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Liquid nitrogen temperature to 700 K Bi3+ thermoluminescence

Toward wide-temperature-range light dosimeters for versatile anti-counterfeiting, information storage, and x-ray imaging

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Liquid nitrogen temperature to 700 K Bi³⁺ thermoluminescence: Toward wide-temperature-range light dosimeters for versatile anti-counterfeiting, information storage, and x-ray imaging

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ABSTRACT

Discovering light dosimeters that can function effectively from liquid nitrogen temperature to 700 K presents significant challenges. Such dosimeters facilitate a range of cutting-edge applications, including anti-counterfeiting measures at low temperature for cryo-preservation. To facilitate such discovery, stacked vacuum referred binding energy diagrams for the LiYGeO₄ cluster of crystals have been first constructed. They offer a robust method for controlling both electron and hole trapping depth in the LiYGeO₄ cluster of crystals. Wide temperature shifting of Bi^{2+} and Eu^{2+} thermoluminescence (TL) glow bands emerges from 200 to 500 K for $LiY_xLu_{1-x}GeO_4:0.01Bi^{3+}$ and $LiY_xLu_{1-x}GeO_4:0.01Bi^{3+}$, $0.001Eu^{3+}$, by changing x, facilitating conduction band tailoring. Wide temperature shifting of Bi^{4+} TL glow bands emerges from 300 to 700 K for $LiYGe_2Si_{1-2}O_4:0.01Bi^{3+}$, by tuning z, facilitating valence band tailoring. TL glow band peaks near 135, 185, 232, and 311 K emerge in $Li_yNa_{1-y}YGeO_4:0.001Bi^{3+}$. Particularly, the discovered Bi^{3+} or/and lanthanide modified $LiYGeO_4$ cluster of crystals exhibit superior charge carrier storage capacity and minimal TL fading properties. For instance, the ratio of TL intensity of the optimized $LiYGe_{0.75}Si_{0.25}O_4:0.001Bi^{3+}$ to that of industrial BaFBr(I): Eu^{2+} is as high as ~4. Interestingly, imaging of intense optically driven Bi^{3+} ultraviolet-A (UVA) luminescence has been validated in 254 nm energized $LiY_{0.25}Lu_{0.75}GeO_4:0.01Bi^{3+}$ with a 100 lux white LED illumination. Together with ZnS: Mn^{2+} , $LiTaO_3:Bi^{3+}$, Sm^{3+} , and $Cs_2ZrCl_6:Sb^{3+}$ perovskites, the realization of wide range liquid nitrogen temperature to 700 K Bi^{3+} thermoluminescence in Bi^{3+} or/and lanthanide modified $LiYGeO_4$ cluster of crystals with superior charge carrier storage capacity offers promising use for versatile anti-counterfeiting, information storage, and delayed x-ray imaging purposes.

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I. INTRODUCTION

A persistent luminescence or radiographic phosphor is known as an energy storage dosimeter, which stores free electrons and holes in traps after being subjected to excitation sources like x-ray, β -ray, γ -ray, or high energy ultraviolet light in the dark.¹ The electrons or holes preserved in traps can be discharged at later times to produce photon emission upon optical,^{2,3} thermal,^{4,5} or mechanical stimulation.^{6–8} Such energy conservation materials then serve various purposes, for instance, in dosimetry,⁹ information storage,¹⁰ anti-counterfeiting,⁸ temperature sensing,¹¹ x-ray computed radiography (CR),^{12,13} and force sensing.^{6,14} However, most energy conservation phosphors are analyzed at room temperature (RT)^{5,15,16} or well above RT.¹⁷ Very rare reports are published that discuss the properties of persistent luminescence or radio-graphic phosphors that can be conducted in the low temperature range from 100 to 300 K. Recently, a Ge, Er, or Ce co-doped BaSi₂O₂N₂:Eu²⁺ energy storage material was reported in Ref.18. Interesting Eu²⁺

11, 041417-1

mechanoluminescence and persistent luminescence features are observed at 77 K. Possibly intrinsic defects behave as charge carrier capturing centers in those materials. However, the energy level locations of these intrinsic defects remain unidentified. The nature of charge carrier capture and discharge processes remains partially unclear. Scientific discovery of such energy storage materials performed at low temperatures then is a crucial scientific question but still remains a challenge.

Bismuth is an interesting element, which has a [Xe]4f¹⁴5d¹⁰6s²6p³ electronic configuration.¹⁹ Bismuth with different valence states can be formed by losing electrons from the outermost shell.²⁰ The most interesting valence states are Bi^{2+} (6p¹), Bi^{3+} (6s²), and Bi^{4+} (6s¹). Bi^{3+} is often doped to crystals to obtain photoluminescent phosphors for white light-emitting diode (WLED) purposes.^{15,21} Interest in energy storage materials modified with Bi has increased during the past years. However, charge carrier trapping and liberation processes in energy storage materials modified with Bi frequently lack of clarity.²² One rationale is that bismuth has many valence states with complicated electronic transitions. The energy level locations in crystals frequently remain unidentified. It becomes problematic to realize a convincing understanding of how electrons or holes are confined or discharged in traps with various excitation sources in Bi²⁺, Bi³⁺, or/and Bi⁴⁺ modified crystals.²³ In 2012, a chemical shift model was proposed in Ref. 24 to establish a vacuum referred binding energy (VRBE) diagram for lanthanides modified inorganic crystals. It facilitates a good discussion on charge carrier capture and discharge processes between lanthanides.

More than 300 h Bi³⁺ persistent luminescence has been claimed in LiYGeO₄:Bi³⁺ after exposure to 254 nm ultraviolet light at room temperature (RT).²⁵ Unique ultraviolet Bi³⁺ A-band mechanoluminescence emerges in LiYGeO₄:Bi³⁺ after exposure to compression force at RT.²⁶ This implies that Bi³⁺ modified LiYGeO₄ is an interesting crystal. However, the storage properties of LiYGeO₄:Bi³⁺ below RT remain unknown. Furthermore, the VRBE diagram with the energy level locations of Bi²⁺, Bi³⁺, and Bi⁴⁺ has not been disclosed yet. This conveys that a convincing understanding of charge carrier capturing and discharge processes is not reached. Particularly, an idea about the realization of liquid nitrogen temperature to 700 K Bi³⁺ thermoluminescence has not been proposed by applying electron discharge from Bi²⁺ or hole discharge from Bi⁴⁺ in LiYGeO₄ cluster of crystals.

Discovering light dosimeters^{9,27} that can work from liquid nitrogen temperature to 700 K is challenging. Such dosimeters facilitate various cutting-edge applications, such as anti-counterfeiting measures at low temperature for cryo-preservation.^{28,29} In this work, to facilitate such discovery, photoluminescence excitation and emission spectra for undoped host, Tb³⁺, Pr³⁺, Eu³⁺, or Bi³⁺ single modified LiYGeO₄ have been first analyzed from deep ultraviolet to visible range at 10 K or RT. Outcomes have been adopted to create a vacuum referred binding energy (VRBE) diagram comprising the energy level locations of excited and ground states of Bi3+ and different lanthanides for LiYGeO₄ as exhibited in Fig. 1(a). The VRBE in the Bi^{2+ 2}P_{1/2} ground state will be experimentally deduced to be $\sim -3.46 \text{ eV}$ in LiYGeO₄ by TL study. Stacked VRBE diagrams for LiYGeO4 cluster of crystals will then be constructed as shown in Fig. 1(b). They provide a powerful method to guide tailoring of both electron and hole trapping depth in the LiYGeO₄ cluster of crystals. As depicted in Fig. 1(c), mechanisms on how electrons or holes are confined or discharged have been unraveled by combining VRBE diagrams with detailed spectroscopy and thermoluminescence studies.

Figure 1(d) illustrates that a recyclable light dosimeter is designed by using wide range liquid nitrogen temperature to 700 K Bi^{3+} thermoluminescence in the Bi^{3+} or/and lanthanides modified LiYGeO₄ cluster of crystals with outstanding charge carrier storage capacity. Such dosimeters have been exploited for potential implementation for versatile anti-counterfeiting, information storage, and x-ray imaging purposes. This work not only initiates how to scientifically realize wide range liquid nitrogen temperature to 700 K Bi^{3+} thermoluminescence, but more crucially can encourage chemists to discover new light dosimeters by creating and applying VRBE diagrams with energy level location of Bi^{2+} , Bi^{3+} , and various lanthanides for inorganic crystals.

II. RESULTS

A. X-ray diffraction patterns and photoluminescence spectroscopy for VRBE diagram establishment

Figures 2(a) and 2(b) present x-ray diffraction (XRD) patterns for the prepared LiY_xLu_{1-x}GeO₄: 0.01Bi³⁺, 0.001Eu³⁺ (x = 0-1) crystals. Compared with the LiYGeO₄ reference card (No. 314874), XRD peaks gradually shift toward a lower 2-theta angle with increasing x. This implies that the cell volume is slightly increased when the smaller Lu³⁺ site is partly occupied by Y³⁺ ions. New solid solutions emerge in LiY_xLu_{1-x}GeO₄:0.01Bi³⁺, 0.001Eu³⁺ when 0<x < 1. The similar applies for the Li_yNa_{1-y}YGeO₄:0.001Bi³⁺ (y = 0-1) in Fig. S2.

Figure 2(c) shows the XRD patterns for the fabricated LiYGe_zSi_{1-z} O₄:0.01Bi³⁺ with different concentrations of Ge⁴⁺. Compared with the LiYSiO₄ reference card (No. 314868), XRD peaks slightly shift toward a smaller 2-theta angle with rising z. This is because the cell volume is slightly increased when the Si⁴⁺ site is occupied by the larger Ge⁴⁺ cations. New solid solutions are created in LiYGe_zSi_{1-z}O₄:0.01Bi³⁺ when 0 < z < 1.

To set up a vacuum referred binding energy (VRBE) diagram for LiYGeO₄, optical properties of undoped, Bi³⁺, or lanthanides modified LiYGeO₄ crystals have been first assessed. Figures 3(a) and 3(b) present photoluminescence excitation (PLE) and emission (PL) spectra for undoped, 0.5% Eu³⁺ or 1% Bi³⁺ modified LiYGeO₄ quantified at 10 K.

Upon 194 nm excitation, the emission spectrum of undoped LiYGeO₄ comprises two broad emission bands peaked near 303 and 446 nm in Fig. 3(b). They will be assigned to recombination emissions from exciton and defect(s), respectively. Monitored at the strongest emission at 303 nm, a strong excitation band peaked at ~194 nm and a narrow band peaked at ~162 nm are found in the excitation spectrum of the undoped LiYGeO₄ and an artifact. The 162 nm artifact arises because the deuterium lamp excitation spectrum exhibits a strong peak at 162 nm that could not be fully corrected.

