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Published in:
Journal of Materials Chemistry C

Link to article, DOI:
10.1039/c9tc01385g

Publication date:
2019

Document Version
Peer reviewed version

Link back to DTU Orbit

Citation (APA):
Kang, F., Sun, G., Boutinaud, P., Gao, F., Wang, Z., Lu, J., ... Xiao, S. (2019). Tuning the Bi\textsuperscript{3+}-photoemission color over the entire visible region by manipulating secondary cations modulation in the Sc\textsubscript{V}xP\textsubscript{1-x}O\textsubscript{4}:Bi\textsuperscript{3+} (0 \leq x \leq 1) solid solution. Journal of Materials Chemistry C, 7(32), 9865-9877. https://doi.org/10.1039/c9tc01385g
Tuning the Bi$^{3+}$-photoemission color over the whole visible region through manipulating secondary cations modulation in the ScV$_x$P$_{1-x}$O$_4$:Bi$^{3+}$ ($0 \leq x \leq 1$) solid solution

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ABSTRACT

Unlike the rare earth (RE) (e.g., Eu$^{2+}$) and non-RE (e.g., Mn$^{2+}$) doped tunable solid solutions that frequently suffer from the visible re-absorption issue, the Bi$^{3+}$ ion features remarkable advantages of strong UV excitation intensity and excitation tail less than 430 nm, allowing the Bi$^{3+}$ to have strong ability of solving the re-absorption issue for future lighting technology. Herein, we report a type of zircon-type ScV$_x$P$_{1-x}$O$_4$:Bi$^{3+}$ ($0 \leq x \leq 1$) emission-tunable solid solution that has a strong UV excitation intensity yet no significant light absorption. We reveal that gradual substitution of larger V ions for smaller P ions, which means expansion of lattice cell, can shift the excitation edge from 295 nm to 385 nm, excitation tail from 340 nm to 425 nm and emission position from 455 nm to 641 nm, without big change of the Stokes shift. This spectral shifting is found to be the consequence of a complex dependence of intra-ion and charge-transfer related transitions of Bi$^{3+}$ with the crystal structure. Because of the remarkable excitation-triggered multi-emission properties, we discover further that the ScV$_x$P$_{1-x}$O$_4$:Bi$^{3+}$ solid solution can serve as a type of potential material for anti-counterfeiting and information protection applications. This work enables providing some design insights into discovering more RE and non-RE doped tunable solid solutions in the future, through modulating the secondary cations in the isostructural crystals.

Key words: Bi$^{3+}$; tunable solid solution; fluorescence; anti-counterfeiting; phospho-vanadates.

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1. Introduction

Spectrally tunable solid solutions based on rare earth (RE) and non-RE doping are a type of highly important phosphor materials in the solid-state lighting technology, which enable device designers to benefit the flexible color-emitting choices but not to consider the complicated lighting system design and integration and the color imbalance problem that results from different responses of different phosphors to variation of external factors such as the LED chip temperature [1-5]. The emission-tunable approaches used for achieving the solid solutions have been widely described in the archival literatures, but strategies are usually focused on isostructural crystals that incorporate dopants like Eu\(^{2+}\) [6], Ce\(^{3+}\) [7], Mn\(^{2+}\) [8], and Bi\(^{3+}\) [9] ions whose spectral characteristics are very sensitive to the nature of their nearby chemical microenvironment, owing to the outer character of the emitting states. As a matter of comparison, the well-shielded 4f ions (e.g., Eu\(^{3+}\) [10], Pr\(^{3+}\) [11], Tb\(^{3+}\) [12], Tm\(^{3+}\) [13], Er\(^{3+}\) [14-15] etc) and other 3d ions like Mn\(^{4+}\) [16], and Cr\(^{3+}\) [17]) usually exhibit their fixed spectral shape and positions, making the tunable-emission being less to realize in single ion doped solid solutions.

In most cases, realization of single Eu\(^{2+}\), Ce\(^{3+}\), Bi\(^{3+}\), or Mn\(^{2+}\) ion doped tunable solid solutions is based upon how to manipulate isostructural ions that feature the same valence but different radii at the same coordination number (CN). For example, Ji et al reported the Ce\(^{3+}\) tunable emission in the Ba\(_{2-x}\)Sr\(_x\)SiO\(_4\):Ce\(^{3+}\) (x = 0 → 1.8, \(\lambda_{em} = 391 \rightarrow 411\) nm) [18]; Fu et al reported the Eu\(^{2+}\) tunable emission in the Sr\(_{2.97}\)Ba\(_x\)MgSi\(_2\)O\(_4\):Eu\(^{2+}\), Dy\(^{3+}\) (x = 0 → 2.0, \(\lambda_{em} = 434 \rightarrow 464\) nm) [19]; Dai et al showed the Eu\(^{2+}\) tunable emission in the (K\(_{1-x}\)Na\(_x\))SrPO\(_4\):Eu\(^{2+}\) (x = 0 → 0.6, \(\lambda_{em} = 446 \rightarrow 498\) nm) [20]; Zhang et al realized and presented the Mn\(^{2+}\) tunable emission in the (Ca\(_{1-x}\)Sr\(_x\))O\(_{10}\)Li(PO\(_4\))\(_7\):0.09Mn\(^{2+}\) (a = 0 → 0.4, \(\lambda_{em} = 642 \rightarrow 632\) nm) [21]; and Kang et al recently reported the (Y\(_{x}\)Lu\(_y\)Sc\(_z\))VO\(_4\):Bi\(^{3+}\) (x → y → z; \(\lambda_{em} = 566 \rightarrow 576 \rightarrow 635\) nm) tunable solid solution [22]. Besides, exemplarily basing upon other reported tunable solid solutions [23-28], it is found further that the isostructural ions involved for modifying the local microenvironments fall into two types, i.e., (i) those ions that can be replaced by the dopants, and (ii) those ions that are not involved in the dopant substitution. The former type (i), for example, in the solid solutions of Sr\(_{2.97-x}\)Ba\(_x\)MgSi\(_2\)O\(_4\):Eu\(^{2+}\), Dy\(^{3+}\) [19], Sr\(_{1.5}\)Ba\(_x\)MgSi\(_2\)O\(_4\):Eu\(^{2+}\) [27], and (Sr\(_{1-x}\)Ba\(_x\))P\(_2\)O\(_5\):Eu\(^{2+}\) [28], features two type of isostructural cations in their intermediate phases that are available for the dopants substitution. In this way, if one wanted to know the intrinsic tunable nature, it has to take into account the site occupancy preferential problem. Although several views have been proposed to explain the intrinsic tunable nature (e.g., the crystal field modulation in (K\(_{1-x}\)Na\(_x\))SrPO\(_4\):Eu\(^{2+}\) [20]), but the final emission bands cannot be excluded from an integrated contribution of multiple emission bands.
Almost all of the reported works seem to be lack of their care to this aspect of tunable luminescence that is associated with a deep-seated issue that involves the distribution and re-distribution of dopant in different isostructural crystal sites. As for type (ii), since the tunable solid solutions involve only a type of crystal sites for the dopant, the question of site occupancy preference is not so critical, like in the Sr₃Mg₃₋ₓZnₓY(PO₄)₃:Eu³⁺ [29].

