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Towards information storage by designing both electron and hole detrapping processes in bismuth and lanthanide-doped LiRE(Si,Ge)O₄ (RE = Y, Lu) with high charge carrier storage capacity

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HIGHLIGHTS
- Rational design of new Ce³⁺ and Bi³⁺ storage phosphors for energy storage.
- Excellent Ce³⁺ and Bi³⁺ storage phosphors were discovered.
- Fully control of trap depth by both CB and VB engineering.
- New mechanism of hole liberation from Bi⁴⁺ and recombination with Bi²⁺.
- New insight of deep understanding storage phosphor mechanisms.

GRAPHICAL ABSTRACT

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ABSTRACT

Guided by vacuum referred binding energy (VRBE) diagrams, both the trapping and detrapping processes of electrons and holes are explored in the bismuth and lanthanide-doped LiRE(Si,Ge)O₄ (RE = Y, Lu) family of compounds. The Tm³⁺ electron trap has been combined with the deep hole traps of Ln⁴⁺ (Ln = Ce, Tb, or Pr) or Bi⁴⁺ in LiLuO₄. During the thermoluminescence readout, the electrons released from Tm²⁺ recombine with holes at Ln⁴⁺ and Bi⁴⁺ to produce typical Ln³⁺ 4f-4f or 5d-4f emission and Bi³⁺ A-band emission. The electron trap depth of lanthanide ions can be tuned by the choice of Ln³⁺ (Ln = Tm or Sm), and for fixed pair of Ln³⁺ and/or Bi³⁺ dopants like in LiLu₁₋ₓYₓSiO₄:0.01Ce³⁺,0.01Ln³⁺ and LiLu₁₋ₓYₓSiO₄:0.01Bi³⁺,0.01Sm³⁺ solid solutions, by adjusting x, resulting in the engineering of the VRBE at the conduction band bottom. The thermoluminescence (TL) intensity of the optimized LiLu₀.₅Y₀.₅SiO₄:0.01Ce³⁺,0.005Sm³⁺ is about 8.5 times higher than that of the commercial X-ray BaFBr(I):Eu²⁺ storage phosphor. By combining deep Eu³⁺ or Bi³⁺ electron traps with Ln³⁺ (Ln = Tb or Pr) or Bi³⁺, Ln³⁺ and Bi³⁺ appear to act as less deep hole capturing centres in LiLuO₄. Here the recombination is achieved through hole liberation rather than the more commonly reported electron liberation. The holes are released from Ln⁴⁺ and Bi⁴⁺ to recombine with electrons at Eu²⁺ or Bi²⁺ to give characteristic Eu³⁺ 4f-4f and Bi³⁺ A-band emissions. The tailoring of Ln³⁺ and Bi³⁺ hole trap depths by crystal composition modulation is discussed in LiLu₁₋ₓYₓSiO₄ and LiLu₀.₂₅Y₀.₇₅Si₁₋ₓGexO₄:0.01Bi³⁺ solid solutions. The TL intensity of the optimized LiLu₀.₂₅Y₀.₇₅SiO₄:0.01Bi³⁺ is ~4.4 times higher than that of the commercial BaFBr(I):Eu²⁺. Proof-of-concept information storage will be demonstrated with X-ray or UV-light charged LiLu₀.₅Y₀.₅SiO₄:0.01Ce³⁺,0.01Sm³⁺ and LiLu₀.₂₅Y₀.₇₅SiO₄:0.01Bi³⁺ phosphors dispersed in silicone gel imaging plates.

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1. Introduction

Charge carrier trapping processes have attracted attention for rational design of afterglow and storage phosphors and from a theoretical point of view [1,2]. The electron capturing and liberation processes have been widely studied for afterglow phosphors [3–8]. Korthout et al. reported the valence change of Eu2+ in the commercial afterglow phosphor SrAl2O4:Eu2+,Dy3+ utilizing X-ray absorption near-edge spectroscopy (XANES) [9]. A partial oxidation of Eu2+ to Eu3+ appears after exposing the phosphor to X-rays. A valence change state of Dy3+ was not detected although it does play a role in the electron trapping process. Eu2+ is proposed to be an electron donor and the electrons liberated by photoionization migrate freely in the conduction band (CB) to be trapped by the electron capturing centre(s). A similar partial oxidation of Ce3+ to Ce4+ and a reduction of Cr3+ to Cr2+ appears in Y2AlGaxOz:Ce3+,Cr3+ afterglow phosphor by XANES [10]. Here Ce3+ is the electron donor and Cr3+ acts as the electron acceptor.

Holes can also be released to recombine with an electron capturing centre through the valence band (VB) or by a migrating Vb centre [2,11]. Hole detrapping processes are rarely reported. In 1988, Chakrabarti et al. reported that Sm3+ is a recombination centre and Ce3+ is a hole capturing centre in MgS:Ce3+,Sm3+ [12]. The holes are liberated from Ce4+ to recombine with electrons trapped at Sm2+ to give typical 4f-4f emission of Sm3+. The other three examples are from recent studies on afterglow phosphors by Lyu et al. on REPO4 [13–15] and Luo et al. on Gd1−xLaxAlO3 [2] and RE2O3S [11] where hole detrapping processes from Bi4+, Tb4+, or Pr3+ were identified in REPO4 and Gd1−xLaxAlO3. For RE2O3S, a hole detrapping process resulting in Ti4+ charge transfer emission is observed. There are rare reports on good storage phosphors discussing the hole-capturing and detrapping processes.

Bi3+ is a famous activator for photonic materials which is widely investigated [16]. However, Bi3+ doped storage phosphors are rarely reported and only a few Bi3+-activated persistent luminescence phosphors have appeared up to now [14,17]. The trapping and detrapping processes regarding bismuth are complex and often remain unclear. A recent study on Bi53+-doped REPO4 indicates that Bi3+ not only can act as an electron trapping centre but also as a hole capturing centre [14]. More studies are required to unravel the charge carrier detrapping processes regarding bismuth to obtain more insights for rational design of bismuth activated storage phosphors.

Methods have been established to derive the energy level locations of the dopants like Cr2+, Cr3+, Bi2+, Bi3+, and divalent and trivalent lanthanides within the band gap of inorganic compounds [5,18–21]. Based on experimental spectroscopy, a vacuum referred binding energy (VRBE) diagram with host band and impurity energy level locations could be established to guide the exploration of charge carrier trapping materials [22]. Knowledge on the VRBE in dopant levels provides a tool to predict the trapping depths and determine what dopant may capture an electron and what dopant may capture a hole, which helps to explain and even adjust carrier trapping processes. The VRBE-aided methodology is so far mainly used in lanthanide and/or transition metal activated garnet compounds [3,23] and other oxide compounds like CaSiO3 [24] and Sr2SiO5 [25,26] to develop persistent luminescence phosphors. To the best of our knowledge, the VRBE-guided exploration of bismuth and/or lanthanide doped storage phosphors is rarely reported up to now.