Upon 232 nm excitation, LiYGeO₄: $0.005Eu^{3+}$ exhibits typical $Eu^{3+} {}^{5}D_{0} \rightarrow {}^{7}F_{j}$ emissions in the spectral range from 500 to 700 nm in Fig. 3(b). Monitored at 612 nm, a broad excitation band that peaks near 232 nm is observed in Fig. 3(a), which compares well with the value tabulated in Ref. 30. It has been assigned to charge transfer (CT) from valence band (VB) to Eu^{3+} , i.e., $VB \rightarrow Eu^{3+}$ CT.³¹

Upon 230 nm excitation, LiYGeO₄:0.01Bi³⁺ exhibits a strong and narrow emission band peaked near 363 nm at 10 K in Fig. 3(b). The full-width at half-maximum (FWHM) for this emission band is \sim 29 nm. 95% emission emerges in the ultraviolet-A (UVA) range from 315 to 400 nm. Like in Ref. 32, the emission band is attributed to



FIG. 1. (a) and (b) Vacuum referred binding energy (VRBE) diagrams for LiYGeO₄ cluster of crystals. The energy level locations of Bi^{3+} , Bi^{2+} , or different lanthanides are exhibited. Experimentally found transitions are also displayed in (a). (c) Illustration of the valence change between Bi^{2+} , Bi^{3+} , and Bi^{4+} . (d) Illustration of a recyclable light dosimeter by engaging Bi^{2+} or Bi^{4+} as electron or hole traps.



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FIG. 3. Photoluminescence excitation (PLE) and emission spectra (PL) for (a) until (d) undoped, Eu³⁺, Pr³⁺, Tb³⁺, or Bi³⁺ single doped LiYGeO₄ at 10 K, (e) and (f) Li_yNa_{1-y}YGeO₄:0.01Bi³⁺ at RT, (g) and (h) LiY_xLu_{1-x}GeO₄:0.01Bi³⁺ at 10 K, and (i) until (l) 2D contour plots of PL spectra and integrated PL intensities as a function of temperature upon excitation at 230 or 292 nm.

Bi³⁺ ³P₁→ ¹S₀ transition. The absolute light yield of LiYGeO₄: 0.01Bi³⁺ in the visible range is about 0.10 and 0.02 cd/cm² in the dark upon and after illumination of a Hg lamp for 60 s. Different from that in Ref. 25, a new and complete excitation spectrum ($\lambda_{em} = 363$ nm) was observed for LiYGeO₄:0.01Bi³⁺ in the spectral range from 145 to 350 nm at 10 K in Fig. 3(a). The excitation spectrum comprises

excitation bands peaked near 202, 230, 297, and 308 nm. Unlike in Ref. 25, the excitation band peaked at 230 nm is not assigned to intrinsic absorption of LiYGeO₄ host, but it will be associated with charge transfer from Bi^{3+} $^{1}\text{S}_{0}$ ground state to the conduction band, i.e., Bi^{3+} D-band.³³ The excitation band peaked at ~202 nm will be assigned to Bi^{3+} $^{1}\text{S}_{0} \rightarrow ^{1}\text{P}_{1}$ transition, i.e., Bi^{3+} C-band. The low energy two

excitation bands peaked near 297 and 308 nm have been assigned to Bi^{3+} Jahn–Teller split ${}^{1}S_{0} \rightarrow {}^{3}P_{1}$ transition.³⁴

To further recheck the created VRBE diagram for LiYGeO₄, Pr^{3+} or Tb^{3+} single modified LiYGeO₄ has been assessed. The excitation spectrum ($\lambda_{em} = 605 \text{ nm}$) of LiYGeO₄:0.01Pr^{3+} observed at 10 K in Fig. 3(c) comprises four excitation bands peaked near 255.5, 237, 195, and 162 nm. They have been associated with Sec. III to intervalence charge transfer (IVCT) from $Pr^{3+} 4f^2$ ground state to conduction band of LiYGeO₄ that overlaps with the first $4f \rightarrow 5d$ excitation band of Pr^{3+} , the second $Pr^{3+} 4f \rightarrow 5d$ transition, host exciton creation, and an artifact by the deuterium lamp correction, respectively.

Figure 3(d) shows the an excitation spectrum ($\lambda_{em} = 548$) of LiYGeO₄:0.01Tb³⁺ at RT. Like in Figs. 3(a) and 3(c), an excitation band peaked near 162 nm is also found, which is attributed to the presence of artifact because of deuterium lamp correction. Unstructured excitation shoulder peaked near 195 nm emerges, which is related to host exciton creation. The low-energy excitation bands peaked near 232, 249, and 296 nm are associated with Tb³⁺ 4f \rightarrow 5d transitions. The excitation band peaked near 265 nm will be associated with Tb³⁺ \rightarrow CB IVCT. The weak and sharp excitation bands peaked near \sim 320 and \sim 379 nm are assigned to typical Tb³⁺ 4f \rightarrow 4f transitions.

To elucidate the nature of Bi³⁺ luminescence, Bi³⁺ single modified LiYGeO₄ cluster of crystals has been assessed. Figures 3(e) and 3(f) show PLE ($\lambda_{em} = 410, 400, 390, \text{ or } 360 \text{ nm}$) and PL ($\lambda_{ex} = 232 \text{ nm}$) spectra for Li_yNa_{1-y}YGeO₄:0.001Bi³⁺ (y = 0-1) crystals. With increasing y, the Bi³⁺ A-, C-, and D-excitation bands remain still, while the Bi^{3+ 3}P₁ \rightarrow ¹S₀ emission band gradually shifts from ~394 to ~360 nm.

Figures 3(g) and 3(h) show the PLE ($\lambda_{em} = 363 \text{ nm}$) and PL ($\lambda_{ex} = 230 \text{ nm}$) spectra for LiY_xLu_{1-x}GeO₄:0.01Bi³⁺ (x = 0-1) at 10 K. With increasing x, the Bi³⁺ A-, C-, and D-excitation bands remain steady, while the Bi³⁺ emission A-band slightly shifts from 361 to 364 nm.

Figures 3(i) and 3(j) show the 2D contour plots of temperature dependent photoluminescence (PL) emission spectra of LiYGeO₄: $0.01Bi^{3+}$ and LiY_{0.25}Lu_{0.75}GeO₄: $0.01Bi^{3+}$ upon 230 nm excitation. The integrated PL intensities as a function of temperature for LiYGeO₄: $0.01Bi^{3+}$ and LiY_{0.25}Lu_{0.75}GeO₄: $0.01Bi^{3+}$ upon 230 or 292 nm excitation are shown in Figs. 3(k) and 3(l). With increasing temperature, negative thermal quenching phenomenon is found. The same applies for other LiYGeO₄ cluster of crystals as shown in Figs. S6–S10.

B. Analyzing recombination and luminescence centers in Bi³⁺ or/and lanthanides modified LiYGeO₄ cluster of crystals

To analyze recombination and luminescence centers, Figs. 4 and S11 show the thermoluminescence emission (TLEM) spectra at $\beta = 1 \text{ K/s}$ for Bi³⁺ or/and lanthanides modified LiYGeO₄ cluster of crystals after being energized by γ -rays. Figure 4(a) first shows the TLEM spectra for γ -ray energized LiYGeO₄:0.01Bi³⁺. TL glow bands peaked near 384 and 436 K with typical Bi³⁺ ${}^{3}P_{1} \rightarrow {}^{1}S_{0}$ emission emerge. They have been related to electron bonding defects. Bi³⁺ behaves as a recombination and luminescence center in Li_{0.5}Na_{0.5}YGeO₄: 0.001Bi³⁺ in Fig. 4(b) and LiLuGeO₄:0.01Bi³⁺ in Fig. 4(c). The same applies to other Bi³⁺ co-doped LiYGeO₄ cluster of crystals as shown in Figs. 4 and S11.

Figure 4(d) shows the TLEM spectra for LiY_{0.75}Lu_{0.25} GeO₄:0.01Bi³⁺. TL glow bands peaked near 382, 442, and 538 K with Bi^{3+ 3}P₁ \rightarrow ¹S₀ emission are observed. They will be assigned to electron

discharge from electron capturing defects and recombination with the hole kept at Bi^{4+} . Figure 4(e) shows the TLEM spectra for $LiY_{0.75}Lu_{0.25}GeO_4:0.01Bi^{3+}, 0.001Eu^{3+}$. Both $Bi^{3+} {}^{3}P_1 \rightarrow {}^{1}S_0$ and $Eu^{3+} {}^{5}D_0 \rightarrow {}^{7}F_j$ emissions are found. Bi^{3+} emission is about 62 times stronger than that of Eu^{3+} . Different than that in Fig. 4(d), only a TL glow band peaked at 464 K is found in Fig. 4(e). It will be attributed to electron discharge from Eu^{2+} and recombination with the hole confined at Bi^{4+} . $Eu^{3+} {}^{5}D_0 \rightarrow {}^{7}F_j$ emissions are achieved via an energy transfer process of $Bi^{3+} \rightarrow Eu^{3+}$.

To further confirm whether Eu^{3+} behaves as an electron bonding center, Figs. 4(f) and 4(g) compare the TLEM spectra of LiYGeO₄:0.005Pr³⁺, 0.001Eu³⁺, and LiYGeO₄:0.005Tb³⁺, 0.001Eu³⁺ after being energized by γ -rays in the dark. A common TL glow band peaked near 492 K but with characteristic Pr³⁺ or Tb³⁺ 4f \rightarrow 4f emissions is found. It will be associated with electron discharge from Eu²⁺ to recombine with the hole preserved at Pr⁴⁺ or Tb⁴⁺, contributing to typical Pr³⁺ or Tb³⁺ 4f \rightarrow 4f transitions.

Figure 4(h) shows the TLEM spectra for LiYGe_{0.5}Si_{0.5}O₄:0.01Bi³⁺ after being subjected to gamma rays. Compared with LiYGeO₄: 0.01Bi³⁺ in Fig. 4(a), typical Bi³⁺ ${}^{3}P_1 \rightarrow {}^{1}S_0$ emission but with a single TL glow band peaked at about 467 K is found. Herein, it is defined as the Bi⁴⁺ TL glow band. It will be assigned in Sec. III to hole discharge from Bi⁴⁺ to recombine with the electron preserved at Bi²⁺, facilitating typical Bi³⁺ ${}^{3}P_1 \rightarrow {}^{1}S_0$ emission. With increasing Si⁴⁺ concentration, a higher temperature Bi⁴⁺ TL glow band peaked near 515 K is found in the temperature range from 400 to 650 K in LiYGe_{0.25}Si_{0.75}O₄:0.01Bi³⁺ as shown in Fig. 4(1). It has been related to increased Bi⁴⁺ hole bonding depth with increased Si⁴⁺ content.

C. Proving electron discharge from ${\rm Bi}^{2+}$ and ${\rm Eu}^{2+}$ in LiYGeO4 cluster of crystals

To elucidate charge carrier trapping and discharge processes, Bi³⁺ or/and lanthanides modified LiYGeO₄ cluster of crystals have been carefully assessed. Figure 5(a) first shows the above 100 K TL glow curves at $\beta = 1$ K/s for LiY_xLu_{1-x}GeO₄:0.01Bi³⁺ (x = 0–1) after being subjected to β -rays at 100 K. For x = 0, a TL glow band peaked near 254 K emerges. Herein, it is defined as a Bi²⁺ TL glow band. It will be ascribed to electron discharge from Bi²⁺ to recombine with the hole preserved at Bi⁴⁺, facilitating Bi³⁺ ${}^{3}P_{1} \rightarrow {}^{1}S_{0}$ emission. Particularly, with increasing x, the Bi²⁺ TL glow band gradually shifts from 254 to 321 K in LiY_xLu_{1-x}GeO₄:0.01Bi³⁺. It will be ascribed to slightly increased Bi²⁺ electron trapping depth because of slight rising of the VRBE at the conduction band bottom of LiY_xLu_{1-x}GeO₄: 0.01Bi³⁺ when x increases.