Significantly, among the Eu³⁺, Ce³⁺, Bi³⁺, and Mn²⁺ ions, previous reports concerning single Eu³⁺, Ce³⁺, or Mn²⁺ ion doped tunable solid solutions are seen more often than that involving single Bi³⁺ solid solutions. As for the Eu³⁺, Ce³⁺, and Mn²⁺ ions, however, one major drawback is the evitable light re-absorption problem in the visible spectral region. Over the past years, a number of works had pointed out the necessity of solving this problem [22, 30-37], but it seems that the d-f (i.e., for Eu³⁺, and Ce³⁺) and 4T₁(4G) → 6A₁(6S) (i.e., for Mn²⁺) transitions feature an inherently-inviolable law, making them impossible to have the tunable-emission and non-visible re-absorption at the same time. By contrast, a dopant like Bi³⁺ ion could be relevant to address well this point [22, 32, 35-36]. Because of a naked 6s electron in the electronic configuration of [Xe]-4f¹⁴5d⁰⁶s² [22, 32-33, 35-38], the Bi³⁺ ion, depending on the specific crystal host it built into, can present the emissions broadly spanning from the UV [39], blue [40], yellow [41] and to reddish/red region [35, 32-33, 42], which are analogous to the Eu³⁺, Ce³⁺, and Mn²⁺ ions. As compared to the frequently reported Eu³⁺, Ce³⁺, and Mn²⁺ tunable solid solutions, however, only a very limited examples of Bi³⁺ emission solid solutions have been reported in the literatures, such as (Yₓ,Luₙ,Sc₂)VO₄:Bi³⁺ (yellow → reddish/red) [22], Ba₃₋ₓSrₓSc₂O₉:Bi³⁺ (blue → green) [43], and YPₓV₁₋ₓO₄:Bi³⁺ (blue → yellow) [44]. Typically, there are still no literatures that have reported the existence of Bi³⁺ doped tunable solid solutions that can show their emissions cover the whole visible spectral region.

Besides, works concerning the luminescent phosphor materials have been widely reported for the solid-state lighting technology such as phosphor-converted white LEDs. Sometimes, some works also propose the phosphor materials for the anti-counterfeiting applications. For example, Chen et al reported that the (Y,Gd)VO₄:Bi³⁺,Eu³⁺ phosphor featured temperature-sensitive luminescence properties and proved it could be used for stealth anti-counterfeiting [45], but the emission tuning come from an integrated emission of Eu³⁺ and Bi³⁺ ions due to the inefficiency energy transfer from Bi³⁺ to Eu³⁺ ions. Moreover, this phosphor has two types of crystal sites (i.e., Y, and Gd) for Bi³⁺ and Eu³⁺ substitution and, thus, involves the complicated site occupy preferential problem. Furthermore, it is found that the Bi³⁺ emission positions as the Y/Gd ratios change did not change in the (Y,Gd)VO₄:Bi³⁺,Eu³⁺ [45-46]. In some already-reported cases, the Bi³⁺ ion is also reported to serve as a role of “sensitizer” to improve the luminescence intensity of RE (e.g., Eu³⁺ [2, 45-46],
Tb$^{3+}$ [47], Tm$^{3+}$ [48] etc and non-RE (e.g., Mn$^{4+}$ [49-50] etc) ions. With temporal fluorescence change like in the (Y,Gd)VO$_4$:Bi$^{3+}$,Eu$^{3+}$ [45-46], the anti-counterfeiting applications are proposed. Some other phosphors like the SiO$_2$@SrTiO$_3$:Eu$^{3+}$,Li$^+$ [51], Y$_2$O$_3$:Eu$^{3+}$ [52], and Tb$^{3+}$,Eu$^{3+}$-Doped Strontium-Aluminum Chlorites [53] have been also proposed for anti-counterfeiting applications. All of these phosphors, however, do not belong to the category of the tunable solid solutions. In addition, their relevant anti-counterfeiting applications actually cannot work without using the RE as the luminescent center. Thus, exploring non-RE doped solid solutions that can use for temporal data storage, information encryption and anti-counterfeiting applications is very meaningful.

To jointly answer the above issues, we designed and reported on the zircon-type ScV$_x$P$_{1-x}$O$_4$:Bi$^{3+}$ (0 $\leq$ x $\leq$ 1) solid solution that enabled featuring strong UV excitation intensity with no significant re-absorption in the visible spectral region and emission positions that were broadly tuned over the whole visible region. The intrinsic processes, which gave rise to the progressive shift of the Bi$^{3+}$ excitation edge from 295 nm to 385 nm, excitation tail from 340 nm to 425 nm and concomitant emission tuning from 455 nm to 641 nm as we gradually moved from ScPO$_4$:Bi$^{3+}$ to ScVO$_4$:Bi$^{3+}$, had been carefully discussed basing upon Rietveld refinements, and semi-empirical models. Such unique spectral properties were discovered to make this type of Bi$^{3+}$ solid solution favorable candidate for anti-counterfeiting and information protection applications.