The research on optical data storage is of interest because of the challenges for storage of fast-growing amount of data [27–34]. Storage phosphors are information storage materials which trap electrons and holes in host related defect traps after absorbing ionizing radiation [35–40]. They have been applied as storage media in information storage applications [41–46], like digital dental radiographic imaging facility [47] and computed radiography (CR) based on an X-ray storage phosphor plate [45]. Today BaFBr(Tl):Eu2+ is the widely utilized commercial X-ray storage phosphor [45,48]. Nevertheless, it is hygroscopic which limits its long-term durability after exposure in air. Scientists are exploring better storage phosphors in various crystals like Ba2Eu2+:Ce3+,Sm3+ [49], CsBr:Eu2+ [50,51], and Lu2O3 [52]. Sidorenko et al. [53] reported the storage properties of LiLu2O4:Ce3+,Sm3+ (Ln = Y or Lu). After charging LiLu2O4, Sm2+ liberates electrons already near room temperature (RT) resulting in strong fading of stored information. Situation is better in LiYSiO4 with the Sm2+ TL glow peak near 390 K but a low density of the host material makes it less suited for application as X-ray storage phosphor. Recently, Dobrovolska et al. [35,54] reported excellent storage capacity of optimized LiLu2O4:Ce3+,Tm3+. Its thermoluminescence (TL) intensity is about 4 times higher than that of commercial BaFBr(Tl):Eu2+ storage phosphor after γ irradiation. However, this phosphor was developed by a trial-and-error approach. The nature of the trap(s) and the role of thulium codoping in LiLu2O4:Ce,Tm are still unclear. This finding motivated a deeper study into the family of related compounds LiLu2O4, LiLuGeO4, and solid solutions NaLu1−xYxGeO4 in Ref. [55] with using other dopants like Bi3+ and Eu3+.

The spectroscopy of Bi3+ in LiYSiO4 and LiLu2O4 and their solid solutions was already discussed in Ref. [55]. Also the spectroscopy of the lanthanides in these compounds is well known and with that information the VRBE schemes with all the relevant levels in the band gap were constructed in the Ref. [55]. In this work, with the knowledge and VRBE diagrams from in Ref. [55], we return to the silicate solid solutions of the family of LiLu2O4, LiYSiO4, and LiLuGeO4. Here the focus is on 1) the engineering aspects of storage and afterglow phosphors and 2) developing and optimizing phosphors for application. Crystal composition modulation and dopant combinations using Bi3+, Pr3+, Tb3+, Ce3+, Tm3+, and Sm3+ are explored with the aim to engineer either the recombination centre, the dominant glow peak temperature, or to optimize the afterglow or storage performance.

The VRBE diagram known for LiLu2O4 is shown in Fig. 1a) [55]. The VRBE of an electron at the ground states of divalent and trivalent lanthanides is linked by two zigzag curves a and b. The VRBE in the ground states of Bi3+ and Bi2+ is also provided. Fig. 1a) illustrates that Tm3+, Sm3+, Bi3+, and Eu3+ act as ~0.62, ~1.08, ~1.81 ± 0.5, and ~2.34 eV deep electron capturing centres, while Ce3+, Pr3+, Tb3+, and Bi3+ act as ~3.89, ~2.04, ~2.22, and ~1.90 eV deep hole capturing centres.

For afterglow phosphor application at RT, shallow trap depth (~ < 1 eV) is required. For storage phosphor application at RT, deep trap depth (> ~1 eV) is needed. Fig. 1a) guides us to choose a proper combination of electron and hole trapping centres to engineer an electron or hole release process for a specific application. It was demonstrated that one may combine a deep hole trap like Ce, Pr, Tb, or Bi with a less deep electron trap like Tm or Sm to arrive at recombination at the hole trap generating either Ce, Tb, Pr, or Bi emission. One may also combine a hole trap like Pr, Tb, or Bi with a deeper electron trap like Eu or Bi to arrive at recombination at the electron trap leading to Eu or Bi emission. For instance, red Eu3+ 4f-4f emission may appear for the Eu3+:Bi3+ or Eu3+:Tb3+ pairs in LiLu2O4 when a hole is liberated from Bi4+ or Tb4+ to recombine with electrons at Eu2+ because Bi3+ and Tb3+ act as less deep hole traps than the electron trap depth on Eu. By making solid solutions like LiLu1−xYxSiO4, LiLu1−xTbxGeO4, or LiLu1−xYxSi1−xGeO4, the VB-top and CB-bottom may be shifted up or down as predicted in the stacked VRBE scheme in Fig. 1b), leading to ~100 K shift of the temperature of glow peak maxima. Herewith one may tune the trap depth.
Lanthanides and/or bismuth activated LiLu$_{1-x}$Y$_x$SiO$_4$ and LiLu$_{0.25}$Y$_{0.75}$Si$_{1-y}$Ge$_y$O$_4$ compounds were synthesized using a high-temperature solid-state reaction method. 0.2–0.7 mm SiO$_2$ (99.99%) crystals were purchased from Umicore company and then milled to small crystals. The other starting reagents were purchased from Sigma-Aldrich and used without further treatment. To compensate for the volatilization of lithium at high temperature, an excess of 10% Li$^+$ above the stoichiometry ratio was used. The appropriate chemicals of rare earth oxides with high purity (99.99%), SiO$_2$ (99.99%), Li$_2$CO$_3$ (99.99%), Bi$_2$O$_3$ (99.999%), and GeO$_2$ (99.99%) were mixed well by adding acetone. The obtained mixture (~0.6 g) was placed in a corundum crucible and then fired at 800 °C for 8 h and at 1150 °C for 15 h in ambient atmosphere. For the compounds without bismuth doping, the mixture was further heated at 1170 °C for 5 h under an atmosphere of H$_2$/N$_2$ (H$_2$: N$_2$ 7%: 93%). To optimize the charge carrier storage capacity for LiLu$_{0.25}$Y$_{0.75}$SiO$_4$:0.01Bi$^{3+}$ solid solution, the starting mixture was first fired at 800 °C for 8 h and then at 1200 °C for 24 h under ambient atmosphere. The optimized LiLu$_{0.5}$Y$_{0.5}$SiO$_4$:0.01Ce$^{3+}$,0.005Sm$^{3+}$ was synthesized at 800 °C for 2 h and then at 1170 °C for 10 h under an atmosphere of H$_2$/N$_2$ (H$_2$: N$_2$ 7%: 93%) for 3 times in a tube furnace. The utilized heating rate for the furnace is 3 °C/min. The obtained crystals were naturally cooled down to room temperature (RT) and ground to fine powders before further measurements.

The synthesized crystal structure was checked by an X-ray diffraction facility (PANalytical XPert PRO) using cobalt Kα radiation (λ = 0.178901 nm) at 45 kV and 40 mA. For the temperature-dependent XRD patterns for LiLu$_{0.25}$Y$_{0.75}$Si$_{1-y}$Ge$_y$O$_4$:0.01Bi$^{3+}$ (y = 0.25), another facility using copper Kα1 radiation (λ = 0.154060 nm) and a temperature-tailorable sample holder were utilized. The utilized heating rate for the furnace is 3 °C/min. The obtained crystals were naturally cooled down to room temperature (RT) and ground to fine powders before further measurements.