Figure 5(b) shows the above 100 K TL glow curves observed at $\beta = 1 \text{ K/s}$ for Li_yNa_{1-y}YGeO₄:0.001Bi³⁺ after being subjected to β -rays at 100 K. For LiYGeO₄:0.001Bi³⁺ (y = 1), a TL glow band peaked near 324 K is found, which is the same as the Bi²⁺ TL glow band in LiYGeO₄:0.01Bi³⁺ in Fig. 5(a). With decreasing y from 1 to 0, the Bi²⁺ TL glow band slightly shifts from 324 K for y = 1-311 K for y = 0 in Fig. 5(b). This will be due to slightly decreased Bi²⁺ electron capturing depth as a result of slight lowering of the VRBE at the conduction band bottom of Li_vNa_{1-v}YGeO₄:0.001Bi³⁺.

 ${\rm Bi}^{3+}$ can confine an electron and also capture a hole in crystals. To verify whether ${\rm Bi}^{3+}$ behaves as a hole trapping and recombination center, ${\rm Bi}^{3+}$ and ${\rm Eu}^{3+}$ co-doped ${\rm LiY_xLu_{1-x}GeO_4}$ crystals have been assessed. Figure 5(c) shows the above 300 K TL glow curves of

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FIG. 4. Thermoluminescence emission (TLEM) plots for (a) until (l) Bi^{3+} or/and Ln^{3+} (Ln = Eu, Pr, or Tb) modified LiYGeO₄ cluster of crystals measured at a heating rate of 1 K/s after being energized by γ -rays.

LiY_xLu_xGeO₄:0.01Bi³⁺, 0.001Eu³⁺ (x = 0-1) after being subjected to β -rays at 300 K in the dark. For x = 0, a TL glow band peaked near 417 K is observed. It will be defined as the Eu²⁺ TL band and assigned to electron discharge from Eu²⁺ to recombine with the hole preserved at Bi⁴⁺ to create Bi³⁺ ³P₁ \rightarrow ¹S₀ luminescence, which is depicted in the legend of Fig. 5(c). Particularly, with increasing x, the Eu²⁺ TL band gradually shifts from 417 K for x = 0 to 473 K for x = 1. Like in Fig. 5(a), it will be ascribed to increased Eu²⁺ electron trap depth owing to the rise of VRBE at the conduction band bottom of LiY_xLu_xGeO₄:0.01Bi³⁺, 0.001Eu³⁺ with increasing x in Fig. 1(b).

Assuming that a TL glow band is realized through a first-order recombination kinetics, one can roughly assess trapping parameters by using a variable heating rate plot with the following equation:³⁵

$$\ln\left(\frac{T_m^2}{\beta}\right) = \frac{E}{kT_m} + \ln\left(\frac{E}{ks}\right),\tag{1}$$

where E implies the trapping depth (eV), T_m is the temperature at the maximum of a TL glow peak (K), β is the adopted heating rate (K/s), k denotes Boltzmann constant (eV/K), and s implies the frequency factor (s⁻¹) for the assessed crystal. Figure 5(d) shows the variable heating rate plots of LiY_xLu_xGeO₄:0.01Bi³⁺, 0.001Eu³⁺. The determined trapping depths and frequency factors are presented in the legend of Fig. 5(d).

To understand how charge carriers are confined, thermoluminescence excitation (TLE) spectra were quantified for Bi³⁺ or/and lanthanides modified LiYGeO₄ cluster of crystals.³⁶ Figures 5(e)–5(h) show the 2D contour plots of TLE spectra of LiYGeO₄:0.01Bi³⁺, LiYGeO₄:0.01Bi³⁺, 0.001Eu³⁺, LiYGeO₄:0.005Tb³⁺, 0.001Eu³⁺, and LiYGeO₄:0.005Pr³⁺, 0.001Eu³⁺. The similar 2D contour plots for other LiYGeO₄ cluster of crystals are shown in Figs. S13–S15. For Bi³⁺ co-doped samples, traps can be filled through the Bi³⁺ D-band excitation. For Tb³⁺ or Pr³⁺ co-doped samples, traps can be filled via the 15 November 2024 10:37:42

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FIG. 5. TL glow curves observed at $\beta = 1 \text{ K/s}$ for (a) LiY_xLu_{1-x}GeO₄:0.01Bi³⁺ (x = 0–1), (b) Li_yNa_{1-y}YGeO₄: 0.001Bi³⁺ (y = 0–1), (c) LiY_xLu_{1-x}GeO₄:0.01Bi³⁺, 0.001Eu³⁺. and (d) Variable heating rate plots for LiY_xLu_{1-x}GeO₄:0.01Bi³⁺, (e)–(h) 2D contour plots of thermoluminescence excitation spectra observed at $\beta = 5 \text{ K/s}$ for Bi³⁺ or/and Li³⁺ modified LiYGeO₄ after being irradiated by different energy photons.

Tb³⁺ 4f \rightarrow 5d, Tb³⁺ \rightarrow CB IVCT, Pr³⁺ 4f \rightarrow 5d, and Pr³⁺ \rightarrow CB IVCT excitations.

D. Scientific design of Bi³⁺ persistent luminescence and radiographic phosphors by tailoring electron discharge from Bi²⁺ and Eu²⁺ in LiYGeO₄ cluster of crystals

The strategy by tailoring electron discharge from Bi²⁺ or Eu²⁺ has been exploited in the LiYGeO₄ cluster of crystals for discovering Bi³⁺ based persistent luminescence and radiographic phosphors. Figure 6(a) presents above 300 K TL glow curves of Li_yNa_{1-y}YGeO₄: 0.001Bi³⁺ (y=0-1) after beta irradiation at 300 K in the dark. The integrated TL intensity from 300 to 723 K of Li_yNa_{1-y}YGeO₄:0.001Bi³⁺ to that of the industrial SrAl₂O₄:Eu²⁺, Dy³⁺, BaFBr(I):Eu²⁺, or Sr₂MgSi₂O₇:Eu²⁺, Dy³⁺ is presented in the legend of Fig. 6(a), respectively. Li_yNa_{1-y}YGeO₄:0.001Bi³⁺ crystals have outstanding charge

carrier storage capacity. A strong TL glow band peaked near 333 K emerges. The close proximity to room temperature implies that intense Bi³⁺ persistent luminescence is expected at RT. This is proved by the persistent luminescence photographs in Fig. 6(b) and more than 2 h RT isothermal decay curves of Li_yNa_{1-y}YGeO₄:0.001Bi³⁺ after being energized by beta irradiation in Fig. 6(c).

Figure 6(d) shows the above 100 K TL glow curves of LiY_xLu_{1-x} GeO₄:0.01Bi³⁺ after being irradiated by beta irradiation at 100 K. For x = 0.5-1, the Bi²⁺ TL glow band covers the temperature range from 300 to 350 K. This implies that recombination of electrons thermally discharged from Bi²⁺ at RT with the holes preserved at Bi⁴⁺ will yield Bi^{3+ 3}P₁ \rightarrow ¹S₀ persistent luminescence. This is proved by RT TL fading properties in Fig. 6(e) and more than 2 h RT isothermal Bi³⁺ decay curves of LiY_xLu_{1-x}GeO₄:0.01Bi³⁺ in Fig. 6(f).

The x = 0.75 sample has relatively strong initial Bi³⁺ ${}^{3}P_{1} \rightarrow {}^{1}S_{0}$ persistent luminescence intensity after being energized by β -ray irradiation at RT in the dark in Fig. 6(f). We therefore analyze it further.



FIG. 6. (a) Above 300 K TL glow curves at $\beta = 1$ K/s, (b) afterglow photographs, and (c) RT isothermal decay curves after β -ray charging for Li_yNa_{1-y}YGeO₄:0.001Bi³⁺. (d) Above 100 K TL glow curves at $\beta = 1$ K/s, (e) TL fading properties, (f) RT isothermal decay curves after β -ray charging, and RT isothermal decay curves after β -ray charging for LiY_xLu_{1-x}GeO₄:0.01Bi³⁺. (g) Above 300 K TL glow curves at $\beta = 1$ K/s, (h) (i) RT isothermal decay curves, and (j) TL fading properties after exposure to β -rays for LiY_{0.75}Lu_{0.25}GeO₄: mBi³⁺. The Bi³⁺ emission was monitored. A SEM image of LiY_{0.75}Lu_{0.25}GeO₄:0.004Bi³⁺ is shown in (i).

Figure 6(g) presents above 300 K TL glow curves of optimized $LiY_{0.75}Lu_{0.25}GeO_4:mBi^{3+}$ (x = 0.0005–0.006) fabricated at 1200 °C for 24 h after being irradiated by β -rays. The ratios of the integrated TL intensity of $LiY_{0.75}Lu_{0.25}GeO_4:mBi^{3+}$ to that of BaFBr(I):Eu²⁺ or SrAl₂O₄:Eu²⁺, Dy³⁺ are presented in the legend of Fig. 6(g). $LiY_{0.75}Lu_{0.25}GeO_4:0.004Bi^{3+}$ has the highest charge carrier storage capacity.

Figure 6(h) shows RT isothermal decay curves of LiY_{0.75}Lu_{0.25}GeO₄:mBi³⁺ after being energized by β -rays. More than 10 h Bi^{3+ 3}P₁ \rightarrow ¹S₀ persistent luminescence is recordable in all LiY_{0.75}Lu_{0.25}GeO₄:mBi³⁺ samples. For the m = 0.004 sample, the Bi³⁺ persistent luminescence intensity is about 87% at t = 0.01 h and \sim 100% at t = 0.6 h of the industrial SrAl₂O₄:Eu²⁺, Dy³⁺. This implies that in terms of persistent luminescence intensity and duration, the material is about the same as that of the most successful industrial persistent luminescence phosphor SrAl₂O₄:Eu²⁺, Dy³⁺. The crucial difference is the emission. SrAl₂O₄:Eu²⁺, Dy³⁺ emits in the green where eye

sensitivity is maximum. The m = 0.004 sample emits in the UVA and blue range from 300 to 500 nm. Particularly, Fig. 6(i) further proves that more than 50 h Bi³⁺ ³P₁ \rightarrow ¹S₀ persistent luminescence is measurable in the best LiY_{0.75}Lu_{0.25}GeO₄:0.004Bi³⁺ after β -ray irradiation. Such long Bi³⁺ A-band persistent luminescence is attributed to gradual thermal discharge of electrons from Bi²⁺, which is indicated by the TL glow curves with different fading times in Fig. 6(j).