2. Experimental Details

2.1 Samples synthesis

Solid solution compounds with nominal chemical composition, i.e., Sc$_{0.98}(V_x,P_{1-x})$O$_4$:Bi$_{0.02}^{3+}$ (0 $\leq$ x $\leq$ 1, with x varying by steps of 0.2), were prepared by high temperature solid state reaction using Sc$_2$O$_3$ (99.95%), NH$_4$H$_2$PO$_4$ (99.999%), NH$_4$VO$_3$ (99.95%), and Bi$_2$O$_3$ (99.9%) as raw chemicals. All the stoichiometric mixtures were fired at 1200 ºC for 3 h in air. To avoid the volatilization of raw chemicals, the heating rate was set to 3 ºC per minute.

2.2 Characterizations

The powder X-ray diffraction (XRD) patterns were recorded by a Bruker D8 ADVANCE powder diffractometer operated at 40 kV, 40 mA, and 1.2°·min$^{-1}$ with the Cu$\text{K}$α radiation ($\lambda = 1.54059$ Å). A Hitachi F-7000 fluorescence spectrophotometer with a Xe lamp as excitation source was used to collect the photoluminescence (PL) spectra at room temperature. In order to precisely achieve the luminescence intensity upon composition and excitation wavelength, the emission and excitation slits and the scanning rate were set to 3.0 nm and 240 nm/min, respectively. The excitation light source utilized for illustrating the anti-counterfeiting and information protection applications was also from the Hitachi F-7000 fluorescence spectrophotometer.
3. Theoretical Details

Our first-principles calculations were performed within framework of density functional theory (DFT) using the Vienna ab initio simulation package (VASP) [54-55]. The projected augmented wave (PAW) [56] potentials were adopted with the valence states of 2s²2p⁴/4s²3d¹/3d¹4s¹/3s²3p³ for O/Sc/N/P, respectively. A plane wave cutoff of 500 eV was used to expand the wave function. The total energy was converged to a level of 0.0001 eV during the self-consistent electron density optimization. All atoms were allowed to relax until the forces on each atom had magnitude less than 0.01 eV Å⁻¹. The Brillouin zone was sampled using the Monkhorst-Pack scheme with 4 × 4 × 4. To describe the V-P alloying, solid solution with the chemical composition of ScVₓPₓO₄ (x = 0, 0.25, 0.5, 0.75, and 1.0) were modeled using the enumerated configurations and super-lattices generated by the Hermite Normal Form (HNF) matrices size of one, two, three, four times than primitive cells, where the degeneracy of each inequivalent configuration was obtained.

4. Results and Discussion

4.1 Electronic bandgap properties of ScVₓPₓO₄

Kang et al [36] and Cavalli et al [44] found respectively in YVₓNb₁₋ₓO₄ and YVₓP₁₋ₓO₄ that the electronic band gap (E₉) as the V/Nb and P/V ratios change can change regularly, which have been proved to use as the fundamental basis of initial consideration to realize the Bi³⁺ spectral tuning in the YVₓNb₁₋ₓO₄:Bi³⁺ and YVₓP₁₋ₓO₂:Bi³⁺ solid solution. In light of this, we therefore calculated the E₉ values of bulk ScVₓPₓO₄ (0.0 ≤ x ≤ 1) using the DFT calculations. It is shown in Figure 1a that the E₉ values as the V/P increases are decreased from 4.11 eV (i.e., x = 0.0) to 2.56 eV (i.e., x = 1.0). Notice that the E₉ values of intermediate Sc(VₓP₁₋ₓ)O₄ (i.e., x = 0.25, 0.50, 0.75) solid solution were calculated basing upon a homogeneous substitution of smaller P ions with larger V ions and without considering the defects such as the oxygen vacancy. Figure 1b gives a typical crystal structure we modeled, i.e., the intermediate ScV₀.₅P₀.₅O₄ compound. The E₉ value of 4.11 eV in ScPO₄ significantly differs in the experimental E₉ value of 7.2 eV reported by Trukhin A et al [57], but it is more close to those values calculated by DFT modeling (Table 1) [58-60]. Noticing in Table 1 reveals that different DFT modeling methods always lead to different E₉ values [58-60, 33, 62-66] of ScPO₄ and ScVO₄. However, as compared to the experimental E₉ values [33, 57-66], the theoretical E₉ values from DFT are obviously underestimated. Such scenarios are frequently reported in previous works like in refs. [33, 62]. Under this consideration, the theoretical E₉ values of 4.11 eV in ScPO₄ and 2.56 eV in ScVO₄ are reasonable, although they are underestimated as
compared to the experimental $E_g$ values of 7.2 eV, 7.73 eV and 6.73 eV in ScPO$_4$ [57] and 2.8 eV in an oxygen-free ScVO$_4$ [37]. Anyway, the regular decrease of variation tendency of $E_g$ values in Sc$_x$P$_{1-x}$O$_4$ (Figure 1b) would be a consideration basis to predict the existence of the Bi$^{3+}$ spectral tuning if one could form the Sc$_x$P$_{1-x}$O$_4$:Bi$^{3+}$ solid solution.

4.2 Analysis on structural properties

The inorganic oxide compounds, shared with the crystallographic structure of LnBO$_4$ (where Ln denotes lanthanide ions; B represents P, V, and Nb ions), are attractive for trivalent ion substitution (e.g., Bi$^{3+}$ [36-40, 44, 45], Eu$^{3+}$ [45, 67], and Tm$^{3+}$ [48]). Among the LnBO$_4$ system, the ScVO$_4$ and ScPO$_4$ crystallize with the zircon-type $I4_1/amd$ structure consisting of interconnected [ScO$_8$] bisphenoids and [BO$_4$] (B = P, V) tetrahedra (Figure 1c). The [ScO$_8$] and [BO$_4$] structures are closely linked with each other by sharing either edge or oxygen atoms, leading to formation of the Sc···O···B (B = P, V) chain. Moreover, there is only one type of Sc$^{3+}$ site available for Bi$^{3+}$ dopant in the lattices, but two type of B-O bonds appear in the ScPO$_4$ and ScVO$_4$, respectively. Once an amount of Bi$^{3+}$ dopants were built into the crystal lattices, it would be expected to change parts of the Sc···O···B (B = P, V) chains into the Bi···O···B (B = P, V) chains.