2. Experimental

Lanthanides and/or bismuth activated LiLu$_{1-x}$Y$_x$SiO$_4$ and LiLu$_{0.25}$Y$_{0.75}$Si$_{1-y}$Ge$_y$O$_4$ compounds were synthesized using a high-temperature solid-state reaction method. 0.2–0.7 mm SiO$_2$ (99.99%) crystals were purchased from Umicore company and then milled to small crystals. The other starting reagents were purchased from Sigma-Aldrich and used without further treatment. To compensate for the volatilization of lithium at high temperature, an excess of 10% Li$^+$ above the stoichiometry ratio was used. The appropriate chemicals of rare earth oxides with high purity (99.99%), SiO$_2$ (99.99%), Li$_2$CO$_3$ (99.99%), Bi$_2$O$_3$ (99.999%), and GeO$_2$ (99.99%) were mixed well by adding acetone. The obtained mixture (~0.6 g) was placed in a corundum crucible and then fired at 800 °C for 8 h and at 1150 °C for 15 h in ambient atmosphere. For the compounds without bismuth doping, the mixture was further heated at 1170 °C for 5 h under an atmosphere of H$_2$/N$_2$ (H$_2$: N$_2$ 7%: 93%). To optimize the charge carrier storage capacity for LiLu$_{0.25}$Y$_{0.75}$SiO$_4$:0.01Bi$^{3+}$ solid solution,
cooled deuterium lamp. The emission from samples was recorded with a PerkinElmer MP-1993 photomultiplier. The excitation spectra were corrected by the wavelength-dependent lamp intensity. The Ce$^{3+}$ and Bi$^{3+}$ fluorescence decay curves were collected by the above facility which further connects with a waveband digitizer module and a pulsed YAG:Nd laser source (NT230-100-SH/DUV-SCU) that contains an optical parametric oscillator (OPO). The laser pulse repetition rate is 100 Hz and the pulse duration is 2–5 ns.

High-temperature thermoluminescence (TL) glow curves ranging from $\sim$300 to 900 K were recorded using a facility which is composed of a RISØ TL/OSL reader model DA-15), a DA-20 controller, and an EMI 9635QA photomultiplier tube. Prior to the TL measurement, the compounds were heated in the dark at a heating rate of 5 K/s from RT to $\sim$900 K to empty all traps and then cooled to room temperature. This was repeated 2 times more. The compounds were then charged by $\beta$-ray irradiation from a $^{90}$Sr/$^{90}$Y source at a dose rate of $\sim$0.7 mGy/s in nitrogen gas atmosphere.

Low-temperature TL (LTL) glow curves were measured with a facility which contains a $^{90}$Sr/$^{90}$Y $\beta$-ray source with a dose rate of $\sim$0.4 mGy/s and a PerkinElmer channel photomultiplier tube (MP-1393) photon detector. Prior to the LTL measurements, the compounds were pressed into pills with mass < 10 mg and then heated to 450 K for 180 s to siberate the randomly trapped charge carriers under vacuum in the dark. The compounds were cooled to 90 K using liquid nitrogen and then irradiated with $\beta$ irradiation. A 600 nm bandpass filter of 600FS40-50 (Andover Corporation) was placed between the compounds and the photomultiplier to select the Pr$^{3+}$ or Eu$^{3+}$ red emission. 350, 400, and 550 nm bandpass filters of 350FS40-50, 400FS40-50, and 550FS40-50 were utilized to select the characteristic ultraviolet Bi$^{3+}$, blue Ce$^{3+}$, and green Tb$^{3+}$ emissions, respectively. For the TL intensity comparison of the synthesized compounds in this work with the commercial BaFBr(1):Eu$^{3+}$ storage phosphor and an Al$_2$O$_3$:C crystal chip, a 300–700 nm bandpass filter of Schott BG-39 was used. The TL intensities were corrected by the sample mass and $\beta$ irradiation time and then expressed in counts/s/g.

To identify the emission centres during TL readout, thermoluminescence emission (TLEM) spectra were recorded on a setup which combines the RISØ TL/OSL reader and a UV/vis QE65000 (Ocean Optics) spectrometer. Prior to the TLEM measurements, the compounds were heated to $\sim$900 K to empty all traps and then cooled to room temperature followed by $\gamma$-ray charging in the dark using a $^{60}$Co source. The TLEM plots measured by QE65000 at a heating rate of 1 K/s were corrected by the wavelength-dependent quantum efficiency of QE65000.

Prior to recording thermoluminescence excitation (TLE) spectra, compounds were heated to $\sim$723 K to empty all traps and cooled to RT. The compounds were then illuminated during 800 s by monochromatic photons from a setup that is composed of a monochromator (Oriel Cornerstone 130) and a 150 W xenon arc lamp (Hamamatsu L2273). This setup has a wavelength resolution of 0.8 nm against 0.1 mm slit width. In this work, a 1 mm slit width was used. The setup is programmed by LabVIEW to automatically collect the TL glow curves from RT to $\sim$723 K when the illumination wavelength ranged from 200 to 400 nm with steps of 10 nm. A TLE plot like in Fig. 7d) was established by integrating TL glow peaks and displaying integrated intensity against the illumination wavelength [11,56]. The measured TL intensities were corrected by the illumination time, compound mass, and the xenon lamp intensities as a function of wavelength. A filter was placed between the compounds and the photomultiplier tube to select the Ce$^{3+}$ or Bi$^{3+}$ characteristic emission.

To compare the readout speed of stored information in storage phosphors, the TL glow curves after $\beta$-ray charging followed by photon stimulation were recorded on the above RISØ TL/OSL reader, which further connects a 475 nm blue LED or a wavelength-tailored laser beam produced from the NT230-100-SH/DUV-SCU facility. The scanning electron microscope (SEM) images and the energy-dispersive X-ray spectroscopy (EDX) mapping for solid solutions LiLu$_{0.5}$Y$_{0.5}$SiO$_4$:0.01Ce$^{3+}$,0.01Sm$^{3+}$, LiLu$_{0.25}$Y$_{0.75}$SiO$_4$:0.01Bi$^{3+}$, and LiLu$_{0.25}$Y$_{0.75}$Si$_{0.75}$Ge$_{0.25}$O$_4$:0.01Bi$^{3+}$ were measured by using JEOL JSM-IT100 facility. A 254 nm Hg lamp and an UV-lamp with the main emission near 365 nm were used to charge the LiLu$_{0.5}$Y$_{0.5}$SiO$_4$:0.01Ce$^{3+}$,0.01Sm$^{3+}$ storage phosphor. An iPhone 8Plus was utilized to take the photographs for Ce$^{3+}$ related emission. For the LiLu$_{0.5}$Y$_{0.5}$SiO$_4$:0.01Ce$^{3+}$,0.01Sm$^{3+}$ dispersed in silicone film, the silicone gel was mixed well with an appropriate amount of storage phosphor to form a gel film on a glass substrate. The film was placed in a vacuum for 300 s to remove air bubbles and then put in air at RT for 10 h.

**Fig. 2.** XRD patterns of (a) LiLu$_{1-x}$Y$_x$SiO$_4$:0.01Ce$^{3+}$,0.01Sm$^{3+}$ (x = 0–1) recorded at RT, and (b) LiLu$_{0.25}$Y$_{0.75}$Si$_{1-y}$Ge$_y$O$_4$:0.01Bi$^{3+}$ (y = 0.25) solid solution recorded at 298, 473, and 598 K.
Fig. 3. TL emission (TLEM) plots for (a) LiLuSiO$_4$:0.01Eu$^{3+}$, (b) LiLuSiO$_4$:0.01Eu$^{3+},0.01$Tb$^{3+}$, (c) LiLuSiO$_4$:0.01Eu$^{3+},0.01$Pr$^{3+}$, (d) LiLu$_{0.5}$Y$_{0.5}$SiO$_4$:0.01Eu$^{3+},0.01$Bi$^{3+}$, (e) LiLu$_{0.5}$Y$_{0.5}$SiO$_4$:0.01Bi$^{3+},0.01$Sm$^{3+}$, and (f) double solid solution LiLu$_{0.25}$Y$_{0.75}$Si$_{0.75}$Ge$_{0.25}$O$_4$:0.01Bi$^{3+}$ recorded at a heating rate of 1 K/s after γ-ray irradiation.
3. Results

3.1. X-ray diffraction patterns for solid solutions

The X-ray diffraction (XRD) patterns for LiLu$_{1-x}$Y$_x$SiO$_4$:0.01Ce$^{3+}$,0.01Sm$^{3+}$ (x = 0–1) with different content of yttrium are shown in Fig. 2a). With increasing x, the XRD peaks slightly shift towards smaller 2θ angles. This confirms that the yttrium cations enter the lutetium site and increase the cell volume because yttrium has a larger ionic radius than lutetium. The patterns evidence that solid solutions appear in the prepared crystals of LiLu$_{1-x}$Y$_x$SiO$_4$:0.01Ce$^{3+}$,0.01Sm$^{3+}$ in Fig. 2a), and for LiLu$_{0.75}$Y$_{0.25}$Si$_{1-y}$Ge$_y$O$_4$:0.01Bi$^{3+}$ the same in Fig. S2.

