Supporting Information

Bi$^{3+}$ acting both as electron and as hole trap in La-, Y-, and LuPO$_4$

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Fig. S1. (a) XRD patterns of Y$_{1-x}$Lu$_x$PO$_4$:0.005Eu$^{3+}$,0.005Bi$^{3+}$ solid solutions (x=0-1). (b) detailed XRD patterns in the range from 28 to 34°.

Fig. S2. Photoluminescence spectra of LaPO$_4$:0.002Bi$^{3+}$ and LuPO$_4$:0.005Bi$^{3+}$ excited at different excitation wavelength recorded at 10 K.

Fig. S2a-2c shows the photoluminescence spectra of LaPO$_4$:0.002Bi$^{3+}$ at different excitation wavelength. All spectra share a same band at 432 nm, and the weaker band at 288
nm only appears when excited at 166 nm and 212 nm. From the study by Boutinaud et al. [1], the band at 432 nm is tentatively attributed to CB→Bi\(^{3+}\) charge transfer emission.

The VRBE diagram in Fig. 1 predicts that Ce\(^{3+}\) acts as a 3.80 eV deep hole trapping center in YPO\(_4\):0.005Bi\(^{3+}\),0.005Ce\(^{3+}\) which is deeper than the 2.7 eV Bi\(^{3+}\) electron trapping center. The electron will be released earlier from Bi\(^{2+}\) than the hole from Ce\(^{4+}\). One then can estimate according to Eq. (1) at the heating rate of 1 K/s that electron release from Bi\(^{2+}\) to the conduction band bottom in YPO\(_4\) will give rise to a glow peak \(T_m\) at \~930 K.

Fig. S3. Thermoluminescence emission (TLEM) plots of Bi\(^{3+}\) single or Bi\(^{3+}\)-Ln\(^{3+}\)-codoped REPO\(_4\) (RE=Y, and Lu; Ln=Tb, Pr, Ce, Eu, and Yb) recorded at a heating rate of 1 K/s. The concentration of each dopant is fixed at 0.5 mol%.
With the VRBE at Bi$^{2+}$ ground state between that of Sm$^{2+}$ and Yb$^{2+}$ we expect that the TL glow appears at between 679 and 965 K as observed for YPO$_4$:Ce$^{3+}$,Ln$^{3+}$ (Ln=Sm, and Yb) in Ref [2]. Clearly, the Bi$^{3+}$ electron trap is too deep to release an electron in the measurement range, which explains why no additional TL band(s) with Ce$^{3+}$ emission appears in Fig. S3b.

Fig. S4. TL glow curves of YPO$_4$:0.005Bi$^{3+}$,0.005Ln$^{3+}$ (Ln=Tb, Pr, and Ce) samples recorded after 4000 s β irradiation monitoring Bi$^{3+}$ emission at a heating rate of 1 K/s.

Fig. S5. Comparison of TL glow peaks IIIa, IIIb, and IIIc for Y$_{1-x}$Lu$_x$PO$_4$:0.005Bi$^{3+}$,0.005Ln$^{3+}$ (Ln=Tb, and Pr) and Y$_{1-x}$Lu$_x$PO$_4$:0.005Eu$^{3+}$,0.005Bi$^{3+}$ solid solutions (x=0-1).
Fig. S6. TL glow curves of LuPO$_4$:0.005Bi$^{3+}$,0.005Ln$^{3+}$ (Ln=Pr, Tb, and Ce) recorded after exposure to β source for 4000 s monitoring Bi$^{3+}$ emission at a heating rate of 1 K/s.