As depicted in Figure 2, gradual substitution of P$^{5+}$ ions with V$^{5+}$ ions does not induce the detectable impurity phase, but brings about a continuous series of solid solution with a progressive shift of XRD position toward low angle direction because of the ionic radii mismatch between the P$^{5+}$ and V$^{5+}$ ions in four-fold coordination [68-69], such as, the shift of (112) plane from 36.536$^\circ$ to 34.671$^\circ$ (Table 2). The splitting of XRD peaks in Figure 2 is produced by the incoming $K_{\alpha1}$ and $K_{\alpha2}$ radiations.

Besides, we further used the Rietveld refinement method to refine the XRD data. The desirable $R_p$, $R_w$, $R_p$, $R_{exp}$, $R_{Bragg}$, $R_f$, and GOF factors (Table 3) reveal that Rietveld results coincide well with the experimental results. Figure 3a and Figure 3b give two typical examples of refinement profiles. In Figure 2c(i-iii) and Table 3, the gradual variation of the refined lattice parameters and unit cell volume as the x value increases matches nicely the Végards’ law [19-20], which confirms the successful formation of the continuous Sc$_x$P$_{1-x}$O$_4$:Bi$^{3+}$ solid solution. Among these cell lattice parameters deduced from the Rietveld refinements, we retain the variation of the average Sc-O bond distance (denoted hereafter $<\text{Sc-O}>$) and shortest Sc-P/V distances with x as key parameters to account for the effect of the Sc$_x$P$_{1-x}$O$_4$ crystal structure on the Bi$^{3+}$-tunable luminescence properties, whereas the composition-dependent average V-O lengths (hereafter $<\text{V-O}>$) accounts for the energy of the O$_{2p}$ $\rightarrow$ V$_{3d}$ charge transfer. All these useful data are listed in Table 3 for further calculations.

6
4.3 Photoluminescence (PL) spectra

Figure 4 shows the excitation and emission spectra (a) of ScVₓP₁₋ₓO₄:Bi³⁺ (0 ≤ x ≤ 1) along with the CIE chromaticity coordinates (b and c). It is not easy for us to locate the lower maximum of their excitation spectra in Figure 4; therefore, we preferred to locate the position of the excitation edge that we have determined from the first derivative. The corresponding values, the wavelength positions of the corresponding emission maxima, and the Full Width at Half Maximum (FWHM) values of the emission bands are given in Table 2 and Table 4.

We observe a gradual redshift of the excitation edge and emission position as the V ions gradually substitute for the P ions (i.e., x increases). The redshift of emission position as x is increased in ScVₓP₁₋ₓO₄:Bi³⁺ is well reflected by the CIE chromaticity coordinates tuning from blue, yellow, and to red. The energy mismatch between the excitation edges and the emission maxima gives rough information on the Stokes shift (ΔS) associated with each composition of the solid solution. These ΔS values are certainly somehow underestimated. In Table 4, we also list the wavelengths corresponding to the cross-over between emission and excitation spectra, the purpose of which is to estimate the spectral overlap between these spectra. Notice that these data were achieved after appropriate normalization of the spectral intensities and integration of the corresponding overlapping areas. As a result, we can acquire the cross points of the excitation and the emission spectra and the percentage of emission area that overlaps the corresponding excitation spectrum (i.e., the spectral overlap) (Table 4). The results vividly exhibit the quantitative information on the little fraction of re-absorbed emission for each member of the present solid solution. Note that the emission spectral region is interrupted at 800 nm. Hence, the light re-absorption essentially occurs in the ScVₓP₁₋ₓO₄:Bi³⁺ solid solution, but except for a very weak visible light re-absorption in the ScVO₄:Bi³⁺ compound (i.e., > 400 nm), other solid solution compounds only show the re-absorption in the near UV spectral region.

4.4 Analysis and discussion on PL properties

The excitation spectrum consists of superimposed electronic transitions with different characters. Transitions within isolated Bi³⁺ ions occur from the fundamental ¹S₀ ground state (6s² configuration) to the excited ³P₀, ³P₂, and ¹P₁ states (i.e., 6s¹6p¹ configuration) and are denoted as A, B, and C, respectively. The spin-allowed C transition is usually intense but its wavelength is usually located far in the UV spectral region (i.e., generally < 250 nm). The B transition is spin forbidden and has low intensity. The A transition has, in contrast, appreciable oscillator strength through the spin-orbit mixing that takes place between ³P₁ and ¹P₁, and it forms the lower lying excitation feature. In addition, transitions with charge transfer character are also observable within Bi³⁺ pairs [70-71] and...
in some oxidic lattices containing metal cations (M\textsuperscript{m+}) having closed-shell \(d^0\) or \(d^{10}\) electron configuration (i.e., titanates, vanadates, niobates, etc) [37]. Note that with a nominal Bi\textsuperscript{3+} doping rate of 2 mol\%, the probability to form Bi\textsuperscript{3+}-pairs in ScV\textsubscript{x}P\textsubscript{1-x}O\textsubscript{4}:Bi\textsuperscript{3+} is low, allowing us not to consider this possibility of Bi\textsuperscript{3+}-pairs in the present work frame. However, the Bi\textsuperscript{3+-to-M\textsuperscript{m+}} transitions are usually referred as D or metal-metal charge transfer (MMCT) transitions. In Bi\textsuperscript{3+-doped vanadates (e.g., the ScVO\textsubscript{4}:Bi\textsuperscript{3+} [33]), additional excitation features belonging to the host-related \([VO_4]^{3-}\) units can appear in case of energy transfer from the host to Bi\textsuperscript{3+} states. At last, the unusual red luminescence and corresponding low-lying excitation in ScVO\textsubscript{4}:Bi\textsuperscript{3+}, which are due to the presence and perturbation of an oxygen vacancy, appear in the first coordination sphere of Bi\textsuperscript{3+} [33]. The global situation looks rather complex, but the origin of the excitation features in the ScV\textsubscript{x}P\textsubscript{1-x}O\textsubscript{4}:Bi\textsuperscript{3+} solid solution can be determined using a few empirical tools. Wang et al reported in 2012 that the energy of A and C transitions can be estimated empirically from the knowledge of the environmental factor \(he\textsubscript{CN}(X)\) [72]:

\[
he\textsubscript{CN}(X) = \sum_{1}^{N_X} f_{c(X-L)} \alpha_{c(X-L)} Q_L^2
\]