Fig. 2b) shows the XRD patterns for the double solid solution LiLu$_{0.75}$Y$_{0.25}$Si$_{1-y}$Ge$_y$O$_4$:0.01Bi$^{3+}$ (y = 0.25). Impurity phases or structural change are absent when the solid solution was heated from 298 to 598 K.

3.2. Engineering hole liberation from Tb$^{4+}$, Pr$^{4+}$, and Bi$^{4+}$ in LiLu$_{1-x}$Y$_x$SiO$_4$ solid solutions

TL emission (TLEM) studies were carried out to identify the recombination centres in Ln$^{3+}$ and/or Bi$^{3+}$ doped LiLu$_{1-x}$Y$_x$SiO$_4$ in Fig. 3. Additional TLEM spectra for other LiLu$_{1-x}$Y$_x$Si$_{1-y}$Ge$_y$O$_4$ phosphors with other combinations of Ln$^{3+}$ doping or different yttrium or germanium content can be found in Figs. S3–S5 and S14.

For LiLu$_{0.1}$SiO$_4$:0.01Eu$^{3+}$ and in Fig. 3a), TL peaks near 373, 420, 497, and 752 K with characteristic Eu$^{3+}$ 4F-4F red emission emerge, that will be referred to as peaks lh, Ih, Ih, and Vh, respectively. Upon co-doping Tb$^{3+}$ in LiLu$_{0.1}$SiO$_4$:0.01Eu$^{3+}$,0.01Tb$^{3+}$ in Fig. 3b), a broad and intense TL peak near 572 K named Tb$^{4+}$ (Tb$^{4+}$), that will be attributed to hole release from Tb$^{4+}$, appears while monitoring the Eu$^{3+}$ red emission. The similar applies to Pr$^{3+}$ co-doping in LiLu$_{0.1}$SiO$_4$:0.01Eu$^{3+}$,0.01Pr$^{3+}$ in Fig. 3c) where a TL peak near 582 K named Pr$^{4+}$ (Pr$^{4+}$) emerges.

Replacing Tb$^{3+}$ or Pr$^{3+}$ by the hole trapping centre of Bi$^{3+}$, again characteristic Eu$^{3+}$ 4F-4F emission appears in LiLu$_{0.1}$SiO$_4$:0.01Eu$^{3+}$,0.01Bi$^{3+}$ with TL glow peaks near 535 and 632 K in Fig. 3d). Fig. 3e) shows the TLEM plot for LiLu$_{0.1}$Y$_{0.5}$Si$_{0.5}$O$_4$:0.01Bi$^{3+}$,0.01Sm$^{3+}$ where Sm$^{3+}$ acts as a less deep electron trap than Bi$^{3+}$ and Eu$^{3+}$. Broad Bi$^{3+}$ A-band emission peaking at ~360 nm with a weak TL peak near 367 K named Sm$^{3+}$, that will be assigned to electron liberation from Sm$^{2+}$, and a broad TL glow peak (Bi$_{h}$) ranging from 425 to 700 K and peaking near 532 K emerges. The
~532 K TL peak is also observed in LiLu<sub>0.5</sub>Y<sub>0.5</sub>SiO<sub>4</sub>:0.01Eu<sup>3+</sup>,0.01Bi<sup>3+</sup> in Fig. 3d), which will be attributed to hole liberation from Bi<sup>4+</sup>. Note that not only characteristic Bi<sup>3+</sup> A-band emission but also typical Sm<sup>3+</sup> red 4f-4f emission appears in Fig. 3e). It is ascribed to an energy transfer process from Bi<sup>3+</sup> to Sm<sup>3+</sup> because the TL glow curves in Fig. 3e) share the same shape when selecting the Bi<sup>3+</sup> A-band emission or when selecting the Sm<sup>3+</sup> 4f-4f emission. This applies also for Li-Lu<sub>1−x</sub>Y<sub>x</sub>SiO<sub>4</sub>:0.01Bi<sup>3+</sup>,0.01Sm<sup>3+</sup> with x = 0.25 and 0.75 in Fig. S14b)-c). The energy transfer from Bi<sup>3+</sup> to Sm<sup>3+</sup> is further evidenced by photoluminescence excitation spectra of LiYSiO<sub>4</sub>:0.01Bi<sup>3+</sup>,0.01Sm<sup>3+</sup> in Fig. S19c). Like in Fig. 3d)-e), a Bi<sup>6</sup> (Bi<sup>4+</sup>) TL peak near 510 K appears in the TL emission plot for the double solid solution Li-Lu<sub>0.25</sub>Y<sub>0.75</sub>Si<sub>0.75</sub>Ge<sub>0.25</sub>O<sub>4</sub>: 0.01Bi<sup>3+</sup> in Fig. 3f).

Fig. 1b) shows that the VRBE in the valence band top of LiYSiO<sub>4</sub> is about 0.1 eV higher than that of LiLuSiO<sub>4</sub>. Because the VBES in the ground states of lanthanides are almost invariant, it implies that the temperature of a TL glow peak due to hole liberation from Tb<sup>3+</sup> or Pr<sup>4+</sup> should decrease. Ln<sup>3+</sup> and/or Bi<sup>3+</sup> doped LiLu<sub>1−x</sub>Y<sub>x</sub>SiO<sub>4</sub> crystals were synthesized to further study and explore such hole trapping process.

Fig. 4a) shows the normalized TL glow curves for LiLu<sub>1−x</sub>Y<sub>x</sub>SiO<sub>4</sub>:0.01Eu<sup>3+</sup>,0.01Tb<sup>3+</sup> solid solutions after β irradiation. The as recorded TL glow curves are shown in Fig. S8a). With increasing x, the Tbh (Tb<sup>4+</sup>) TL glow peak near 614 K shifts about 37 K towards lower temperature, confirming the above prediction. The same applies to LiLu<sub>1−x</sub>Y<sub>x</sub>SiO<sub>4</sub>:0.01Eu<sup>3+</sup>,0.01Pr<sup>3+</sup> solid solutions as shown in Fig. 4b), where a ~43 K TL peak lowering appears with increasing x. Note that the Tb<sub>h</sub> (Tm<sub>h</sub>) and Pr<sub>h</sub> (Tm<sub>h</sub>) in LiLuSiO<sub>4</sub> in Fig. 4a)-b) are about 35 K higher than that in Fig. 3b)-c). The compounds in Fig. 4 were synthesized ~2 years later with respect to that in Fig. 3b)-c), and the synthesis conditions may have been slightly different.