For use in radiographic phosphor technology, deep traps (>~0.9 eV) are required to prevent rapid fading of preserved information at RT. Bi³⁺ and Eu³⁺ are therefore co-doped into the LiYGeO₄ cluster of crystals to discover radiographic phosphors. Figure 7(a) shows TL glow curves at $\beta = 1$ K/s of β -ray energized LiY_xLu_{1-x}GeO₄: 0.01Bi³⁺, 0.001Eu³⁺. The ratios of integrated TL intensity from 300 to 723 K of LiY_xLu_{1-x}GeO₄: 0.01Bi³⁺, 0.001Eu³⁺ to that of the industrial BaFBr(I):Eu²⁺ radiographic phosphor are presented in the legend of Fig. 7(a). All crystals offer good charge carrier storage capacity. The

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FIG. 7. (a)–(e) TL glow curves collected at $\beta = 1$ K/s, RT isothermal decay curves, and TL fading properties after being irradiated by β -rays in the dark for LiY_xLu_{1-x}GeO₄:0.01Bi³⁺, 0.001Eu³⁺ and LiY_xLu_{1-x}GeO₄:0.001Bi³⁺, 0.001Eu³⁺. (f) TL glow curves at $\beta = 1$ K/s of LiY_{0.5}Lu_{0.5}GeO₄:0.01Bi³⁺, 0.001Eu³⁺ after being energized by β -rays with different durations from 30 to 600 s. (g) TL glow curves at $\beta = 5$ K/s after first being irradiated by β -rays for 60s and then triggered by 475 nm light for 10s. (h), (k) Stability test of TL glow curves after β -ray charging for a typical LiY_{0.5}Lu_{0.5}GeO₄:0.01Bi³⁺, 0.001Eu³⁺.

Eu²⁺ TL glow band shifts from 417 K for x = 0 to 473 K for x = 1. Figure 7(b) shows RT isothermal decay curves of LiY_xLu_{1-x}GeO₄: 0.01Bi³⁺, 0.001Eu³⁺ after being energized by β -rays. The Bi³⁺ persistent luminescence intensities from LiY_xLu_{1-x}GeO₄:0.01Bi³⁺, 0.001Eu³⁺ are much weaker compared with the industrial SrAl₂O₄: Eu²⁺, Dy³⁺ persistent luminescence phosphor. Figure 7(c) shows TL fading properties of LiY_xLu_{1-x}GeO₄:0.01Bi³⁺, 0.001Eu³⁺ with different delay time prior to TL-readout after being energized by β -rays in the dark. The ratios of the integrated TL intensity without delay time to that with 2 h delay are labeled as percentages in the legend of Fig. 7(c). About 20% of the preserved electrons at Eu²⁺ are discharged during the 2 h delay time.

To discover more stable radiographic phosphor at RT, the effect of Bi³⁺ concentration on the discharge process of preserved electrons at Eu²⁺ is further analyzed in Figs. 7(d), 7(e), and S20. Figure 7(d) shows TL glow curves at $\beta = 1$ K/s for LiY_xLu_{1-x}GeO₄:0.001Bi³⁺,

0.001Eu³⁺ after being subjected to β -rays in the dark. The Eu²⁺ TL glow band shifts from 434 to 490 K with increasing x. Compared with the TL curves in Figs. 7(a), 7(d), and S20(a), the decrease in Bi³⁺ concentration from 0.01 to 0.001 contributes to about 20 K shifting of the Eu²⁺ TL glow band toward higher temperature. This implies that the electrons preserved at Eu²⁺ are becoming more thermally stable with decrease in the added Bi³⁺ concentration. This is proved by the TL fading properties as shown in Figs. 7(c), 7(e), and S20(b). For LiY_xLu₁, xGeO₄:0.001Bi³⁺, 0.001Eu³⁺ with 2 h delay time after β -ray charging, all TL intensities remain above 91%, which is about 4% higher than that of the industrial BaFBr(I):Eu²⁺. Particularly, the TL intensity remains 99% for x = 0.25 after 2 h delay.

The discovered Bi³⁺ or/and Eu³⁺ modified LiY_xLu_{1-x}GeO₄ crystals are further assessed as dosimeters for radiation detection. Figure 7(f) shows the TL glow curves quantified at $\beta = 1$ K/s for a typical LiY_{0.5}Lu_{0.5}GeO₄:0.01Bi³⁺, 0.01Eu³⁺ after being irradiated by β -rays

with different durations from 30 until 600s in the dark. As shown in the inset of Fig. 7(f), the integrated TL intensity from 300 to 723 K linearly increases with increasing β -ray exposure duration. The similar applies to other LiY_xLu_{1-x}GeO₄ in Fig. S21. This implies that the Bi³⁺ or/and Eu³⁺ modified LiY_xLu_{1-x}GeO₄ can behave as potential dosimeters for radiation detection.

The readout of preserved charge carriers in traps by optically triggered luminescence is crucial for dosimeters.¹³ The discovered LiYGeO₄ cluster of crystals are further analyzed with optical illumination in Figs. 7(g), S22, and S23. Figure 7(g) presents TL glow curves observed at $\beta = 5 \text{ K/s}$ of a typical LiY_{0.5}Lu_{0.5}GeO₄:0.001Bi³⁺, 0.001Eu³⁺ sample with 10s of 475 nm light illumination after being energized by β -rays for 60 s. The preserved charge carriers discharge ~73% with 10s of 475 nm stimulation. Particularly, the amount of discharged electrons preserved at Eu²⁺ in LiY_{0.5}Lu_{0.5}GeO₄:0.001Bi³⁺, 0.001Eu³⁺ with 10s of 475 nm stimulation is about 1.3 times higher compared with that of industrial BaFBr(I):Eu²⁺ in Fig. S23(h). Moreover, the electrons preserved at Eu²⁺ can be fully discharged with 300s of 475 nm stimulation in LiY_{0.25}Lu_{0.75}GeO₄:0.005Bi³⁺, 0.001Eu³⁺ in Fig. S23(d).

The stability of readout of preserved charge carriers in traps is vital for application. Figure 7(h) suggests that a TL glow curve was repeatedly quantified for a typical $\text{LiY}_{0.5}\text{Lu}_{0.5}\text{GeO}_4:0.001\text{Bi}^{3+}$, 0.001Eu³⁺ after being energized by β -rays for 10s. The integrated TL intensity as a function of cyclic number is labeled in Fig. 7(k). An outstanding repeatability of TL-readout is found.

E. Scientific design of Bi³⁺ radiographic phosphors by tailoring hole discharge from Bi⁴⁺ in LiYGeO₄ cluster of crystals

To explore the development of radiographic phosphors by using hole discharge from Bi⁴⁺, Bi³⁺ modified LiYGe_zSi_{1-z}O₄ crystals were analyzed. Figures 8(a) and S24 show normalized and unnormalized TL glow curves observed at $\beta = 1$ K/s for LiYGe_zSi_{1-z}O₄:0.01Bi³⁺ after being subjected to β -rays in the dark. The ratios of integrated TL intensities of LiYGe₇Si₁₋₇O₄:0.01Bi³⁺ to that of the industrial BaFBr(I):Eu²⁺ are presented in the legend of Fig. 8(a). For z = 0, a TL glow band peaked near 524 K emerges. Herein, it is abbreviated as a Bi4+ TL band. It will be attributed to thermally triggered hole discharge from Bi^{4+} to recombine with the electron preserved at Bi^{2+} to yield Bi^{3+} ${}^{3}P_{1} \rightarrow {}^{1}S_{0}$ luminescence. The Bi^{4+} TL glow band gradually shifts from 524 K for z = 0 toward 396 K for z = 0.75. Such 128 K TL band shifting toward a lower temperature will be assigned to decreased Bi4+ hole trapping depth. For z = 1, the VB-bottom rises slightly and the CB has lowered quite a lot such that the e-trap depth on Bi²⁺ becomes smaller than the h-trap depth on Bi^{4+} in Fig. 1(b). The TL glow band peaked at 339 K will then be assigned to electron discharge from Bi^{2+} .

Figure 8(b) presents RT isothermal decay curves for LiYGe₂Si_{1-z}O₄: 0.01Bi³⁺ after β -ray charging. With increasing z from 0 to 1, the Bi³⁺ initial ³P₁ \rightarrow ¹S₀ persistent luminescence increases. Figure 8(c) further gives the TL fading properties of LiYGe₂Si_{1-z}O₄:0.01Bi³⁺ with different delay times prior to TL-readout after being energized by β -rays in the dark. The hole preserved at Bi⁴⁺ is more thermally unstable to be discharged. This is consistent with the Bi⁴⁺ TL glow band shifting toward a lower temperature in Fig. 8(a) and the increased Bi³⁺ initial ³P₁ \rightarrow ¹S₀ persistent luminescence in Fig. 8(b) with increasing z. To determine trapping parameters, Fig. 8(d) presents variable heating rate plots for LiYGe_zSi_{1-z}O₄: 0.01Bi³⁺ after β -ray exposure. The obtained trapping depths and frequency factors are presented in the legend of Fig. 8(d). The Bi⁴⁺ hole trapping depth decreases from \sim 1.35 eV for z = 0 to \sim 0.83 eV for z = 0.75.

The effect of Bi³⁺ concentration on charge carrier storage capacity has been analyzed to obtain better radiographic phosphors. Figure 8(e) shows TL glow curves of β -ray irradiated LiYGe_zSi_{1-z}O₄:0.001Bi³⁺ fabricated at 1200 °C for 24 h. The ratios of integrated TL intensities of LiYGe_zSi_{1-z}O₄:0.001Bi³⁺ to that of state-of-the-art BaFBr(I):Eu²⁺ or SrAl₂O₄:Eu²⁺, Dy³⁺ are given in the legend of Fig. 8(e), respectively.

For z = 0.75, good charge carrier storage capacity emerges in Fig. 8(e). The LiYGe_{0.75}Si_{0.25}O₄ composition is therefore analyzed further. Figure 8(f) gives TL glow curves at $\beta = 1$ K/s for β -ray energized LiYGe_{0.75}Si_{0.25}O₄:nBi³⁺ (n = 0.0005–0.006) crystals fabricated at 1250 °C for 24 h. The ratios of integrated TL intensities of LiYGe_{0.75}Si_{0.25}O₄:nBi³⁺ to that of industrial BaFBr(I):Eu²⁺ or SrAl₂O₄: Eu²⁺, Dy³⁺ have been given in the legend of Fig. 8(f). A record ratio of ~4 emerges for the optimized LiYGe_{0.75}Si_{0.25}O₄:0.001Bi³⁺.

The optimized LiYGe_{0.75}Si_{0.25}O₄:0.001Bi³⁺ has been assessed as a dosimeter. Figure 8(g) compares TL fading properties for LiYGe_{0.75}Si_{0.25}O₄:nBi³⁺ with different delay time prior to TL-readout after being subjected to β -rays in the dark. The ratios of the integrated TL intensities with 2 h delay to that with no delay are given as percentages in the legend of Fig. 8(g). For n = 0.0005–0.004, the ratio is about 92%, which is about 8% higher than that of BaFBr(I):Eu²⁺. It suggests that the holes preserved at Bi⁴⁺ are very thermally stable. This is proved by the TL fading curves of the optimized LiYGe_{0.75}Si_{0.25}O₄: 0.001Bi³⁺ in Fig. 8(h).