For a given cationic site \((X)\) occupied by Bi\textsuperscript{3+} in the host lattice, with coordination number (here, \(CN = 8\)), the quantity \(he\textsubscript{CN}(X)\) is connected to the nephelauxetic effect at site \(X\) and gives relevant information on the influence of the nearby chemical environment on a given Bi\textsuperscript{3+} ion in the lattice. The \(f_{c(X-L)}\) and \(\alpha_{c(X-L)}\) represent respectively the fractional covalency and the volume polarization of each chemical bond separating cation \(X\) to its nearby ligands \(L\) (here \(L = \text{oxygen}\)) in binary units to which the initial host lattice is decomposed. In particular, these parameters strongly depend on the \(X-L\) distances in the crystal lattices. The procedure for crystal lattice decomposition in binary units is described by previous works [73-75] and is not reproduced here for sake of brevity. \(Q_L\) is the effective charge carried by ligand \(L\) in each given \(X_mL_n\) unit, and it can be further calculated using the expression of \(Q_L = \frac{m}{n} Q_X\) (where \(Q_X\) denotes the effective charge of the considered cation \(X\)). In present work, this charge was taken as the bond valence sum of atom \(X\) in its polyhedron and was obtained from the crystal structure of the host lattice using VESTA software [76]. The necessary values of bond valence parameters were obtained from [77]. So, once \(he\textsubscript{CN}(X)\) is known, the energy \(E\textsubscript{A,CN}(X)\) in cm\textsuperscript{-1} of the A transition of Bi\textsuperscript{3+} in a given site \(X\) of a given host lattice can be obtained empirically from the following equation [72]:

\[
E\textsubscript{A,CN}(X) = 23970 + 50051\exp \left( - \frac{he\textsubscript{CN}(X)}{0.551} \right)
\]

In our case, \(X\) is Sc\textsuperscript{3+} with 8 oxygen neighbors in the regular zircon structure of ScV\textsubscript{x}P\textsubscript{1-x}O\textsubscript{4}. Owing
to the ionic mismatch between Sc³⁺ and Bi³⁺ ions, a local expansion of the crystallographic site, as the “4.1 Analysis on structural properties” section describes, occurs in the ScVₓP₁ₓO₄:Bi³⁺. This local expansion amounts ≈ 6 % in ScVO₄:Bi³⁺ [33], i.e., <Bi-O> = 1.06 <Sc-O>, taking the <Sc-O> bond distances from Table 3. This value is assumed as indicatively representative of the average local site expansion of Bi-O bonds within the entire ScVₓP₁ₓO₄:Bi³⁺ system. Hence, we calculated the environmental factors heₓ(Bi) on this ground for all values of x in the solid solution. Values are given in Table 4. The corresponding E₁ₓₓₓ(Bi) energies are then easily obtained by mean of equation 2. In case that an oxygen vacancy is present in the first neighborhood of Bi³⁺ ion, as identified earlier in ScVO₄:Bi³⁺ [33], the coordination number of Bi³⁺ will be reduced to 7 with a resulting local expansion of the crystallographic site by ≈ 14 % with respect to virgin ScVO₄. We obtain heₓ(Bi) = 1.405 and E₁ₓₓₓ(Bi) = 27880 cm⁻¹ (359 nm) for this specific case.

The energy of D transitions in cm⁻¹ (i.e., Bi³⁺ -to-V⁵⁺ MMCT) can be estimated using [37]:

\[ E_{D, CN}(B_i - V) = k_{CN}^{CN} \left[ \chi_{CN}(B_i^{3+}) - \alpha_{CN}^{CN} \chi_{CN}(V^{5+}) \right] \]  

(3)

where \( \chi_{CN}(B_i^{3+}) \) and \( \chi_{CN}(V^{5+}) \) are the electronegativities of Bi³⁺ and V⁵⁺ in CN and CN’-fold coordination, respectively, as calculated by Li et al [78]; for the specific purpose of the present work, we need \( \chi_{m}(B_i^{3+}) = 1.34 \) (i.e., Bi³⁺ in regular eight-fold coordination) and \( \chi_{d}(V^{5+}) = 2.46 \) (i.e., V⁵⁺ in tetrahedral coordination); \( d_{corr} \) is the shortest Bi³⁺-V⁵⁺ interatomic distance corrected for the doping effect defined as \( d_{corr} = d_{host} + 1/2 \Delta r_{CN} \), where \( d_{host} \) is the shortest distance separating V⁵⁺ and Sc³⁺ cation sites in the undoped lattice (i.e., the Sc-P/V distances given in Table 3). Here we have \( \Delta r_{s} = r_{Sc} - r_{Bi} \), where \( r_{Sc} \) and \( r_{Bi} \) are the crystal radii of Sc³⁺ and Bi³⁺ in eight-fold coordination [68]. Table 4 gives all \( d_{corr} \) values for all x values in ScVₓP₁ₓO₄:Bi³⁺. \( k_{CN}^{CN} \) and \( \alpha_{CN}^{CN} \) are the crystal-structure related quantities available from [37]. Here, we need \( k_{4}^{CN} = 52239 \text{ cm}^{-1} \) and \( \alpha_{4}^{CN} = 0.99 \) for the calculation of all \( E_{D, CN}(B_i-V) \) energies by means of equation (3). At this stage, it should be kept in mind that the intensity of the Bi-V MMCT bands depends on the probability for a given Bi³⁺ ion to find a V⁵⁺ (or a [VO₄]³⁻ unit) in its immediate neighborhood. This probability writes \( P(x) = 1-(1-x)^{n} \), where x is the molar ratio in ScVₓP₁ₓO₄ and n is the number of V⁵⁺ (P⁵⁺) sites contained in the first coordination sphere of a given Bi³⁺, i.e., \( n = 2 \) in the zircon structure. All the values are given in Table 4. They give information on the probability of Bi-V MMCT transitions to occur in the ScVₓP₁ₓO₄:Bi³⁺ and therefore on the intensity of the transition. At last, we also provide in Table 4 some available information on the host fundamental excitation (HFE) in virgin ScVₓP₁ₓO₄ that depend on the <V-O> distances [78]. Figure 4(d) shows the variation of HFE, excitation tail, excitation edge, \( E_{L, x}(Bi) \) and \( E_{D, x}(Bi-V) \) against x. Meanwhile, energy \( E_{L, x}(Bi) \) is also added for
the specific ScVO₄:Bi³⁺ composition and $E_{A,8}(Sc)$ for $x \leq 0.2$.