Fig. 4c) shows the TL glow curves for LiLu<sub>1−x</sub>Y<sub>x</sub>SiO<sub>4</sub>:0.01Eu<sup>3+</sup>,0.01Bi<sup>3+</sup> after β irradiation. The TL glow peak Bi<sub>h</sub> near 553 K gradually shifts ~35 K towards lower temperature when x increases. Note that the TL glow peak near 647 K named peak host<sub>h</sub>, that will be attributed to hole liberation from intrinsic host-related hole trap(s), shifts only about 10 K towards lower temperature with increasing x. The derived energy level locations of the intrinsic defect(s) corresponding with these host<sub>h</sub> TL peaks for x = 0 and x = 1 are shown in Fig. 1b). They are determined by adding the derived hole trap depths to the valence band top. Considering that hole liberation and transport...
may be realized via V₄ centre creation, the derived level locations of the intrinsic hole defect(s) may move up in the VRBE diagram in Fig. 1b).

### 3.3. Engineering electron liberation from Tm²⁺ and Sm²⁺ in LiLu₁₋ₓYₓSiO₄ solid solutions

In Fig. 1b) the conduction band bottom moves ~0.17 eV upward with the full substitution of Lu³⁺ by Y³⁺ in LiLu₁₋ₓYₓSiO₄ solid solutions, and an increase of the La³⁺ electron trapping depths is then expected. Fig. 5a) shows the low-temperature TL glow curves for LiLu₁₋ₓYₓSiO₄:0.01Ce³⁺,0.01Tm³⁺ solid solutions after β irradiation. Here Ce³⁺ acts as a deep hole trap and Tm³⁺ as a less deep electron trap. With increasing x, the TL glow peak named peak Tmₑ (Tm²⁺) near 144 K shifts ~42 K towards higher temperature.

The Tmₑ TL glow peak in LiLu₁₋ₓYₓSiO₄ in Fig. 5a) is at a too low temperature of 144–186 K for afterglow or storage phosphor applications. It needs to be shifted close to 400 K or even higher in order to avoid TL fading at RT for storage phosphor application. Fig. 1a) shows that Sm³⁺ acts as a ~0.47 eV deeper electron trap than Tm³⁺. The storage phosphor properties of Sm³⁺ co-doped LiLu₁₋ₓYₓSiO₄ (x = 0–1) crystals were therefore explored. Fig. 5b) and S11a) show the normalized and unnormalized TL glow curves for LiLu₁₋ₓYₓSiO₄:0.01Ce³⁺,0.01Sm³⁺ solid solutions after β irradiation. With increasing x, the TL glow peak named peak Smₑ (Sm²⁺) that will be assigned to electron liberation from Sm³⁺, gradually shifts about 54 K from 348 K towards higher temperature in Fig. 5b). The shifting leads to almost 3 orders of magnitude decreased initial Ce³⁺ persistent luminescence in Fig. S11b), and less TL fading as shown in Fig. S11c). For the x = 0.75 phosphor after 100 min delay time, the integrated TL intensity between 300 and 723 K remains ~85%, which is comparable to that of BaFBr(I):Eu²⁺ (87%). The optimal combination of the Sm³⁺ co-dopant at which Smₑ glow is most intense, is about 1% in LiLu₀.₂₅Y₀.₇₅Si₁₋ₓGexO₄:0.01Ce³⁺,0.01Sm³⁺ (x = 0.1%), that will be assigned to electron liberation from Sm³⁺, gradually shifts near 490 K towards higher temperature in Fig. S11c).

As Bi³⁺ can also act as a hole capturing centre, LiLu₁₋ₓYₓSiO₄:0.01Bi³⁺,0.01Sm³⁺ was explored and its normalized TL glow curves after β irradiation are shown in Fig. 5c). The as recorded TL glow curves are shown in Fig. S15a). With increasing x, the Smₑ TL glow peak near 343 K shifts ~53 K towards higher temperature in the inset of Fig. 5c), the conduction band bottom moves ~0.17 eV upward from host intrinsic defect(s) in Refs. [53,54], first shifts ~30 K towards higher temperature from x = 0 to x = 0.5, but then remains constant near 520 K with further increasing x in LiLu₁₋ₓYₓSiO₄:0.01Ce³⁺,0.01Sm³⁺.

Since Bi³⁺ can also act as a hole capturing centre, LiLu₁₋ₓYₓSiO₄:0.01Bi³⁺,0.01Sm³⁺ was explored and its normalized TL glow curves after β irradiation are shown in Fig. 5c). The as recorded TL glow curves are shown in Fig. S15a). With increasing x, the Smₑ TL glow peak near 343 K shifts ~53 K towards higher temperature in the inset of Fig. 5c), the conduction band bottom moves ~0.17 eV upward from host intrinsic defect(s) in Refs. [53,54], first shifts ~30 K towards higher temperature from x = 0 to x = 0.5, but then remains constant near 520 K with further increasing x in LiLu₁₋ₓYₓSiO₄:0.01Ce³⁺,0.01Sm³⁺.

### 3.4. Engineering Bi⁴⁺ hole detrapping in LiLu₀.₂₅Y₀.₇₅Si₁₋ₓGexO₄ solid solutions

We explored further tailoring of the Biₑ (Bi⁴⁺) TL glow peak in Bi⁴⁺ single doped LiLu₀.₂₅Y₀.₇₅Si₁₋ₓGexO₄:0.01Bi³⁺ solid solutions. Fig. 1b) illustrates that the main effect of adding germanium is the ~0.6–1.0 eV lowering of the CB-bottom and in addition, the VB-top may change a few 0.1 eV. Fig. 5a) and S16 show the normalized and unnormalized TL glow curves for LiLu₀.₂₅Y₀.₇₅Si₁₋ₓGexO₄:0.01Bi³⁺ solid solutions after β irradiation. The Biₑ TL glow peak near 538 K gradually shifts ~144 K towards 394 K from y = 0 to y = 0.75, implying that the VB-top moves up or the Bi³⁺ ground state moves down or both movements are combined. For the y = 1 phosphor, TL glow peaks near 327 K (weak), 371, 425, and 520 K emerge. Due to the lowering of the CB-bottom, we arrive at a situation where the Biₑ (Bi⁴⁺) electron trap depth of ~0.74 ± 0.5 eV becomes less deep than the Bi³⁺ hole trap depth of ~1.33 eV in LiLu₄₀Ge₃₇O₄ as shown in Fig. 1b). The same will apply to LiLu₀.₂₅Y₀.₇₅Si₁₋ₓGexO₄. The dominant TL peak near 371 K is therefore tentatively attributed to electron release from Bi⁴⁺ to recombine with holes trapped at Bi³⁺ to give Bi⁵⁺ A-band emission as shown in Fig. S14h).