Figure 8(i) presents TL glow curves at $\beta = 5$ K/s of the optimized LiYGe_{0.75}Si_{0.25}O₄:0.001Bi³⁺ after β -ray exposure and then irradiation by 475 nm light with different duration from 0 to 300 s in the dark. The ratios of the integrated TL intensities with 475 nm stimulation to that obtained without 475 nm stimulation are presented as percentages in the legend of Fig. 8(i). For 10 s of 475 nm stimulation, the amount of discharged charge carriers in LiYGe_{0.75}Si_{0.25}O₄:0.001Bi³⁺ is about 2.5 times higher compared with that of industrial BaFBr(I):Eu²⁺. With increase in the stimulation duration to 300 s, the holes preserved at Bi⁴⁺ can be fully discharged.

To understand how holes are confined at Bi⁴⁺, thermoluminescence excitation (TLE) spectra were observed for LiYGe_zSi_{1-z}O₄: 0.01Bi³⁺, which are shown in Figs. 8(j), 8(k), and S25. Figure 8(l) compares the TLE plots of LiYGe_zSi_{1-z}O₄:0.01Bi³⁺ with the photoluminescence excitation (TLE) spectrum ($\lambda_{em} = 360$ nm) of the z = 0.75 sample. The traps in LiYGe_zSi_{1-z}O₄:0.01Bi³⁺ can be filled via Bi³⁺ D-band excitation instead of the A-band excitation.

F. Evaluating the discovered Bi³⁺ radiographic phosphors for anti-counterfeiting and information storage purposes

Figures 9(a1) and 9(a2) illustrate how to make a semitransparent flexible film with a diameter of ~6 cm by dispersing phosphors in silicone gel. Herein, it is referred to as film A. Different than a traditional film with only one phosphor composition, film A is unique for multimode purposes because the top and bottom layers are dispersed with $LiY_{0.25}Lu_{0.75}GeO_4:0.01Bi^{3+}$ and $LiTaO_3:0.006Bi^{3+}$, $0.002Sm^{3+}$ perovskite.³⁷ LiTaO_3:0.006Bi^{3+}, $0.002Sm^{3+}$ was selected because it exhibits



FIG. 8. (a) Normalized TL glow curves at $\beta = 1$ K/s, (b) RT isothermal decay curves, (c) TL fading properties, and (d) variable heating rate plots for LiYGe_zSi_{1+z}O₄:0.01Bi³⁺ after β -ray charging. (e)–(i) TL glow curves at $\beta = 1$ K/s, TL fading properties, and TL glow curves at $\beta = 5$ K/s with 475 nm stimulation for LiYGe_zSi_{1+z}O₄:0.01Bi³⁺ and LiYGe_{0.75}Si_{0.25}O₄:nBi³⁺ (n = 0–0.006) after being energized by β -rays. (j) (k), and (l) Thermoluminescence excitation (TLE) curves for LiYGe_zSi_{1+z}O₄:0.01Bi³⁺. The photoluminescence excitation spectrum (PLE, $\lambda_{em} = 360$ nm) for LiYGe_zSi_{1+z}O₄:0.01Bi³⁺ (z = 0.75) is also shown in (l).

intense persistent luminescence and fast photochromic feature upon 254 nm illumination for information storage.³⁸ Figure 9(b1) presents a TL glow curve quantified at a heating rate of 1 K/s for LiY_{0.25}Lu_{0.75}GeO₄:0.01Bi³⁺ after β -ray exposure at 100 K. The Bi³⁺

A-band emission was monitored during TL-readout. Four TL glow bands peaked near 172, 269, 332, and 375 K are found. Film A then can be adopted to sense whether the phosphor has been exposed to temperatures in the range from 100 to 450 K for cryo-preservation.^{29,39}

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FIG. 9. Proof-of-concept purposes of sensing ultralow temperature and information encryption by employing a smart label. (a1) and (a2) Illustration of how the flexible label is constructed by using two silicone gel layers dispersed with LiY_{0.25}Lu_{0.75}GeO₄:0.01Bi³⁺ or LiTaO₃:0.006Bi³⁺, 0.002Sm³⁺ perovskite, respectively. (b1)–b6) Illustration of the realization of sensing ultralow temperature and information encryption. (c1)–c3) Illustration of high resolution x-ray imaging for chicken claws with the smart label.

For example, a film A that has been energized can be used as a smart label to be positioned on a surface of a bottle like in Fig. 9(a2). The bottle contains vaccines or biological samples that should always be kept at ultralow temperatures like -70 °C. If the temperature of the bottle is accidentally increased to room temperature, charge carriers in traps will be discharged to give Bi³⁺ A-band persistent luminescence from LiY_{0.25}Lu_{0.75}GeO₄:0.01Bi³⁺. One then cannot observe the TL glow curves below RT anymore. This implies that the vaccines or biological samples in the bottle are possibly damaged. This indicates that LiY_{0.25}Lu_{0.75}GeO₄:0.01Bi³⁺ has potential use in sensing whether the phosphor has been heated to some specific temperature in the past for anti-counterfeiting purposes.

Figure 9(b2) shows a red persistent luminescence photograph of film A, which is observed at 10s after being irradiated by 254 nm ultraviolet light for 30s in the dark at RT. Its persistent luminescence spectrum is shown in Fig. 9(b3). The persistent luminescence spectrum is composed of the Bi^{3+} A-band emission from $LiY_{0.25}Lu_{0.75}GeO_4$: 0.01 Bi^{3+} from layer A of the film together with the Bi^{3+} 460 nm

emission and Sm³⁺ 4f \rightarrow 4f emissions from LiTaO₃:0.006Bi³⁺, 0.002Sm³⁺ perovskite in layer B of the film. The Bi³⁺ A-band persistent luminescence from LiY_{0.25}Lu_{0.75}GeO₄:0.01Bi³⁺ is mainly located below 400 nm in the special ultraviolet-A (UVA) range from 314 to 400 nm. It can only be detected by a spectrometer and not by the naked eye. This concealment feature can be adopted in anti-counterfeiting applications. The persistent luminescence spectrum in the visible range in Fig. 9(b3) is mainly constituted of Sm³⁺ 4f \rightarrow 4f emissions from the LiTaO₃:0.006Bi³⁺, 0.002Sm³⁺ perovskite. The persistent luminescence film A then emerges as a red disk in Fig. 9(b2), which can be easily observed by the naked eye in the dark. By combining LiY_{0.25}Lu_{0.75}GeO₄: 0.01Bi³⁺ with UVA persistent luminescence and LiTaO₃:0.006Bi³⁺, 0.002Sm³⁺ perovskite. The persistent in Fig. 9(b4) and 9(b5), fast photochromic feature in Fig. 9(b6), and x-ray induced charge carrier storage in Figs. 9(c1)–9(c3), film A can be potentially used for advanced anti-counterfeiting purposes.

To discover a smart film for multimode applications, a multifunctional film with three layers has been explored. Figure 10(a1) illustrates



FIG. 10. Proof-of-concept purposes of anti-counterfeiting and x-ray imaging by utilizing a smart label. (a1) and (a2) Illustration of how the smart label is designed by creating three silicone gel layers dispersed with $LiYGe_{0.75}Si_{0.25}O_4:0.01Bi^{3+}$, industrial $ZnS:Mn^{2+}$, or $Cs_2ZrCl_6:0.005Sb^{3+}$ perovskite, respectively. (b1)–(b4) Illustration of anti-counterfeiting application with multimode luminescence. (c1)–c6) Illustration of high resolution x-ray imaging for a pen and dried fishes by employing the smart label.

how such a film is constituted by dispersing LiYGe_{0.75}Si_{0.25}O₄: 0.01Bi³⁺, industrial ZnS:Mn^{2+,40} and Cs₂ZrCl₆:0.005Sb³⁺ perovskite⁴¹ in three layers with silicone gel, respectively. ZnS:Mn²⁺ is the state-of-the-art mechanoluminescence (ML) material. It gives bright mechanoluminescence upon weak mechanical stimulation. Cs₂ZrCl₆:0.005Sb³⁺ perovskite was selected because it emits bright blue or yellow emission upon 254 or 365 nm illumination in the dark. Herein, the film is

named as a film B. It is flexible to be positioned on a curved surface of a bottle as shown in Fig. 10(a2). Upon mechanical excitation, Mn^{2+} ${}^4T_1 \rightarrow {}^6A_1$ mechanoluminescence emerges in film B in Fig. 10(b1). This implies that film B can be potentially adopted for force sensing. Upon 254 nm ultraviolet light excitation, film B emits bright cyan light in the dark in Fig. 10(b2). This is because of exciton emission from Cs₂ZrCl₆ host.⁴² Like 254 nm excitation, x-ray excitation can also

trigger out such exciton emission from Cs₂ZrCl₆ host, which can be adopted for direct x-ray imaging purposes.⁴³ Different than that by 254 nm excitation, 365 nm ultraviolet light excitation induces bright yellow light in the dark in Fig. 10(b3). This is assigned to Sb³⁺ related emission from Cs₂ZrCl₆:0.005Sb³⁺⁴¹. Figure 10(b4) shows that a thermally triggered emission text of "Lyu" is realized in film B kept at ~350 K after first being energized by 254 nm ultraviolet light and then selectively irradiated by 656 nm red laser beam in the dark. The appearance of emission is due to the ~350 K thermally triggered Bi³⁺ ³P₁→ ¹S₀ luminescence from LiYGe_{0.75}Si_{0.25}O₄:0.01Bi³⁺. A combination of ML from ZnS:Mn²⁺, color-tailorable emission from Cs₂ZrCl₆:0.005Sb³⁺ perovskite, and smart realization of thermally triggered emission texts from LiYGe_{0.75}Si_{0.25}O₄:0.01Bi³⁺ with 656 nm laser stimulation has potential applications for advanced anticounterfeiting purposes.

Figures 10(c1)–10(c3) show film B positioned underneath a ballpoint, two dried fishes, or a lead-based resolution test plate for x-ray imaging, respectively. They are exposed to x rays at a perpendicular angle in the dark. After exposure to x rays, the ballpoint, two dried fishes, and test plate are extracted from film B. X ray imaging photographs of the ballpoint and two dried fishes are shown in Figs. 10(c4) and 10(c5) when the film is kept at \sim 373 K in the dark. This is attributed to the thermally triggered Bi³⁺ ${}^{3}P_{1} \rightarrow {}^{1}S_{0}$ luminescence from LiYGe_{0.75}Si_{0.25}O₄:0.01Bi³⁺ in the visible range. Figure 10(c6) shows that a high-resolution x-ray image can be achieved.

To create a smart label for anti-counterfeiting purposes, $LiY_{0.25}Lu_{0.75}GeO_4:0.01Bi^{3+}$ has been further explored. As shown in Fig. S28, its Bi^{3+} ultraviolet-A (UVA) persistent luminescence at RT can be imaged for 10 min by using a corona camera (WNZW-01). The absolute light yield of the persistent luminescence in the visible range of $LiY_{0.25}Lu_{0.75}GeO_4:0.01Bi^{3+}$ after exposure to a Hg lamp for five min is about 0.08 cd/m^2 . To demonstrate special optically triggered Bi^{3+} UVA emission, $LiY_{0.25}Lu_{0.75}GeO_4: 0.01Bi^{3+}$ was first energized by

254 nm ultraviolet light for 300s and then irradiated by a 100 lux white LED. As shown in Fig. 11, the optically triggered Bi^{3+} UVA emission from $LiY_{0.25}Lu_{0.75}GeO_4:0.01Bi^{3+}$ with white LED illumination can be imaged for more than 22 min. It is ~2 times higher compared with that obtained without white LED illumination. The intense optically triggered Bi^{3+} UVA luminescence then has promising use for developing smart labels for anti-counterfeiting purposes.