We note that the host fundamental excitation (HFE) of virgin ScVₓP₁₋ₓO₄ and energy position of excitation edge of ScVₓP₁₋ₓO₄:Bi³⁺ vary similarly with $x$. The energy downshift in the latter case is attributed to Bi³⁺ doping. The noticeable thing is the very peculiar behavior of ScVO₄:Bi³⁺ that shows a pronounced redshift of its excitation edge, as pointed out already [33]. Figure 4d exhibits information on the energy level structure of Bi³⁺ in ScVₓP₁₋ₓO₄. In this case, here we can confirm that D (Bi-V MMCT) and A transitions ($^1S_0 \rightarrow ^3P_1$) of Bi³⁺ have similar energy in such systems (ScPO₄:Bi³⁺ excepted) [80]. The calculation locates a cross-over for $x = 0.8$, meaning that the lowest-lying excitation has an A character in ScV₀.₉P₀.₁O₄:Bi³⁺ and ScVO₄:Bi³⁺. In the latter case, the calculated energy $E_{A,7}(Bi)$ corresponding to an $^1S_0 \rightarrow ^3P_1$ transition of Bi³⁺ having an oxygen vacancy in its immediate neighborhood reproduces reasonably the spectacular redshift of the first derivative of excitation edge in this vanadate. Moving to the other side, the D band is predicted slightly below the A transition, but here it should be reminded that the probability for the Bi-V MMCT to occur drops as $x$ is decreased. This is indicated in Figure 4d by the size of the spots that are drawn in proportion with probability $P(x)$. In other words, the D band becomes in practice too weak to be observed in the spectra for $x \leq 0.4$ and presumably the A transition dominates here. For $x < 0.2$, i.e., in the phosphorous-rich systems, we observe a noticeable deviation between the experimental edge and the predicted $E_{A,8}(Bi)$ energies. This reveals that the 6% local site expansion of Bi-O bonds that has been considered for the calculation of $E_{A,8}(Bi)$ does not hold anymore, which may be due to the increasing stiffness of the lattice as the amount of [PO₄]³⁻ units grows. To illustrate this point, we have calculated $E_{A,8}(Sc)$ energies without considering any local expansion of the crystal site (i.e., as if we were considering virgin ScVₓP₁₋ₓO₄). The values are plotted in Figure 4d and better corresponds to the excitation edge. Presumably, the A energies associated with Bi³⁺ in the phosphorous-riche members of solid solution are located between $E_{A,8}(Sc)$ and $E_{A,8}(Bi)$ extrema. Further work needs to be done here to clarify the situation. At last, we find that HFE (i.e., the [VO₄]³⁻ excitation) overlaps the A and D bands for $x > 0.4$ and can contribute to the excitation spectrum if the excitation energy is transferred to Bi³⁺ ion. Considering a doping rate of 2%, the probability that a [VO₄]³⁻ group possesses a Bi³⁺ ion in its immediate neighborhood in ScVO₄:Bi³⁺ is less than 4%, meaning that host sensitization of the Bi³⁺ luminescence needs energy migration among vanadate units prior the energy transfer to Bi³⁺. Diluting the vanadates in the solid solution ScVₓP₁₋ₓO₄:Bi³⁺ makes this migration less and less probable as $x$ decreases. This specific point has been examined by G. Blasse in the late 60’s and was concluded that the critical concentration for energy migration in this system is $x \approx 0.25$ [79]. This means that we can expect a contribution of HFE in the excitation
spectra of ScV₄P₁₋ₓOₓ:Bi³⁺ for 1 ≤ x ≤ 0.25. Excepting the two extreme members of the solid solution, we thus can ascribe the emission of ScV₄P₁₋ₓOₓ:Bi³⁺ to thermalized A and D states giving ΔS shifts of ≈ 9000 to ≈ 12000 cm⁻¹. The emission of ScVO₄:Bi³⁺ is confirmed to have an A character, but the origin of the blue emission in ScPO₄:Bi³⁺ is still unsure at this stage, especially if we compare with the isostructural YPO₄:Bi³⁺ compound which regularly emits at 245 nm for an excitation at 230 nm [44] with a very small Stokes shift.

Looking in details, however, we find a low-lying excitation feature with low intensity in the 325 - 425 nm region, with a maximum at ≈ 365 nm that is responsible for the 8.7 % spectral overlap with the blue emission. This denotes the presence of an electronic state that could be responsible for the blue emission, with a Stokes shift of ≈ 5000 cm⁻¹. The nature of this state, however, is at the moment not fixed and, thus, needs a further study.