The 371 K TL glow peak is referred to as the Biₑ (Bi⁴⁺) glow peak. The TL peak shifting in Fig. 6a) results in more than a factor of 100 increased initial Bi⁴⁺ afterglow intensity in Fig. 6b), and stronger TL

### Table 1

| x     | s     | Tₑ₀, Biₑ | E_Biₑ | Tₑ₀, Tmₑ | E_Tmₑ | Tₑ₀, Prₑ | E_Prₑ | Tₑ₀, Smₑ | E_Smₑ | Tₑ₀, Tmₑ | E_Tmₑ |
|-------|-------|----------|-------|----------|-------|----------|-------|----------|-------|----------|-------|
| 0     | 3.19 × 10⁻³ | 553      | 1.62  | 614      | 1.80  | 611      | 1.79  | 348      | 1.00  | 144      | 0.40  |
| 0.25  | 1.29 × 10⁻³ | 543      | 1.55  | 610      | 1.74  | 605      | 1.73  | 367      | 1.03  | 158      | 0.43  |
| 0.5   | 3.42 × 10⁻³ | 538      | 1.47  | 607      | 1.67  | 592      | 1.52  | 396      | 1.05  | 167      | 0.44  |
| 0.75  | 1.16 × 10⁻² | 527      | 1.40  | 592      | 1.57  | 575      | 1.52  | 396      | 1.04  | 178      | 0.46  |
| 1     | 1.26 × 10⁻² | 518      | 1.38  | 577      | 1.53  | 568      | 1.51  | 402      | 1.06  | 186      | 0.48  |
fading as demonstrated in Fig. 6c). The ratios of integrated TL between 300 and 723 K of LiLu$_{0.25}$Y$_{0.75}$Si$_{1-y}$Ge$_y$O$_4$:0.01Bi$^{3+}$ to that of BaFBr (I):Eu$^{2+}$ are shown in the legend of Fig. 6a) and S16. The maximal ratio of 1.7 is obtained when $y = 0.75$.

The trapping depths $E$ (eV) for the Bih (Bi$^{4+}$) and Bie (Bi$^{2+}$) TL glow peaks in LiLu$_{0.25}$Y$_{0.75}$Si$_{1-y}$Ge$_y$O$_4$:0.01Bi$^{3+}$ in Fig. 6a) were derived from variable heating rate plots using Eq. (1) where the heating rate changes between 0.08 and 5 K/s after β irradiation. Fig. 6d) shows the plots for LiLu$_{0.25}$Y$_{0.75}$Si$_{1-y}$Ge$_y$O$_4$:0.01Bi$^{3+}$ that gives the trapping depths and the frequency factors as listed in the legend of Fig. 6d).

Fig. 7a) and b) show the TL excitation (TLE) spectra for LiLu$_{0.25}$Y$_{0.75}$SiO$_4$ with Bi$^{3+}$,Sm$^{3+}$ and with Bi$^{3+}$ only. For the LiLu$_{0.25}$Y$_{0.75}$Si$_{0.75}$Ge$_{0.25}$O$_4$:0.01Bi$^{3+}$ solid solution, the TLE spectrum is shown in Fig. 7c). Additional TLE spectra for other LiLu$_{0.25}$Y$_{0.75}$Si$_{1-y}$Ge$_y$O$_4$:0.01Bi$^{3+}$ that gives the trapping depths and the frequency factors as listed in the legend of Fig. 7d).

3.5. Evaluating the potential application for information storage

The crystal synthesis of LiLu$_{0.25}$Y$_{0.75}$SiO$_4$:0.01Bi$^{3+}$ and LiLu$_{0.5}$Y$_{0.5}$SiO$_4$:0.01Ce$^{3+}$,0.005Sm$^{3+}$ solid solutions was optimized in order to further increase the charge carrier storage capacity for achieving more efficient information storage. Fig. 8a) and 8c) show the TL glow curves and TL fading characteristics for the optimized samples. The ratio of integrated TL intensity between 300 and 800 K of LiLu$_{0.25}$Y$_{0.75}$SiO$_4$:0.01Bi$^{3+}$ to that of commercial Al$_2$O$_3$:C or BaFBr (I):Eu$^{2+}$ is about 1.1 and 4.4. For LiLu$_{0.25}$Y$_{0.75}$SiO$_4$:0.01Bi$^{3+}$ after 10 h delay time, the integrated TL intensity remains 96%, which is ~20% higher than that of BaFBr(I):Eu$^{2+}$. The ratio of integrated TL intensity between 300 and 723 K of LiLu$_{0.25}$Y$_{0.75}$SiO$_4$:0.01Bi$^{3+}$ to that of BaFBr(I):Eu$^{2+}$ is about 8.5, which is higher than that of ~4 in the...
optimized LiLuSiO₄:Ce³⁺,Tm³⁺ in Ref. [35] and of ~7 in the optimized NaYGeO₄:0.01Bi³⁺,0.001Eu³⁺ in Ref. [55].

For storage phosphor application, the stored charge carriers during X-ray or other excitation source exposure are often read out by photon stimulation. Fig. 9 compares the TL glow curves of the optimized samples in this work after photon stimulation with various duration times. Additional TL curves for other LiLu₃₋ₓYₓSi₁₋ₚGeₚO₄ can be found in Fig. S24.

**Table 2**

Comparison of the TL excitation (TLE) plots, the Bi³⁺ and Bi I, TL glow peaks, and the Bi³⁺ D-excitation bands from spectroscopy for LiLu₀.₂₅Y₀.₇₅S₁₋ₚGeₚO₄:0.01Bi³⁺ (y = 0–1).

| y   | TLE peak | Bi³⁺ D-band | Bi³⁺ TL peak at β = 5 K/s | Bi³⁺ TL peak at β = 1 K/s |
|-----|----------|-------------|--------------------------|--------------------------|
| 0   | 210 nm   | 207 nm      | 566 K                    | 538 K                    |
| 0.25 | 220 nm   | 214 nm      | 532 K                    | 510 K                    |
| 0.5  | 230 nm   | 223 nm      | 471 K                    | 450 K                    |
| 0.75 | 230 nm   | 227 nm      | 408 K                    | 394 K                    |
| 1    | 230 nm   | 230 nm      | 396 K (Bi₆⁺)             | 371 K (Bi₀⁺)             |

source: Fig. 7d, Fig. S19a, Fig. 7b-c, and S18, Fig. 6a

Fig. 9 and S24 demonstrate that 10 s of 475 nm photon stimulation releases ~38, 54, 49, and 41% of the charge carriers stored during β irradiation of LiLu₀.₅₇₅S₁₋ₚGeₚO₄:0.01Ce³⁺,0.01Sm³⁺, LiLu₀.₅₇₅S₁₋ₚGeₚO₄:0.01Bi³⁺, BaFBr(I):Eu³⁺, and Al₂O₃:C, respectively. The relative amount of released charge carriers in LiLu₀.₅₇₅S₁₋ₚGeₚO₄:0.01Ce³⁺,0.01Sm³⁺ in Fig. 9a) or LiLu₀.₅₇₅S₁₋ₚGeₚO₄:0.01Bi³⁺ in Fig. 9c) is smaller than that in BaFBr(I):Eu³⁺, but their absolute amount is ~2.4, 5.2 times, and ~1.3, 2.7 times higher than that in BaFBr(I):Eu³⁺ and Al₂O₃:C, respectively.

Fig. 9b-c) shows that ~94% and ~98% of stored charge carriers can be liberated when the stimulation time increases to 1800 s. The same applies to other LiLu₀.₅₇₅S₁₋ₚGeₚO₄ phosphors as shown in Fig. S24g-h). Fig. 9d) shows the stimulation spectra with different stimulation photon wavelength. For the LiLu₀.₅₇₅S₁₋ₚGeₚO₄:0.01Ce³⁺,0.01Sm³⁺ phosphor, a stimulation peak near 580 nm appears. The information stored by the LiLu₀.₅₇₅S₁₋ₚGeₚO₄:0.01Bi³⁺ phosphor is erased more efficiently at 410 nm.