Fig. S6 shows the TL glow curves for LuPO$_4$:0.005Bi$^{3+}$,0.005Ln$^{3+}$ (Ln=Pr, Tb, and Ce) samples. Similar as in Fig. 3a and S4 for YPO$_4$, Tb and Pr also give rise to two peaks IIIa and IIIb in LuPO$_4$:0.005Bi$^{3+}$,0.005Tb$^{3+}$ and LuPO$_4$:0.005Bi$^{3+}$,0.005Pr$^{3+}$. The TL glow curves of the single Bi$^{3+}$ and the Bi$^{3+}$-Ce$^{3+}$-codoped samples are shown to illustrate the absence of peaks IIIa and IIIb. These results further support that the glow peaks IIIa and IIIb are due to hole release from Tb$^{3+}$ and Pr$^{4+}$ and recombination on Bi$^{2+}$.
Fig. S7. Thermoluminescence emission (TLEM) plots of (a) LaPO$_4$:0.005Eu$^{3+}$,0.005Bi$^{3+}$, (b) LaPO$_4$:0.005Eu$^{3+}$,0.005Tb$^{3+}$, and (c) LaPO$_4$:0.005Eu$^{3+}$,0.005Ce$^{3+}$ at a heating rate of 1 K/s.

Fig. S8. (a) TL glow curves of LaPO$_4$:0.005Eu$^{3+}$,0.005Bi$^{3+}$ and LaPO$_4$:0.005Eu$^{3+}$,0.005Tb$^{3+}$ monitoring the red emission from Eu$^{3+}$ recorded at a heating rate of 1 K/s. The data on LaPO$_4$:0.005Eu$^{3+}$,0.005Tb$^{3+}$ were obtained from Lyu et al. [3].
Fig. S9. (a) TL glow curves charged by β irradiation at different dose, (b) repeatability test of TL glow curves after 20 s β irradiation, and (c) integrated TL glow intensity as a function of cyclic number for LaPO₄:0.005Eu³⁺,0.005Bi³⁺.

Fig. S9a shows the TL glow curves for LaPO₄:0.005Eu³⁺,0.005Bi³⁺ charged by a β dose of 70 to 1400 mGy. All TL glow curves show their maxima at the same temperature $T_m$ (± 6 K), suggesting that the first-order TL recombination approximation is justified⁴.

Note that a proportional increase of the TL intensity appears when irradiation time increases. This shows that this phosphor has potential application as energy storing materials or as a dosimeter for detection of ionizing radiation. Fig. S9b shows a repeatability test of TL glow curves of LaPO₄:0.005Eu³⁺,0.005Bi³⁺. The integrated TL intensities in Fig. S9c suggest that this phosphor is relatively stable during the 40 cycle test.
Fig. S10. (a) Isothermal decay curve monitoring the Eu$^{3+}$ emission recorded at room temperature and (b) TL glow curves with different waiting time after 2000 s β irradiation for LaPO$_4$:0.005Eu$^{3+}$,0.005Bi$^{3+}$.

Fig. S10a shows that the persistent luminescence from Eu$^{3+}$ can still be detected after 12 h at RT. In order to identify the origin of the afterglow, Fig. S10b shows the TL glow curve of LaPO$_4$:0.005Eu$^{3+}$,0.005Bi$^{3+}$ without and with 12 h waiting time after β irradiation. It shows that glow peak IIc disappears almost entirely after 12 h. This suggests that the hole release from a shallow host related hole trap at RT and recombination on Eu$^{2+}$ may be responsible for the Eu$^{3+}$ afterglow.

Fig. S11. Thermoluminescence excitation (TLE) spectrum of LaPO$_4$:0.005Eu$^{3+}$,0.005Bi$^{3+}$ and photoluminescence excitation (PLE) spectrum of LaPO$_4$:0.005Eu$^{3+}$ monitoring the Eu$^{3+}$ 590 nm emission recorded at room temperature.

TL excitation (TLE) spectra for LaPO$_4$:0.005Eu$^{3+}$,0.005Bi$^{3+}$ were recorded by first illuminating the samples during 4000 s with a monochromatic photon beam generated using a 150 W xenon arc lamp (Hamamatsu L2273) filtered by a monochromator (Oriel Cornerstone...
This system has a wavelength resolution of 0.8 nm against 0.1 mm slit width. The slit width was set to 1 mm and the wavelength step as 10 nm. A LabVIEW program was used to record TL glow curves in 300-700 K at a heating rate of 5 K/s when the excitation wavelengths change between 200 and 300 nm.