4.5 UV-triggered anti-counterfeiting and information protection application

A closer re-inspection into Table 2 reveals that the excitation tails between the different solid solution are different from each other. For example, an excitation tail wavelength gap of 61 nm appears between ScPO₄:Bi³⁺ (337 nm) and ScV₀.₈P₀.₂O₄:Bi³⁺ (398 nm); there is a tail gap of 62 nm between ScV₀.₈P₀.₄O₄:Bi³⁺ (i.e., 365 nm) and ScVO₄:Bi³⁺ (i.e., 427 nm). Moreover, as Figure 4a depicts, by exciting with different wavelengths, different solid solutions show different emission positions and the FWHM values. Hence, the spectral properties of ScV₄P₁₋ₓOₓ:Bi³⁺ solid solution appear very attractive for temporal data storage, information encryption, and anti-counterfeiting applications. As a proof of concept, we first have built a home-built setup consisting of a Hitachi F-7000 fluorescence spectrophotometer, a Lumenera camera (INFINITY 1) and a high-resolution fiber optical spectrometer (FG4000) (Figure 5a). Then, various compositions of ScV₄P₁₋ₓOₓ:Bi³⁺ solid solution, i.e., ScV₀.₂P₀.₈O₄:Bi³⁺ and ScV₀.₈P₀.₂O₄:Bi³⁺ with a mass (denoted hereafter) ratio of 4:1 (blend 1), ScV₀.₇P₀.₃O₄:Bi³⁺ and ScV₀.₃P₀.₇O₄:Bi³⁺ with a ratio of 5:2 (blend 2), ScV₀.₆P₀.₄O₄:Bi³⁺ and ScVO₄:Bi³⁺ with a ratio of 3:5 (blend 3), and ScV₀.₄P₀.₆O₄:Bi³⁺ and ScVO₄:Bi³⁺ with a ratio of 7:2 (blend 4), were employed and deposited onto a piece of quartz glass (Figure 5b). After positioned the phosphors-covered quartz glass onto this home-built setup, we could captured the photographs and allowed the blended phosphors to have selective excitation wavelengths at the same time. It is shown in Table 2 that the gap of excitation tails between the ScV₀.₂P₀.₈O₄:Bi³⁺ and ScV₀.₈P₀.₂O₄:Bi³⁺ is 52 nm, which is large enough to cover the beam width (~2 mm) and length (~4 mm) of UV excitation and thus can allow to having enough resolution to distinguish the emission colors of the two blended samples. More specifically, when the excitation wavelengths of 260 nm and 380 nm were used, temporal variation of emission colors is observable. In Figure 5b and Figure
5c, the former excitation wavelength can excite all blended phosphors, leading to the superimposed luminescence contribution of each phosphor in the blend that can be finely tuned by appropriate adjustment of the mass ratios. The latter wavelength, however, only selectively excites the phosphors that can show an excitation tail exceeding to this wavelength, e.g., the solid solution of ScV₃P₁₋ₓO₄:Bi³⁺ with x > 0.7. Thus, exciting at 380 nm, such as in the blended ScV₀.₈P₀.₂O₄:Bi³⁺ and ScV₀.₈P₀.₂O₄:Bi³⁺ phosphors, pumps the color analogous to that of the ScV₀.₈P₀.₂O₄:Bi³⁺ solid solution, while upon excitation at 260 nm enables giving rise to a color that differs in that of each ScV₀.₈P₀.₂O₄:Bi³⁺ and ScV₀.₈P₀.₂O₄:Bi³⁺ solid solution. Hence, blend 1 enables featuring a temporal information encryption behavior, allowing to possessing the multiple UV light-converted anti-counterfeiting feature. Figure 5d gives the CIE chromaticity coordinates and related digital photos taken upon at different excitation wavelengths. When taken into account a variety of emission colors the ScV₄P₁₋ₓO₄:Bi³⁺ solid solution, a wide range of temporal colors, derived from any two or more types of the solid solution (i.e., the examples shown in Figure 5b and Figure 5c), can be anticipated, and they enable covering the whole visible spectral region.

5. Conclusion and Outlook

In summary, a new type of full-color tunable ScVₓP₁₋ₓO₄:Bi³⁺ (0 ≤ x ≤ 1) solid solution with strong UV excitation intensity yet featured no significant excitation in the visible spectral region is reported in this work. We reveal that gradual substitution of P ions with larger V ions in the ScVₓP₁₋ₓO₄:Bi³⁺ solid solution induces a progressive shift the excitation edge from 295 nm to 385 nm, excitation tail from 340 nm to 425 nm, and corresponding emission maximum from 455 nm to 641 nm. The redshift of the excitation edge as the x value is increased in the ScVₓP₁₋ₓO₄:Bi³⁺ is well explained by considering the overlapping contribution of features having different origins, either intra-ionic A-type transitions or transitions with charge transfer character. Emission in these systems arises from the lower-lying excitation levels and shifts concomitantly with these levels with an almost constant Stokes shift. Moreover, blending the ScVₓP₁₋ₓO₄:Bi³⁺ (0 ≤ x ≤ 1) solid solution with adjusted mass ratios has been proved to be promising candidates for use in security and authenticity purposes, such as temporal information encryption and decryption and UV-converted anti-counterfeiting. This work not only have contributed a new type of Bi³⁺-doped tunable member to the big family of solid solutions, but also progresses in the understanding of the intrinsic luminescence-structure relationships in ScVₓP₁₋ₓO₄:Bi³⁺ (0 ≤ x ≤ 1) solid solution. Thereby, we expect that this work could participate to the design and discovery of more Bi³⁺ doped tunable solid solutions that are able to address the visible re-absorption problem for feature solid-state lighting technology. Meanwhile, we expect that more RE and non-RE doped tunable solid solutions and
relevant new application possibilities based upon their spectral features can be discovered through modulating the secondary cations in the isostructural crystals.

**Acknowledgement**

Here, we would like to acknowledge the financial supports from the Innovation and Technology Commission of HKSAR through Hong Kong Branch of National Precious Metals Material Engineering Research Center, City University of Hong Kong (Projects no. 9667143, and 7004902), and the European Union’s Horizon 2020 research and innovation program under the Marie Skłodowska-Curie grant agreement no. 713683.

**Table 1** Summarization on electronic bandgap ($E_g$) values of bulk ScPO$_4$ and ScVO$_4$ crystals. Noted that the theoretical $E_g$ values highlighted by $a$ contain 2H$_2$O, while those denoted by $b$ are
based upon using a GGA + \( U \) extension method. As the experimental \( E_g \) value highlighted by c, it is achieved using the Urbach rule’s approximation method.

<table>
<thead>
<tr>
<th>ScPO(_4)</th>
<th>Exptl ( E_g )/eV</th>
<th>Calcd ( E_g )/eV</th>
<th>ScVO(_4)</th>
<th>Exptl ( E_g )/eV</th>
<th>Calcd ( E_g )/eV</th>
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<tr>
<td>7.2</td>
<td>---</td>
<td>2.8</td>
<td>2.70 (GGA)(^b)</td>
<td>[57]</td>
<td>[33]</td>
</tr>
<tr>
<td>---</td>
<td>4.52 (GGA)</td>
<td>2.8</td>
<td>2.75 (GGA)(^b)</td>
<td>[58]</td>
<td>[62]</td>
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<td>---</td>
<td>5.07 (LDA)</td>
<td>---</td>
<td>2.57 (GGA)</td>
<td>[59]</td>
<td>[63]</td>
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<td>---</td>
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<td>2.56 (GGA)</td>
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<td>[64]</td>
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<td>2.48 (GGA)</td>
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<td>[65]</td>
<td>[66]</td>
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<tr>
<td>6.73</td>
<td>4.11 (GGA)</td>
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GGA --- Generalized Gradient Approximation  
LDA --- Local density approximation

**Table 2** XRD position of planes spacing (112) and corresponding calculated \( d \) values of the Sc(V\(_x\),P\(_{1-x}\))O\(_4\):Bi\(^{3+}\) (0 \( \leq x \leq 1 \)) solid solution. Besides, experimental and fitted emission positions as well as emission fwhm values and excitation tails of the solid solution are also included here.

