transfer transitions in $[\text{VO}_4]^{3-}$ group. This shows that the phosphor absorption can perfectly match with emission spectrum of near UV-LED chips (360–400nm), which is essential for improving the efficiency of white LEDs. The nearly same excitation spectrum is in agreement with the conclusion suggested by Ronde et al., [4] that the position of the excitation bands is slightly influenced by the vanadate host.

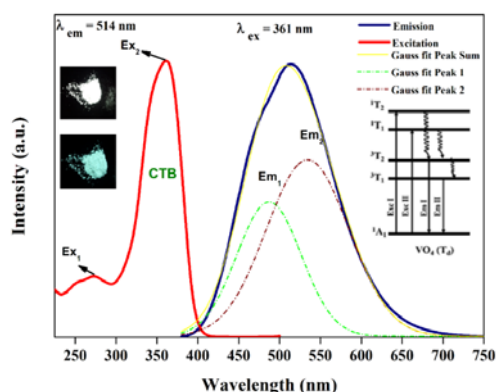


Figure-3. Photoluminescence of undoped $\text{CsK}_2\text{La}(\text{VO}_4)_2$

The luminescence of vanadate host lattice arises from the charge transfer (CT) bands ($2p$ orbital of $\text{O}^{2-} \rightarrow$ orbital of V^{5+}) in ligand–metal localized tetrahedral coordinated $[\text{VO}_4]^{3-}$ groups [14,15]. From the inset figure–3, one can observe that the ground state of VO_4 is 1A_1 and the excited states are 1T_1 , 1T_2 , 3T_1 , and 3T_2 . The electronic transitions from the ground state 1A_1 to 1T_1 , 1T_2 are permitted, but the emission transitions from the excited state 3T_1 , 3T_2 to ground state 1A_1 are forbidden by the spin selection rule in the ideal Tetrahedral symmetry. However, due to the spin-orbit interaction, the spin-forbidden transition is allowed partially. This is because spin-orbit interaction not only rely on the spin and orbital angular momentum but along with the central-field potential and also it is enhanced by the distortion of VO_4 tetrahedron [16]. In addition, due to the presence of the heavy atom effect of VO_4 , which contains the vanadium atom, the luminescence-process transition is allowed by

the spin-orbit interaction. As a result, an intense 514 nm emission is observed (figure–3), which is due to CT emission transition in $[\text{VO}_4]^{3-}$.

The broad emission band of the undoped sample has a peak at 514 nm and extends from 400 to 700 nm. Therefore, taking into consideration that its emission spectrum is similar to the solar spectrum regarding the peak wavelength and broad band in the visible region, this material is useful for lighting when it is pumped with near UV-LED. Besides, the broad band is analysed using Gaussian multi-peaks fitting and the results is shown in the figure-3 as Em_1 and Em_2 . The result shows that the broad emission band can be decomposed into two Gaussian peaks, indicating that the Gauss fit peak 2 is from CT band $\text{O}^{2-} \rightarrow \text{V}^{5+}$ in relatively high intensity than the Gaussian fit peak 1, which is relatively weak intensity. Inset (right) in the figure-3 is the schematic model to display the excitation and emission processes in VO_4 tetrahedron [14]. The molecular orbitals of V^{5+} ion with T_d symmetry are expressed as a ground 1A_1 state and excited 1T_1 , 1T_2 , 3T_1 , and 3T_2 states. The absorption bands for Ex_1 and Ex_2 in the PLE spectra are corresponding to the spin-allowed transitions from the ground state 1A_1 to the excited states 1T_2 and 1T_1 levels, respectively [17].

3.3.2 PL of Eu^{3+} - activated $\text{CsK}_2\text{La}_{(1-x)}(\text{VO}_4)_2$

The Photoluminescence excitation and emission spectra of Eu^{3+} doped $\text{CsK}_2\text{La}_{(1-x)}(\text{VO}_4)_2$: Eu_x ($x=0.6$) is shown in Figure-4. The broad emission, observed in an undoped compound (Figure-4), was also observed in the Eu^{3+} doped compositions and along with some sharp emission lines were also observed in Eu^{3+} doped $\text{CsK}_2\text{La}(\text{VO}_4)_2$. These sharp emission lines ranging from 580 to 700 nm, which are associated to the transitions from the excited 5D_0 state to the Stark components of the 7F_J ($J=0,1,2,3$ and 4) levels in Eu^{3+} . The red emission at 615 nm is an electric dipole transition, while the orange emission range at 593 nm is a

typical magnetic dipole transition. The emission spectra are dominated by the transitions of ${}^5D_0 \rightarrow {}^7F_1$.