Fig. 9a) demonstrates proof-of-concept information storage and readout using the developed phosphor. LiLu₀.₅₇₅S₁₋ₚGeₚO₄:0.01Ce³⁺,0.01Sm³⁺ phosphor is first dispersed in a ~2 mm thick silicone gel to form “plate I”, which is then placed underneath a chicken bone to be X-ray exposed as demonstrated in Fig. 10a2). “Plate I” was heated to ~370 K and after 12 and 32 s a photo
of the afterglow was made. The X-ray image of the chicken bone shape appears as a weaker thermally stimulated Ce\(^{3+}\) emission intensity in Fig. 10a3) and a4). This is due to the absorption of X-rays by the chicken bone during X-ray exposure. The resolution of the image in Fig. 10a3) and a4) is rather poor, but when an image was made with a ~0.5 mm thick plate II it improves as shown in Fig. 10a6). The similar applies to another X-ray image of a chicken bone stored in "plate III" in Fig. S31a4)–a6), where the LiLu\(_{0.25}\)Y\(_{0.75}\)SiO\(_4\):0.01Bi\(^{3+}\),0.01Sm\(^{3+}\) storage phosphor was used. Here the X-ray image is obtained because of afterglow from hole liberation from Bi\(^{4+}\) and recombination with Bi\(^{2+}\) followed by energy transfer from Bi\(^{3+}\) to Sm\(^{3+}\), as illustrated in Fig. S31a7). Note that the used optical sensor of the smartphone is not sensitive to the main thermally stimulated Bi\(^{3+}\) emission near 360 nm in LiLu\(_{0.25}\)Y\(_{0.75}\)SiO\(_4\):0.01Bi\(^{3+}\),0.01Sm\(^{3+}\).

"Plate I" in Fig. 10b1) is placed underneath a black mask as shown in Fig. 10b2). LiLu\(_{1-x}\)Y\(_x\)SiO\(_4\):0.01Ce\(^{3+}\),0.005Sm\(^{3+}\) can be charged by 260 nm light as shown in Fig. S13. When the UV-light near 260 nm passes through the open area of the black mask it charges "plate I". The information of text of "LMG TUD TSL Ce\(^{3+}\)" is then stored in the "plate I" in Fig. 10b3). The text is not visible in the dark when the UV-light is switched off in Fig. 10b4). The text emerges again in Fig. 10b5) when the "plate I" is heated to ~370 K with duration time of ~15s because of thermally stimulated Ce\(^{3+}\) emission. The mechanism is demonstrated in Fig. 10b6).

A QR code printed on a sheet of white paper in Fig. 10c1) was generated by the text of "This is a nice storage phosphor for information..."
storage from TUD!” with computer software. The QR code is visible in the dark in Fig. 10c2) because of the ~370 K thermally stimulated Ce³⁺ emission from “plate I” underneath the paper as a backlight display source shining through the sheet in Fig. 10c2). The QR code was scanned using a mobile phone software in the dark to read out the hidden text above as demonstrated in Fig. 10c3).

4. Discussion

Based on low-temperature (10 K) photoluminescence spectroscopy in Ref. [55], the constructed vacuum referred binding energy (VRBE) diagrams including bismuth and lanthanide levels for LiLuSiO₄ related family of compounds are shown in Fig. 1 and S1. We will show how these VRBE schemes can be verified and made more accurate by thermoluminescence study, and how they guide the design of both the electron and hole trapping processes in the lanthanide and/or bismuth doped Li(RE,Ge)O₄ (RE = Y or Lu) towards storage phosphors with high charge carrier storage capacity for information storage. Here let us call this approach the ‘engineering game’.

The essence of the game is to combine a hole trapping defect with an electron trapping defect in a controlled fashion. In sequence of decreasing hole trap depths in Fig. 1a) and b) one may select Ce³⁺, Pr³⁺~Tb³⁺, and Bi³⁺ where Ce³⁺ is the deepest h-trap and Bi³⁺ is the shallowest h-trap. In sequence of decreasing electron trap depths one may select Eu³⁺, Bi³⁺, Yb³⁺, Sm³⁺, and Tm³⁺. We will call these trapping centres ‘the players’.

In addition to these controlled trapping centres one has to deal with the intrinsic e-traps and h-traps, and in this work we will show how one may discriminate one type from another. Fig. 1b) illustrates that our ‘playing field’ are the solid solutions LiLu₀.5Y₀.5SiO₄ where we have focused on the silicates (y = 0). A small excursion was made for x = 0.75 where y was changed from 0 to 1.

The ‘rules of the game’ are actually the physical mechanism of carrier trapping and recombination. 1) If the hole trap is deeper than the electron trap, then the electron is released at a lower temperature than the hole. Recombination takes place at the hole centre leading to hole-trap luminescence. 2) if the e-trap is deeper than the h-trap, the hole will be released at a lower temperature to recombine with the electrons.
Fig. 10. Proof-of-concept information storage application by using LiLu$_{0.5}$Y$_{0.5}$SiO$_4$: 0.01Ce$^{3+}$, 0.01Sm$^{3+}$ dispersed in the silicone gel plates I and II. Information storage and display of an X-ray photograph of a chicken bone in a1)–a6), of text of LMG TUD TSL Ce$^{3+}$ in b1)–b5), and of a QR code on a paper in the dark in c1)–c3). b6) illustrates the thermally stimulated luminescence process for b5). The chicken bone was removed before heating in a3)–a4), and a6), and the mask was not removed during heating in b5). The thickness is ~2 mm for plate I in a2) and ~0.5 mm for plate II in a5). Both the plates in a2) and a5) were heated to ~370 K for 3 min to empty all traps in the dark before X-ray exposure.
at the e-trap leading to e-trap emission. 3) by changing the VRBE at the VB-top via changing x or y in solid solutions the hole trapping depths will change likewise. 4) changing the VRBE at the CB-bottom by changing x or y in solid solutions affects the e-trapping depths.

The ‘strategy of the game’ is to find combinations of e-trap and h-trap for a specific purpose and then engineer x and y towards either optional storage phosphor or optimal afterglow phosphor performance.

4.1. Playing with the colour of recombination emission

Guided by the VRBE diagram in Fig. 1a), the combination of a deep h-trap formed by Ln3+ (Ln = Ce, Tb, or Pr) or Bi3+ with a less deep e-trap formed by Tb3+ or Sm3+ was explored with the aim to engineer the recombination emission in LiLu1−xYxSiO4. Compared with the Ce3+ or Bi3+ single doped LiLuSiO4 in Fig. S7a), an additional TL glow peak near 144 K emerges in Tb3+-co-doped LiLuSiO4 in Fig. 5a) and S7a). The corresponding 0.40 eV electron trap depth in Table 1 is smaller than the predicted hole trap depths of Ce3+, Tb3+, Pr3+, and Bi3+. Considering the largely systematic error margins of few 0.1 eV in VRBE diagrams based on broad charge transfer band transitions [13,60], the 0.40 eV is still regarded as consistent with the −0.62 eV electron trap depth of Tb3+ in the VRBE diagram in Fig. 1a). The 144 K Tb3+ TL glow peak is therefore attributed to electron liberation from Tb3+ to recombine with holes at Ce4+, Pr4+, Tb4+, and Bi4+ to give characteristic 5d-4f or 4f-4f emission of Ce3+, Pr3+, and Tb3+, and Bi3+ A-band emission in Fig. S7a). This is further supported in Fig. S7b) where a same Tb3+ TL peak near 186 K appears in all four Tb3+-co-doped LiYSiO4:0.01Ln3+, 0.01Sm3+ TL glow peaks (Ln = Ce, Pr, or Tb) and LiYSiO4:0.01Bi3+, 0.01Sm3+ samples. These results imply that one may engineer the recombination emission by the choice of deep hole trapping centres of Ce3+, Pr3+, Tb3+, or Bi3+ when combined with the less deep Tb3+ electron trapping centre.