III. DISCUSSION

A. Vacuum referred binding energy (VRBE) diagram with level locations of lanthanides in LiYGeO₄

Scientific control of trapping and discharge processes of electrons and holes in traps in inorganic crystals is crucial but challenging for discovering good persistent luminescence and radiographic phosphors. There are ongoing arguments on this issue. In Ref. 44, a synergistic defect tailoring strategy is proposed for systematic tuning of persistent luminescence in CaZnOS modified with lanthanides, Cu^+ , Pb^{2+} , Mn^{2+} , Sb^{3+} , or Bi^{3+} . In Ref. 45, persistent luminescence is reported in NaYF₄ modified with different lanthanides after being subjected to x rays. However, whether lanthanides, Cu⁺, Pb²⁺, Mn²⁺, Sb³⁺, or Bi³⁺ can behave as electron or hole trapping centers is not known. The trapping and discharge processes of electrons and holes in traps then are not fully clear. Herein, we propose that an understanding of the trapping and discharge processes can be realized by constructing vacuum referred binding energy (VRBE) diagrams for LiYGeO4 cluster of crystals using data from detailed spectroscopy and thermoluminescence studies.2

With a U value of 6.90 eV and the determined values for host exciton (E^{ex}), VB \rightarrow Eu³⁺ CT (E^{CT}), Pr³⁺ \rightarrow CB IVCT, and Tb³⁺ \rightarrow CB IVCT, a vacuum referred binding energy diagram for LiYGeO₄ is constructed and shown in Fig. 1(a). It comprises energy level locations of different divalent and trivalent lanthanides. Note that the values for the IVCT energies, the Eu³⁺ CT-energy, and the host



FIG. 11. Imaging for ultraviolet-A (UVA) emission from $LiY_{0.25}Lu_{0.75}GeO_4:0.01Bi^{3+}$ after being energized by a Hg lamp (254 nm ultraviolet light) and then irradiated by a 100 lux white LED.

bandgap energy are mutually consistent with the VRBE diagram. It will serve as a useful tool to explain and even to scientifically design confining and discharge processes of charge carriers in lanthanides modified LiYGeO₄.

To exploit more experimental data for establishing the VRBE diagram, data on electron transfer from the 4f ground states of Tb³⁺ and Pr³⁺ to the conduction band (CB) bottom have been adopted. Generally, such electron transition is referred to as intervalence charge transfer (IVCT).⁴⁷ Such IVCT transition often is found when lowest excited 5d states of Tb³⁺ and Pr³⁺ are positioned within the conduction band, like in CdGeO₃.⁴⁸ YInGe₂O₇.⁴⁹ and Ca₂Nb₂O₇.⁵⁰ For a radiographic phosphor, electron capturing traps can be filled by free electrons created via Tb³⁺ \rightarrow CB or Pr³⁺ \rightarrow CB IVCT excitation. Another deployment of the IVCT transition is that its energy gives information about energy level locations of 4f ground states of Tb³⁺ and Pr³⁺ with respect to the CB-bottom. In Ref. 51, data on IVCT transitions are collected and compiled for 27 inorganic crystals. The energy of Tb³⁺ \rightarrow CB IVCT is often close to that of Pr³⁺ \rightarrow CB IVCT.

The excitation spectrum ($\lambda_{em} = 605 \text{ nm}$) of LiYGeO₄:0.01Pr³⁺ at 10 K is shown in Fig. 3(c). Two excitation bands peaked near 237 and 255.5 nm are found. The thermoluminescence excitation (TLE) spectra of Pr³⁺ co-doped LiYGeO₄:0.005Pr³⁺, 0.001Eu³⁺ in Fig. 5(h) prove that the Eu³⁺ electron trapping center can be filled by free electrons yielded through excitation of the two bands peaked near 237 and ~255.5 nm. The lowest energy excitation band peaked near 255.5 nm is therefore attributed to Pr³⁺ \rightarrow CB IVCT. The higher energy excitation band peaked near 237 nm is assigned to the second Pr³⁺ 4f \rightarrow 5d transition.

The excitation spectrum ($\lambda_{em} = 548 \text{ nm}$) of LiYGeO₄:0.01Tb³⁺ is shown in Fig. 3(d). The weak excitation peaks in the range from 310 to \sim 400 nm are ascribed to characteristic Tb³⁺ 4f \rightarrow 4f transitions. The thermoluminescence excitation (TLE) spectra of Tb3+ co-doped LiYGeO₄:0.005Tb³⁺, 0.001Eu³⁺ in Fig. 5(g) prove that the Eu²⁺ electron trap center can be energized by free electrons created via two excitation bands peaked near 245 and 260 nm. The low energy excitation shoulder band peaked near 265 nm (4.68 eV) in Fig. 3(d) is close to the $Pr^{3+} \rightarrow CB$ IVCT band peaked near 255.5 nm in Fig. 3(c), which is then assigned to the $\text{Tb}^{3+} \rightarrow \text{CB}$ IVCT band. The higher energy excitation bands peaked near 232 and 249 nm are assigned to spin allowed electron transitions from the Tb³⁺ 4f ground state to its first two excited 5d states. The weak band at 296 nm is then attributed to the first spin-forbidden $4f \rightarrow 5d$ transition. The energy difference of $0.79\,\mathrm{eV}$ with the 249 nm band corresponds with the expected exchange splitting between the first spin allowed and first spin forbidden $4f \rightarrow 5d$ transition. Based on the first $5d_1$ band of Tb^{3+} , the first 5d band of Pr^{3+} is at 255 nm and that is precisely underneath the CT-band in Fig. 3(c). The band at 237 nm in the Pr^{3+} PLE spectrum in Fig. 3(c) must then be the transition to the second 5d band of Pr^{3+} .

B. VRBE at Bi³⁺ ground and excited states in LiYGeO₄

In Ref. 52, energies of the Bi^{4+/3+} and Bi^{3+/2+} charge transition levels in LiYGeO₄ were computed by employing the first principles approach. The computed ground states of Bi³⁺ and Bi²⁺ are about 2.16 and 5.98 eV above the valence band top, respectively. This implies that the calculated Bi^{3+ 1}S₀ ground state level is about 0.83 eV higher compared with that in the vacuum referred binding energy (VRBE) diagram as shown in Fig. 1(a). The calculated Bi^{2+ 2}P_{1/2} ground state

level is consistent compared with that in our VRBE in Fig. 1(a). However, no experimental evidence has been reported on VRBEs in the Bi^{3+} and Bi^{2+} ground state levels in LiYGeO₄ yet.

Figure 3(a) shows the excitation spectrum ($\lambda_{em} = 363 \text{ nm}$) of LiYGeO₄:0.01Bi³⁺ at 10 K. In Ref. 53, energies of Bi³⁺ excitation A-band (E_A) and C-band (E_{BiC}) are compiled, which can be related by utilizing the following formula:⁵³

$$E_{BiC} = 3.236 + 2.290 \times (E_A - 2.972)^{0.856}.$$
 (2)

Using Eq. (2) with the energy of the $Bi^{3+1}S_0 \rightarrow {}^{3}P_1$ band peaked around 297 and 308 nm for LiYGeO₄: $0.01Bi^{3+}$ at 10 K in Fig. 3(a), the energy of the Bi^{3+ 1}S₀ \rightarrow ¹P₁ C-band peak (E_{BiC}) can be calculated to lie in the range from \sim 5.92 eV (209 nm) to \sim 5.63 eV (220 nm). This predicted Bi3+ C-band is close to the excitation band peaked near 202 nm in Fig. 3(a). We therefore assign that band to the Bi^{3+} excitation C-band, i.e., $Bi^{3+1}S_0 \rightarrow {}^1P_1$ transition. The slightly lower energy excitation band peaked at \sim 230 nm (5.39 eV) is then ascribed to the Bi³⁺ excitation D-band, i.e., an electron transfer band from the Bi³⁺ ¹S₀ ground state to the conduction band bottom of LiYGeO₄.⁵⁴ This assignment implies that electron trapping centers can be filled by the free electrons produced via Bi³⁺ D-band excitation. This prediction is proved by the thermoluminescence excitation (TLE) spectra for Bi³⁺ modified LiYGeO₄:0.01Bi³⁺ in Fig. 5(e) and LiYGeO₄:0.01Bi³⁺, 0.001Eu³⁺ in Fig. 5(f). During Bi³⁺ D-band excitation, Bi⁴⁺ is formed from Bi^{3+} when an electron is excited from the $Bi^{3+} {}^{1}S_{0}$ ground state to the conduction band of LiYGeO4. The free electrons freely migrate in the conduction band. Part of the free electrons can be confined by intrinsic electron trapping centers associated with TL glow bands peaked near 370, 403, 466, and 565 K for LiYGeO₄:0.01Bi³⁺ in Fig. 5(e). Part of the free electrons can be confined by a Eu^{3+} electron capturing center associated with a TL glow band peaked around 506 K for LiYGeO₄: $0.01Bi^{3+}$, $0.001Eu^{3+}$ in Fig. 5(f). Part of the free electrons can be confined by Bi^{3+} to form Bi^{2+} , which is associated with the Bi^{2+} TL glow band in Figs. 5(a) and 5(b).

Subtracting the energy value of the Bi³⁺ D-band peak (5.39 eV) from the value of VRBE at the conduction band bottom, the VRBE in the ¹S₀ ground state of Bi³⁺ has been deduced to be ~-8.0 eV. It is about 0.83 eV lower than that computed by first principles in Ref. 52. It agrees with the statistical result in Ref. 33 where the VRBEs in the Bi³⁺ ¹S₀ ground state are found to range from -5 to -10 eV for different types of oxide based inorganic crystals. Based on the experimentally obtained VRBE in the Bi³⁺ ¹S₀ ground state level (~-8.0 eV) and energies of the Bi³⁺ excitation A-band and C-band for LiYGeO₄: 0.01Bi³⁺ at 10 K in Fig. 3(a), the VRBEs in the Bi³⁺ ³P₁ and ¹P₁ excited states can then be deduced. Figure 1(a) shows a full picture with Bi³⁺ ground and excited state levels in LiYGeO₄ together with the experimentally observed transitions.

Figures 3(e) and 3(f) show the excitation and emission spectra for $\text{Li}_{y}\text{Na}_{1-y}\text{YGeO}_4:0.001\text{Bi}^{3+}$. With increasing y, the Bi^{3+} excitation A-, C-, and D-bands remain stationary, while the $\text{Bi}^{3+} {}^3\text{P}_1 \rightarrow {}^1\text{S}_0$ emission A-band gradually shifts from 394 nm for y = 0 to 360 nm for y = 1 upon 232 nm excitation. This implies that a weaker host lattice relaxation emerges with increase in the composition ratio of Li⁺ to Na⁺, contributing to creation of higher energy emission photons. Figures 3(g) and 3(h) show the excitation ($\lambda_{em} = 363 \text{ nm}$) and emission ($\lambda_{ex} = 230 \text{ nm}$) spectra of LiY_xLu_{1-x}GeO₄:0.01Bi³⁺ solid solutions. They share almost the same Bi³⁺ A-, C-, and D-excitation bands in

Fig. 3(g). The $Bi^{3+3}P_1 \rightarrow {}^{1}S_0$ emission A-band only slightly shifts from 361 nm for x = 0 to 364 nm for x = 1. The above results elucidate that these fabricated $LiY_xLu_{1-x}GeO_4:0.01Bi^{3+}$ solid solutions have a very similar structure, resulting in the same nephelauxetic effect on the nature of Bi^{3+} luminescence.