<table>
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<tr>
<th>( x )</th>
<th>(112) ( /^0 )</th>
<th>( d )/(Å)</th>
<th>( \lambda_{em} ) peak /nm</th>
<th>Fitted ( \lambda_{em} )/nm</th>
<th>FWHM /cm(^{-1})</th>
<th>( \lambda_{ex} ) tail /nm</th>
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<td>507.55</td>
<td>6250</td>
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**Table 3** Rietveld refined XRD results for the Sc(V\(_x\),P\(_{1-x}\))O\(_4\):Bi\(^{3+}\) (0 \( \leq x \leq 1 \)) solid solution.
### Table 4 Corrected Bi-V distances, environmental factor and spectral properties of Bi$^{3+}$ in the ScV$_x$P$_{1-x}$O$_4$ solid solution

<table>
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<tr>
<th>x</th>
<th>$d_{	ext{corr}}$/Å</th>
<th>$P$ (x)</th>
<th>$h_n$ (Bi)</th>
<th>HFE /cm$^2$</th>
<th>Edge /cm$^2$</th>
<th>$\Delta S$ /cm$^2$</th>
<th>Crossing point /nm</th>
<th>Spectral overlap /%</th>
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<td>36800</td>
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<td>26040</td>
<td>10440</td>
<td>416</td>
<td>2.41</td>
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---

**Figure captions**

Noted that the abbreviations of $R_p$, $R_{wp}$, $R_{\text{exp}}$, $R_{\text{Bragg}}$ and $R_F$ denote Profile factor, Weighted profile, factor Expected weighted profile factor, Bragg factor, and Crystallographic factor, respectively.

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...
**Figure 1** (a) Calculated density of state (DOS) of Sc(V\textsubscript{x},P\textsubscript{1-x})O\textsubscript{4} (x = 0, 0.25, 0.50, 0.75, 1.00), where the E\textsubscript{g} values are also given; (b) Crystal structure of intermediate Sc(V\textsubscript{x},P\textsubscript{1-x})O\textsubscript{4} (x = 0.50) compound; (c) Lattice cells of ScPO\textsubscript{4} (i.e., from ICSD file no. 74483) and ScVO\textsubscript{4} (i.e., from ICSD file no. 78074) as well as the cationic coordination environments and schematic illustration of the substitution process that involves the substitution of the Sc site with the Bi dopant and the P atom with the V atom. The Sc-O and P-O lengths in the ScPO\textsubscript{4} lattice, along with the Sc-O and V-O lengths in the ScVO\textsubscript{4} lattice are also given in Figure 1c.

**Figure 2** XRD patterns of Sc(V\textsubscript{x},P\textsubscript{1-x})O\textsubscript{4}:Bi\textsuperscript{3+} (0 < x < 1) solid solution and the corresponding enlarged diffraction patterns within the range of 34-37°.

**Figure 3** Refined XRD patterns (−) of ScPO\textsubscript{4}:Bi\textsuperscript{3+} (a) and Sc(V\textsubscript{0.5},P\textsubscript{0.5})O\textsubscript{4}:Bi\textsuperscript{3+} (b) compounds, where the Rietveld refining results, Bragg reflections, profile differences between experimental and calculated values are denoted using the ×, | and − symbols, respectively; (c), (d) and (e) are the x-dependent cell lattice parameters a/b, c and V, where the linear fitting are based upon the equation of y = m + nx.

**Figure 4** (a) Excitation and emission spectra of the Sc(V\textsubscript{x},P\textsubscript{1-x})O\textsubscript{4}:Bi\textsuperscript{3+} (0 < x < 1) solid solution, all spectra are normalized to unity; (b) CIE chromaticity coordinates calculated using the emission of (a), the cross points of the excitation and the emission spectra, along with the emission wavelengths used for monitoring the excitation spectra, are also denoted beside each excitation curve; (c) Energy level structure of Bi\textsuperscript{3+} in ScV\textsubscript{x}P\textsubscript{1-x}O\textsubscript{4}, where (i) is the host fundamental excitation (HFE), excitation edge and tail, (ii) is the calculated position of A and D transitions.

**Figure 5** (a) Home-built PL setup of how to collect the digital photos (b) and emission spectra (c) of the blended phosphors upon excitation at different wavelengths, as well as the related CIE values (d). In (b-e), the blended phosphors are ScV\textsubscript{0.2}P\textsubscript{0.8}O\textsubscript{4}:Bi\textsuperscript{3+} and ScV\textsubscript{0.3}P\textsubscript{0.7}O\textsubscript{4}:Bi\textsuperscript{3+} with a mass (denoted hereafter) ratio of 4:1 (blend 1, points 1-2), ScV\textsubscript{0.2}P\textsubscript{0.8}O\textsubscript{4}:Bi\textsuperscript{3+} and ScV\textsubscript{0.3}P\textsubscript{0.7}O\textsubscript{4}:Bi\textsuperscript{3+} with a ratio of 5:2 (blend 2, point 3), ScV\textsubscript{0.6}P\textsubscript{0.4}O\textsubscript{4}:Bi\textsuperscript{3+} and ScVO\textsubscript{4}:Bi\textsuperscript{3+} with a ratio of 3:5 (blend 3, point 4), and ScV\textsubscript{0.1}P\textsubscript{0.9}O\textsubscript{4}:Bi\textsuperscript{3+} and ScVO\textsubscript{4}:Bi\textsuperscript{3+} with a ratio of 7:2 (blend 4, point 5). The excitation wavelengths and the corresponding CIE values have been also labeled besides each curve and/or suitable place.

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Figure 1
Figure 2
Figure 4
Figure 5