To investigate the origin of glow peaks I and IIC, Fig. S11 shows the thermoluminescence excitation (TLE) spectrum of the TL glow peak between 300-500 K for LaPO₄:0.005Eu³⁺, 0.005Bi³⁺. A broad TL excitation band extending from 200 to 300 nm and peaking at 240 nm is detected. The position and width resembles with the VB→Eu³⁺ charge transfer band of LaPO₄:0.005Eu³⁺, where the band width is identical but it appears 10 nm blue shifted corresponding with 0.2 eV. During CT band excitation, electrons are excited from the valence band to 4f⁷⁶ (⁸S⁷/₂) of Eu²⁺ and holes are generated in the valence band which can then be trapped by host intrinsic hole trapping center. During TL readout, the holes release from hole trapping centers and then recombine with Eu²⁺ to yield Eu³⁺ 4f-4f emission. The 0.2 eV blue shift in band location may imply that the hole trap is far from Eu³⁺, which is not conducive to hole release.

![Graph](image)

Fig. S12. Fluorescence lifetimes of YPO₄:0.005Bi³⁺,0.005Ln³⁺ (Ln=Pr, Tb, and Ce) samples monitoring Bi³⁺ emission at 245 nm.

From the study in Ref. [5, 6] there are spectral overlaps between the Bi³⁺ A-band emission and the excitation bands of Ce³⁺, Pr³⁺, and Tb³⁺, which suggests that there is a probability for the energy transfer from Bi³⁺ to Ce³⁺, Pr³⁺, or Tb³⁺⁷⁻⁹. To further show the energy transfer processes, Fig. S12 shows photoluminescence decay curves of the Bi³⁺ A-band emission in YPO₄:0.005Bi³⁺,0.005Ln³⁺. For YPO₄:0.005Bi³⁺, the decay curve can be well fitted by a single exponential function which can be written as

\[ I(t) = I_0 \times \exp\left(-\frac{t}{\tau}\right) \]  

(1)
where \( I_0 \) and \( I_1 \) are emission intensities of a sensitizer Bi\(^{3+}\) in the absence and presence of an activator Ce\(^{3+}\), Tb\(^{3+}\), or Pr\(^{3+}\), respectively. The lifetime of the Bi\(^{3+}\) A-band emission in YPO\(_4\):0.005Bi\(^{3+}\) is derived to be 0.98 \( \mu \)s using Eq. (1). With the co-doping of Ce\(^{3+}\), Tb\(^{3+}\), or Pr\(^{3+}\), decay curves deviate from single exponential function and the Bi\(^{3+}\) lifetime decreases. This indicates that the co-doping Ln\(^{3+}\) modifies the luminescence dynamic of Bi\(^{3+}\) because of the energy transfer from Bi\(^{3+}\) to Ln\(^{3+}\).

![TL glow curves of YPO\(_4\):0.005Bi\(^{3+}\),0.005Ce\(^{3+}\) recorded at different heating rates of 1 and 5 K/s after 400 s \( \beta \) source irradiation. A Hoya C5-58 filter was utilized to select Ce\(^{3+}\) emission.](image1)

![TL glow curve of YPO\(_4\):0.005Eu\(^{3+}\),0.005Bi\(^{3+}\) charged by a laser beam at 212 nm for 600 s recorded at a heating rate of 5 K/s. The Eu\(^{3+}\) red emission was monitored.](image2)
Fig. S15. X-ray excited emission spectrum for YPO₄: 0.05mol%Bi sample recorded at room temperature. The data were obtained from Awater et al. [10].

The emission band peaked at 670 nm has been ascribed in Ref. [10] to Bi²⁺ ²P₃/₂→²P₁/₂ transition, which is induced via the capturing of an electron from the conduction band by Bi³⁺ to form the excited state of Bi²⁺.

Reference