C. VRBE at $Bi^{2+2}P_{1/2}$ ground state in LiYGeO₄ deduced by electron discharge from Bi^{2+}

The above 100 K TL glow curve observed at $\beta = 1$ K/s for LiYGeO₄:0.01Bi³⁺ after being energized by β -rays at 100 K is shown in Fig. 5(a). An intense TL glow band peaked near 321 K is found, which is assigned to the Bi²⁺ electron trapping center. Using Eq. (1) with $T_m = 321$ K, $\beta = 1$ K/s, and $s = 4.15 \times 10^{11}$ s⁻¹, the Bi²⁺ electron trapping depth has been calculated to be \sim 0.81 eV. Subtracting the energy of this electron trapping depth from the VRBE in the CB-bottom, the VRBE in the $Bi^{2+2}\hat{P}_{1/2}$ ground state in LiYGeO₄ has been determined to be \sim -3.46 eV. This value compares very well with the findings in Ref. 55. During exposure to β -rays at 100 K, a part of Bi³⁺ can confine holes from valence band to form Bi4+. A part of Bi3+ can trap electrons from conduction band to form Bi²⁺. Since the Bi²⁺ electron trapping depth of \sim 0.81 eV is lesser than the Bi⁴⁺ hole trapping depth of \sim 1.40 eV, the electron preserved at Bi²⁺ can be discharged at a lower temperature compared with the hole preserved at Bi⁴⁺. During TL-readout, the electrons are discharged from Bi²⁺ to recombine with the holes confined at Bi⁴⁺ to yield Bi³⁺ typical ${}^{3}P_{1} \rightarrow {}^{1}S_{0}$ luminescence.

D. Tailoring electron discharge from Bi²⁺ and Eu²⁺ toward light dosimeters

Figure 1(a) predicts that Bi²⁺ and Eu²⁺ serve as about 0.81 and 1.3 eV deep electron trapping centers, while Bi⁴⁺ serves as an ~1.4 eV deep hole trapping center in LiYGeO₄. Combining Bi⁴⁺ with Bi²⁺ or Eu²⁺, electrons confined at Bi²⁺ or Eu²⁺ will be discharged at a lower temperature than holes confined at Bi⁴⁺. Figure 1(b) illustrates that the VRBE in the CB-bottom of LiLuGeO₄ is about ~0.1 eV lower than that of LiYGeO₄. This implies that the electron trapping depths of Bi²⁺ and Eu²⁺ can be engineered in LiY_xLu_{1-x}GeO₄ by tailoring x, contributing to conduction band tailoring. This prediction is verified by the TL glow curves of LiY_xLu_{1-x}GeO₄:0.01Bi³⁺ in Fig. 5(a) and LiY_xLu_{1-x}GeO₄:0.01Bi³⁺, 0.001Eu³⁺ in Fig. 5(c). With increasing x, 60–70 K shifting toward a higher temperature of the Bi²⁺ and Eu²⁺ TL glow bands is found. This is ascribed to the increased ~0.19 eV activation energy determined in Fig. 5(d) for electron discharge from Bi²⁺ and Eu²⁺ because of the rising of conduction band with increasing x as shown in Fig. 1(b).

Figure 1(a) also predicts that Pr^{4+} and Tb^{4+} serve as about 2 eV deep hole trapping centers in LiYGeO₄. Similar to LiYGeO₄:0.01Bi³⁺, 0.001Eu³⁺, combining Eu²⁺ with Pr^{4+} or Tb^{4+} , electrons preserved at Eu²⁺ will be discharged earlier than holes confined at Pr^{4+} or Tb^{4+} in LiYGeO₄. To prove this, Fig. S12(b) compares the TL glow curves of Bi³⁺ or/and Ln³⁺ (Ln = Tb, Pr, or Eu) modified LiYGeO₄. Compared with Bi³⁺, Tb³⁺, or Pr³⁺ single modified LiYGeO₄, a common TL glow band peaked near 488 K is found in Eu³⁺ co-doped LiYGeO₄:0.001Bi³⁺, 0.001Eu³⁺, LiYGeO₄:0.005Pr³⁺, 0.001Eu³⁺, and LiYGeO₄:0.005Tb³⁺, 0.001Eu³⁺. During TL-readout, the electrons bonded at Eu²⁺ are discharged earlier to combine with holes confined

at Bi^{4+} , Pr^{3+} , or Tb^{4+} , facilitating typical $Bi^{3+3}P_1 \rightarrow {}^{1}S_0$, Pr^{3+} , or Tb^{3+} 4f \rightarrow 4f emissions as shown in Figs. 4(e)–4(g).

Figures 7(a) and 7(d) compare the TL glow curves at $\beta = 1$ K/s for β -ray energized LiY_xLu_{1-x}GeO₄:0.01Bi³⁺, 0.001Eu³⁺ and LiY_xLu_{1-x}GeO₄:0.001Bi³⁺, 0.001Eu³⁺, 0.001Eu³⁺. Decreasing the Bi³⁺ concentration from 1% to 0.1% contributes to ~17 K shifting of the Eu²⁺ TL glow band toward a higher temperature. Potentially, the energy barrier between Bi³⁺ and Eu³⁺ is increased when Bi³⁺ is positioned farther away from Eu³⁺. A higher activation energy is then required to discharge the electrons confined at Eu²⁺ to recombine with the holes bonded at Bi⁴⁺ to create Bi³⁺ $^{3+}$ $^{3+}$ $^{3+}$ $^{1+}$ $^{5-}$ $^{1+}$ $^{5-}$ $^{1+}$ $^{5-}$ $^{1+}$ $^{5-}$ $^{1+}$ $^{5-}$ $^{1+}$ $^{5-}$ $^{1+}$ $^{5-}$ $^{1+}$ $^{5-}$ $^{1+}$ $^{5-}$ $^{1+}$ $^{1+}$ $^{5-}$ $^{1+}$ $^{1+}$ $^{5-}$ $^{1+}$

E. Tailoring hole discharge from Bi⁴⁺ toward light dosimeters

Compared with LiYGeO₄, the stacked VRBE diagram in Fig. 1(b) shows that about 1.2 eV rising of the conduction band bottom is found in LiYSiO₄. This implies that the Bi^{2+} electron trap depth will be increased by $\sim 1.2 \text{ eV}$ when LiYGeO₄ is reconfigured by LiYSiO₄. For LiYSiO₄, Bi²⁺ serves as a \sim 2.1 eV deep electron trap and Bi⁴⁺ serves as a \sim 2.0 eV deep hole trap. For LiYGeO₄, Bi²⁺ behaves as a \sim 0.81 eV deep electron trap and Bi^{4+} behaves as a $\sim 1.4 \text{ eV}$ deep trapping center. This implies that the Bi4+ hole trap depth will be decreased by ${\sim}0.6\,\text{eV}$ when LiYSiO₄ is reconfigured by LiYGeO₄. Figure 8(a) shows the TL glow curves for β -ray irradiated LiYGe_zSi_{1-z}O₄:0.01Bi³⁺. With increasing z, a nice TL glow band shifts from 524 K (1.35 eV) for z = 0to 396 K (0.83 eV) for z = 0.75. The establishment of the VRBE diagram does not take into account the lattice relaxation that may shift energies perhaps by 0.5 eV. Furthermore, with increase in temperature the bandgap lowers, and that will affect also trapping depths. At the temperature of TL-peak, the bandgap is smaller than the value at 10 K. Considering these factors, the TL glow bands for z = 0-0.75 are assigned to hole discharge from Bi⁴⁺ to recombine with the electrons bonded at Bi²⁺ to create the Bi³⁺ A-band emission. The 128 K shifting of the Bi⁴⁺ TL glow band toward a lower temperature is associated with decreased activation energy for hole discharge from Bi⁴⁺ owing to the VB-top rising as proved in Fig. 1(b). For z = 1, i.e., LiYGeO4:0.01Bi3+, an intense TL glow band peaked near 339 K is seen, which has been ascribed to electron discharge from Bi2+ to recombine with the holes confined at Bi^{4+} to create $Bi^{3+} P_1 \rightarrow {}^1S_0$ luminescence as analyzed in Fig. 5(a).

F. Liquid nitrogen temperature to 700 K Bi³⁺ thermoluminescence for versatile anti-counterfeiting, information storage, and x-ray imaging purposes

Typically, radiographic phosphors are created by a trial-and-error approach. Properties of radiographic phosphors are often reported above room temperature.^{2,56} Reports are infrequently published to discuss trapping and discharge processes of charge carriers below room temperature in radiographic phosphors.¹⁸ Herein, a new idea is proposed to realize light dosimeters that function over a wide temperature range from liquid nitrogen temperature to 700 K as depicted in Fig. 1(c). TL glow bands peaked near 135, 185, 232, and 311 K with Bi³⁺ A-band emission are found in Li_vNa_{1-v}YGeO₄:0.001Bi³⁺ by

combining intrinsic defects and Bi2+ electron trapping centers with Bi^{4+} as a hole trap in Fig. 5(b). Wide temperature shifting of Bi^{2+} and Eu^{2+} TL glow bands in the temperature range from 200 to 500 K is found in LiY_xLu_{1-x}GeO₄:0.01Bi³⁺ and LiY_xLu_{1-x}GeO₄:0.01Bi³⁺, 0.001Eu³⁺ owing to conduction band tailoring by adjusting x as shown in Figs. 5(a) and 5(c). Herein, Bi^{4+} is testified as a deep hole trap, while Bi²⁺ and Eu²⁺ are found to behave as less deep electron traps in LiY_xLu_{1-x}GeO₄. Wide temperature shifting of Bi⁴⁺ TL glow bands in the temperature range from 300 to 700 K is discovered in LiYGe_zSi_{1-z} $O_4:0.01Bi^{3+}$ (z = 0–0.75) due to valence band tailoring by altering z as shown in Fig. 8(a). Together with ZnS:Mn²⁺, LiTaO₃:Bi³⁺, Sm³⁺, and $\text{Cs}_2\text{ZrCl}_6\text{:Sb}^{3+}$ perovskites, the realization of wide range liquid nitrogen temperature to 700 K Bi³⁺ thermoluminescence in the discovered Bi³⁺ or/and lanthanide modified LiYGeO₄ cluster of crystals as discussed in Figs. 6-8 has potential applications for anti-counterfeiting, information storage, and x-ray imaging purposes as shown in Figs. 9 and 10. Compared with a scintillation crystal based x-ray imaging technique, a radiographic phosphor based x-ray imaging technique is cheap and also offers special delayed thermally and optically triggered luminescence features for various cutting-edge uses, such as delayed three-dimensional or flexible x-ray imaging for identifying curved substances.