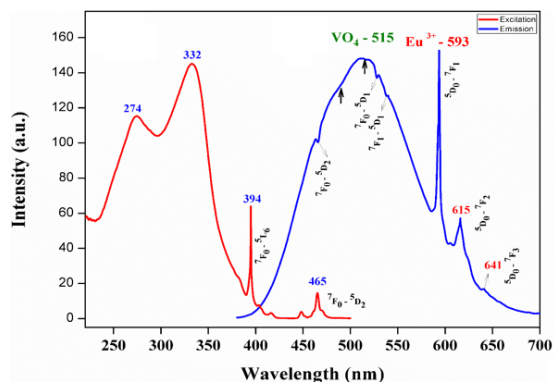


Figure-4. shows Photoluminescence ex. and em spectra of $\text{CsK}_2\text{La}_{1-x}\text{Eu}_x[\text{VO}_4]_2$; ($x=0.6$)

According to the Judd–Ofelt theory, the magnetic dipole transition is permitted. However, the electric dipole transition is allowed only when the europium ion occupies a site without an inversion center and the intensity is significantly affected by the symmetry in local environments around Eu^{3+} ions [18].

If the Eu^{3+} ions occupy an inversion symmetry site, the orange emission (magnetic dipole transition) ${}^5D_0 \rightarrow {}^7F_1$ (at 593 nm) is the dominant electronic transition. On the contrary, the electric dipole transition ${}^5D_0 \rightarrow {}^7F_2$ (at 612 nm) is the dominant one, when the Eu^{3+} occupies in the non-centrosymmetric site in the host lattice [19]. According to these sharp emission lines, it can be concluded that most Eu^{3+} ions have inversion centers and the magnetic dipole transition ${}^5D_0 \rightarrow {}^7F_1$ (at 593 nm) is dominant. In the emission band, there are five tiny dips have been observed, which is due to the presence of $[\text{VO}_4]^{3-}$. In these five tiny dips, three are sharper and two are broader. Due to the self-absorption of the dopant Eu^{3+} ion, three sharp tiny dips were observed at 465 (${}^5D_2 \leftarrow {}^7F_0$), 527 (${}^5D_1 \leftarrow {}^7F_0$) and 537 nm (${}^5D_1 \leftarrow {}^7F_1$). The other two tiny depressions which are broader and weaker dips observed at 490 and 516 nm (clearly depicted

by arrows in the emission spectra) which are ascribed to extra source such as other impurity. Similar kind of observation is made in the $\text{CsK}_2\text{Gd}(\text{VO}_4)_2$ [11]. Reports has been made earlier on the effect of concentration quenching in Eu^{3+} -doped orthovanadates such as $\text{YVO}_4:\text{Eu}^{3+}$ [20], $\text{LaVO}_4:\text{Eu}^{3+}$, $\text{Gd}(\text{V}_{0.6}\text{P}_{0.4})\text{O}_4:\text{Eu}^{3+}$ [21] and $\text{Dy,Bi:K}_3\text{Y}(\text{VO}_4)_2$ [22]. From these reports, one can conclude that the emission lines are well dominated by the dopant Eu^{3+} ions, whereas the host emission from the $[\text{VO}_4]^{3-}$ is nearly quenched. This is because there is an efficient energy transfer from the host lattice $[\text{VO}_4]^{3-}$ to the dopant Eu^{3+} ions. However, the presently studied Eu^{3+} activated $\text{CsK}_2\text{La}(\text{VO}_4)_2$ compound still show the host emission at around 514 nm and not been quenched. The emission due to host lattice is not quenched even when the concentration of the Eu^{3+} is at $x = 0.6$ in the host lattice, which clearly indicates that the energy transfer from VO_4^{3-} to Eu^{3+} is inefficient in $\text{CsK}_2\text{La}(\text{VO}_4)_2$. Blasse argued that the energy transfer from host lattice to Eu^{3+} ion is determined by orbital overlap. “This overlap depends strongly on the angle between the center of the absorbing group, the O^{2-} ion, and the rare – earth ion. If this angle is 90° , the overlap is assumed to be small (using π bonding), if it is 180° , the orbital overlap is assumed to be much larger (using σ bonding)” [23]. In the present case, the V-O-Eu bond angle is about 160° , which reduces the wave function overlap and the exchange energy transfer efficiency. Hence, the host emission from VO_4 is always appears. The PL excitation spectra (PLE) for 514 nm emission consists of two broad bands with maxima at 332 and about 274 nm, which are ascribed to the CT transition in VO_4^{3-} as the case in the undoped sample. On the other hand, the PLE spectra for 593 and 615 nm emissions of Eu^{3+} ions consist of sharp lines at 394 and 465 nm, which are due to the transitions of ${}^5L_6 \leftarrow {}^7F_0$ and ${}^5D_2 \leftarrow {}^7F_0$ of Eu^{3+} , respectively. These dominated sharp lines in the wavelength region of 350–500 nm are from