IV. CONCLUSIONS

In this work, a new idea on wide range liquid nitrogen temperature to 700 K Bi3+ thermoluminescence has been proposed to discover light dosimeters for use in anti-counterfeiting, information storage, and x-ray imaging purposes. To achieve this goal, tailoring of both electron and hole trapping depths has been exploited in LiYGeO4 cluster of crystals by the choice of Bi3+ or/and lanthanides doping or solid solution composition optimization. Mechanisms on how electrons or holes are confined or discharged have been unraveled by combining vacuum referred binding energy (VRBE) diagrams with detailed spectroscopy and thermoluminescence studies. Photoluminescence excitation and emission spectra for undoped host, Tb³⁺, Pr³⁺, Eu³⁺, or Bi³⁺ single modified LiYGeO4 have been first examined in the deep ultraviolet and visible range quantified at 10K or RT. The outcomes have been used to create the VRBE diagram comprising the energy levels of excited and ground states of Bi3+ and different lanthanides for LiYGeO₄. The VRBE in the Bi^{2+ 2}P_{1/2} ground state was experimentally found to be $\sim -3.46 \text{ eV}$ in LiYGeO₄.

The stacked VRBE diagrams for LiYGeO₄ cluster of crystals serve as a powerful tool to guide the realization of wide range liquid nitrogen temperature to 700 K Bi³⁺ thermoluminescence. Wide temperature shifting of Bi²⁺ and Eu²⁺ TL glow bands with Bi³⁺ ³P₁ \rightarrow ¹S₀ emission is found in the temperature range from 200 to 500 K for LiY_xLu_{1-x} GeO₄:0.01Bi³⁺ and LiY_xLu_{1-x}GeO₄:0.01Bi³⁺, 0.001Eu³⁺, by altering x, facilitating conduction band tailoring as shown in Figs. 5(a) and 5(c). Herein, Bi⁴⁺ is proved to be a deep hole trap, while Bi²⁺ and Eu²⁺ are verified as less deep electron traps in LiY_xLu_{1-x}GeO₄. Wide temperature shifting of Bi⁴⁺ TL glow bands with Bi³⁺ ³P₁ \rightarrow ¹S₀ emission is obtained in the temperature range from 300 to 700 K for LiYGe_zSi_{1-z} O₄:0.01Bi³⁺ (z = 0-0.75), by tuning z, facilitating the tailoring of valence band as shown in Fig. 8(a). TL glow bands peaked near 135, 185, 232, and 311 K with Bi³⁺ ³P₁ \rightarrow ¹S₀ emission emerge in Li_yNa_{1-y} YGeO₄:0.001Bi³⁺ by combining less deep intrinsic defects and Bi²⁺ electron traps with Bi⁴⁺ as a deeper hole trap in Fig. 5(b). Particularly, the discovered Bi³⁺ or/and lanthanide modified LiYGeO₄ cluster of

crystals offer outstanding charge carrier storage capacity and minimal TL fading properties. For instance, the ratio of the integrated TL intensity of the optimized LiYGe_{0.75}Si_{0.25}O₄:0.001Bi³⁺ after being subjected to β -rays to that of industrial BaFBr(I):Eu²⁺ is as high as ~4. It is a recordable value for a hole discharge from Bi⁴⁺ and recombination with the electron confined at Bi²⁺ so far.

The realization of wide range liquid nitrogen temperature to 700 K Bi³⁺ thermoluminescence in the Bi³⁺ or/and lanthanide modified LiYGeO₄ cluster of crystals with outstanding charge carrier storage capacity as analyzed in Figs. 6–8 has potential for use in anticounterfeiting, information storage, and x-ray imaging applications as shown in Figs. 9 and 10. This work not only initiates how to scientifically realize wide range liquid nitrogen temperature to 700 K Bi³⁺ thermoluminescence, but more importantly can stimulate chemists to discover new light dosimeters by creating and using VRBE diagrams with energy level location of Bi²⁺, Bi³⁺, and various lanthanides for inorganic crystals.

V. EXPERIMENTAL

Crystals of LiYGeO₄ modified with lanthanides or Bi³⁺, LiY_xLu_{1-x} GeO₄:0.01Bi³⁺, 0.001Eu³⁺, Li_vNa_{1-v}YGeO₄:0.001Bi³⁺, and LiYGe_zSi_{1-z} O4:0.01Bi³⁺ were fabricated by a high temperature solid state reaction technique. The concentration of the dopant (lanthanide or bismuth) has been determined based on the molar ratio of the dopant to the crystal host. SiO₂ (99.99%) was bought from Umicore. The other starting chemicals were bought from Sigma-Aldrich. An excess of 10% lithium above crystal proportion of Li⁺ was used. Raw chemicals of Li₂CO₃ (99.99%), Na₂CO₃ (99.99%), Y₂O₃ (99.99%), Lu₂O₃ (99.99%), SiO₂ (99.99%), GeO₂ (99.99%), Bi₂O₃ (99.999%), and other lanthanide oxides with a high purity of 99.99% have been carefully balanced and then thoroughly blended in an agate mortar by using acetone solution. The mixed powder (\sim 1 g) was positioned in a covered corundum crucible. It was first kept at 800 °C for 8 h and then at 1200 °C with a duration of 24 h under surrounding environment in a tube furnace. After cooling to room temperature (RT, ~298 K), the fabricated crystals were ground to be homogeneous powders before performing optical quantifications.

A PANalytical XPert PRO x-ray diffraction apparatus was used to determine the structures of the fabricated crystals. The apparatus contains an x-ray tube that functions at 45 kV and 40 mA, contributing to Co K α irradiation ($\lambda = 0.178901$ nm). A JEOL JSM-IT100 apparatus was used to take scanning electron microscope (SEM) images. The detailed photoluminescence excitation (PLE) and emission (PL) spectra were collected in the spectral range from 100 to 750 nm and in the temperature range from 10 to ~400 K by using an apparatus comprising of a deuterium lamp, a 500 W Hamamatsu xenon lamp, a photomultiplier (PerkinElmer MP-1993), a cryostat, and a Gemini 180 monochromator. Corrections for wavelength-dependent excitation intensities were implemented for the PLE spectra. Corrections for detection efficiencies of the photomultiplier at different wavelengths were applied to the PL spectra. Powder crystals were pressed into disks approximately 0.5 cm in diameter. They were then directly subjected to excitation light during PLE and PL quantification.

Above 298 K thermoluminescence (TL) glow curves, TL emission (TLEM) spectra, RT isothermal decay curves, and TL excitation (TLE) curves were acquired with a RISØ TL/OSL apparatus. It comprises of a photomultiplier (EMI 9635QA), an industrial 475 nm light-emitting diode (\sim 8 mW/cm²), a beta excitation source ⁹⁰Sr/⁹⁰Y with a dose rate

of about 0.7 mGy/s, and a 150 W Hamamatsu xenon arc lamp (L2273) with a monochromator. Before TL recording, samples were kept at \sim 723 K for a duration of \sim 100s to discharge randomly preserved charge carriers in traps under nitrogen gas atmosphere. For fair TL intensity comparison, a constant sample mass of \sim 0.04 g was adopted and each sample was uniformly positioned in a metal disk with a diameter of \sim 0.8 cm. The quantified TL intensities have been corrected by the sample mass and the beta-ray exposure time and therefore a notation of "s⁻¹.g⁻¹" has been used in TL spectra.

The observed TL intensities are comparable because they are quantified by the same RISØ TL/OSL instrument with a fixed configuration. For the TLEM spectra, samples were subjected to a cobalt-60 (60 Co) gamma source to an absorbed dose of ~3.0 kGy in the dark. For TLEM quantification, a QE65000 spectrometer (Ocean Optics) has been used, which can rapidly track a full spectrum, but a strong emission is required. Gamma irradiation has a very high energy. A sample then can be energized by gamma irradiation to a high dose and then can emit strong TL emission to be possibly detected by the QE65000 spectrometer (Ocean Optics).

Above 100 K TL (LTTL) glow curves were quantified with an apparatus by employing liquid nitrogen as a cooling medium. The apparatus is comprised of a cryostat, a ⁹⁰Sr/⁹⁰Y beta excitation source with a dose rate of about 0.4 mGy/s, a vacuum pump, and a PerkinElmer photomultiplier (MP-1393). For LTTL quantification, powders have been pressed into disks approximately 0.5 cm in diameter. Each disk was positioned on the heater of the used cryostat by using conductive silver paste in vacuum (10^{-7} mbar). Before LTTL documenting, disks were kept at 450 K for 150s to discharge randomly confined charge carriers in traps in the dark. In this work, Bi²⁺, Bi⁴⁺, and Eu²⁺ TL glow bands are abbreviated for clarity because the TL combination is respectively ascribed to the discharge of electrons from Bi²⁺, the generation of holes from Bi⁴⁺, and the discharge of electrons from Eu²⁺.

For exploring advanced information encryption applications, multilayer flexible films like in Figs. 9(a1) and 10(a1) were assembled by dispersing radiographic and luminescent phosphors into silicone gel (Sylgard 184, Dow Corning). Phosphors were first sifted by a 200 mesh screen. For each layer, about 0.3 g sifted phosphor was dispersed into 2.1 g silicone gel. Each layer was kept at 75 °C for 4 h in air. The LiTaO₃:0.006Bi³⁺, 0.002Sm³⁺ perovskite was fabricated by applying a high temperature solid-state reaction method at 1200 °C for 10 h. The industrial ZnS:Mn²⁺ mechanoluminescence phosphor was bought from Shanghai Keyan Phosphor. The Cs₂ZrCl₆:0.005Sb³⁺ perovskite was fabricated by a chemical coprecipitation method like in Refs. 41 and 42. For x-ray imaging, an x-ray TUB00154-9I-W06 tube (MOXTEK, Ltd.) was adopted. It was used at 58 kV, 190 μ A, and 11 W. A Nikon D850 camera has been used to capture the x-ray imaging photographs.

For thermoluminescence excitation spectra, a heating rate of 5 K/s was applied because quantification can be finished in few hours. The thermoluminescence excitation spectra in Figs. 5(e)-5(h) and 8(j)-8(l) have been corrected by wavelength-sensitive excitation intensities. Beta irradiation was adopted for TL quantification because TL intensities can be fairly compared. X-ray source was adopted for x-ray imaging since x rays can penetrate objects. The 475 nm LED has been adopted for optically triggered luminescence quantification. This is because that it was installed in the RISØ TL/OSL facility and the

illumination time can be easily controlled. It can be modified by 450 nm or 980 nm light source. Thermal quenching of Bi^{3+} emission has no effect on the TL glow curve of $LiYGeO_4:0.01Bi^{3+}$ as shown in Fig. S7.

SUPPLEMENTARY MATERIAL

See the supplementary material for supporting SEM photographs, x-ray diffraction patterns, PLE spectra, PL spectra, thermoluminescence emission spectra, TL glow curves, and photographs of the prepared crystals for potential utilizations.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Tianshuai Lyu: Conceptualization (equal); Formal analysis (equal); Funding acquisition (equal); Investigation (equal); Writing – original draft (equal); Writing – review & editing (equal). **Pieter Dorenbos:** Formal analysis (supporting); Resources (supporting); Writing – review & editing (supporting).

DATA AVAILABILITY

The data that support the findings of this study are available within the article and its supplementary material.

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