the f–f transitions within $4f^6$ configuration of Eu^{3+} ions.

3.5 Commission International del'Eclairage (CIE) chromaticity coordinates

The CIE chromaticity coordinates for the host lattice $\text{CsK}_2\text{La}(\text{VO}_4)_2$ and the $x\text{Eu}^{3+}$ doped $\text{CsK}_2\text{La}_{(1-x)}[\text{VO}_4]_2$ ($x=0.6$) phosphor excited by 324 nm were calculated and are indicated by black encircled mark in figure-5.

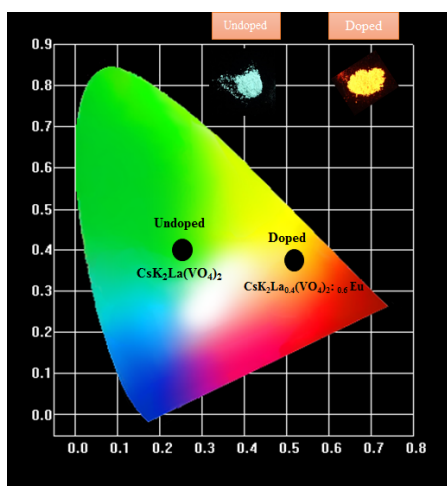


Figure-5. The CIE chromaticity coordinates of $\text{CsK}_2\text{La}(\text{VO}_4)_2$ and $\text{CsK}_2\text{La}_{0.4}\text{Eu}_{0.6}(\text{VO}_4)_2$ orange red phosphor excited by 324 nm.

The CIE color chromaticity coordinates are $x = 0.247$ and $y = 0.402$ for host lattice and $x = 0.523$ and $y = 0.381$ for Eu^{3+} doped phosphor, respectively. The presently studied orange-red phosphor can be used with other suitable phosphor to compensate the lack of color if any. Hence, this phosphor material is suggested to be used as an orange-red phosphor and may find potential applications in phosphor converted WLEDs.

4. Conclusions

In summary, the new rare-earth free self-activated and Eu^{3+} activated $\text{CsK}_2\text{La}(\text{VO}_4)_2$ with Glaserite-type orthovanadates phosphors were successfully synthesized by solid state reaction method. XRD revealed that undoped and Eu^{3+} doped phosphor materials crystallize

in monoclinic structure with space group of $P2_1/m$. The FESEM with EDX spectra showed the presence of the elements are confirmed in both undoped and Eu^{3+} doped phosphor materials. A broad-band green emission was observed from the as-prepared $\text{CsK}_2\text{La}(\text{VO}_4)_2$ compound, originating from the VO_4^{3-} emission. Eu^{3+} substituted compound showed orange-red emission. The colour coordinates, CIE values supported the PL emission for the host lattice and Eu^{3+} activated phosphor materials. The optical properties of the currently synthesised self-activated and Eu^{3+} doped $\text{CsK}_2\text{La}(\text{VO}_4)_2$ phosphors show great potential for near-UV based white LEDs.

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