Fig. 1a) illustrates that one may also engineer the recombination colour by combining the deep e-traps of Eu3+ and Bi3+ with less deep h-traps of Tb3+, Pr3+, and Bi4+ in LiLuSiO4. Indeed hole liberation from Tb3+, Pr3+, and Bi4+ that recombines with electrons at Eu4+ to give characteristic Eu3+ 4f-4f emission was identified, which is evidenced by the Tm emission spectra and the corresponding TL glow peaks Tb4+, Pr4+, and Bi4+ in Fig. 3b)–d). If the e-trap of Eu3+ is not present as in Fig. 3e) and 3f), the Bi4+ TL glow peaks near 532 K and near 510 K with Bi4+ A-band emission appear because of the hole liberation from Bi4+ to recombine with electrons captured at Bi4+. Here it demonstrates that one can tailor the recombination emission from Eu3+ 4f-4f emission to Bi3+ A-band emission by replacing the e-trap of Eu3+ by that of Bi3+ and using the hole liberation from Bi4+.

4.2. Playing with the electron trapping depth

Fig. 1a) and 1b) predict that Sm3+ acts as a ~0.46 eV deeper electron trap than Tb3+ which would correspond to a higher Tm for the corresponding TL glow peak. Fig. S7c) shows that indeed an additional TL peak near 345 K emerges in all the three Sm3+-co-doped LiLuSiO4:0.01Ln3+, 0.01Sm3+ (Ln = Pr, Tb, or Ce) compared with the Ln3+ single doped samples. The −345 K TL peak also appears in LiLuSiO4:0.01Bi3+, 0.01Sm3+ in Fig. 5c). The experimentally derived 1.0 eV electron trap depth for the 345 K TL peak in Table 1 is consistent with the predicted ~1.0 eV electron trap depth of Sm3+ and is less deep than the predicted hole trap depths of Pr3+, Tb3+, Ce3+, and Bi3+ based on the VRBE scheme in Fig. 1a). We therefore attribute the TL peak near 345 K to the electron release from Sm3+ to recombine with holes at Pr4+, Tb4+, Ce4+, and Bi4+ generating characteristic Pr3+, Tb3+, Ce3+, and Bi3+ emission, respectively. The above result implies that one may engineer the electron trap depth by the choice of lanthanides like Tb3+ and Sm3+. Since the TL peak shifts about 200 K close to room temperature by replacing the e-trap of Sm3+ by that of Sm3+ in the LiLuSiO4:0.01Ce3+, 0.01Ln3+ in Fig. 5a)–b), Ce3+ afterglow emerges in LiLuSiO4:0.01Ce3+, 0.01Sm3+ in Fig. S11b). One may again engineer the afterglow colour by replacing the hole trapping centre of Ce3+ by Tb3+ or Pr3+ producing typical Tb3+ and Pr3+ afterglow as demonstrated in Fig. S10.

Above the players were Tm and Sm but one may also enlarge the playing field by studying solid solutions. The results for Ln3+ and/or Bi3+ doped LiLu1−xYxSiO4 solid solutions in Fig. 5a)–c) demonstrate the electron trap depth tailoring of Tm3+ and Sm3+ by conduction band engineering. Here Ce3+ and Bi3+ act as deep hole capturing centres and Tm3+ and Sm3+ are less deep electron trapping centres. An about 0.1 eV electron trap depth increase is determined from both the Sm3+ and Tm3+ TL glow peaks in columns 10 and 12 of Table 1 when x increases from 0 to 1. It indicates that the conduction band bottom moves up by ~0.1 eV in LiLu1−xYxSiO4 with increasing x, which is to be compared with the predicted 0.17 eV increase in the stacked VRBE scheme as shown in Fig. 1b). We therefore attribute the about 50 K shifting of Tm3+ and Sm3+ TL peaks towards higher temperature to the increased activation energy for electron liberation from Tm3+ and Sm3+ as a result of conduction band rising with increasing x in LiLu1−xYxSiO4. The above result also demonstrates that thermoluminescence is a sensitive technique to determine a small (~0.1 eV) energy difference in a VRBE scheme.

The above results imply that one may design a storage phosphor via tailoring the electron trap depth by a combination of conduction band engineering and a choice of Ln3+ like the above Tm3+ and Sm3+ co-dopants. By further synthesis optimization, a good storage phosphor may appear like LiLu0.5Y0.5SiO4:0.01Ce3+, 0.005Sm3+ in Fig. 8a)–b) where after β irradiation its integrated TL intensity between 300 and 723 K is about 2 and 8.5 times higher than that of commercial Al2O3:C and BaFBr(1):Eu3+ storage phosphors.

Intrinsic host-related electron traps can also be very important for a high charge carrier storage capacity [35]. Using Eq. (1) with the frequency factor in column 2 of Table 1 and β = 1 K/s, the trapping depths for the host, TL peaks in LiLu1−xYxSiO4:0.01Ce3+, 0.01Sm3+ in Fig. 5b) are determined between ~1.43 and ~1.38 eV. They are ~3 eV less deep than the predicted Ce3+ hole trap depth in Fig. 1a). We therefore attribute these TL peaks to host-related intrinsic electron traps. The VRBE at the intrinsic defect(s) corresponding with these TL peaks is indicated in Fig. 1b). It is derived by subtracting the experimentally determined electron trap depth from the conduction band bottom. The VRBE in LiYSiO4 is different from that in LiLuSiO4 indicating that the VRBE at the intrinsic defect(s) is more dependent on the compound composition than that of Sm2+ in LiLu1−xYxSiO4:0.01Ce3+, 0.01Sm3+.

4.3. Playing with the hole trapping depth

The vacuum referred binding energy (VRBE) scheme for LiLuSiO4 in Fig. 1a) illustrates that Ce3+, Pr3+, Tb3+, and Bi3+ will act as ~3.89, ~2.04, ~2.22, and ~1.90 eV deep hole trapping centres, while Eu3+, Yb3+, and Bi3+ will act as ~2.34, ~1.90, and ~1.81 ± 0.5 eV deep electron trapping centres in LiLuSiO4. Holes captured to form Pr4+, Tb4+, and Bi4+ are then predicted to be released earlier, i.e., at a lower temperature, than the electrons at Eu4+ to upon recombination produce characteristic red 4f-4f emission of Eu3+.

Using Eq. (1) with the frequency factor in column 2 of Table 1 and β = 1 K/s, the trapping depths for TL peaks denoted Ith to Vth in LiLuSiO4 in Fig. 3a) are determined to be ~1.08, 1.22, 1.45, and 1.63, and 2.21 eV, which are less deep than the predicted Eu3+ electron trap depth of ~2.34 eV in Fig. 1a). These Ith–Vth TL peaks are therefore attributed to host-related intrinsic hole traps. We have drawn the derived level location for the Ith hole trap in Fig. 1b). The trapping depths for TL peaks Thb near 572 K and Pth near 582 K in Fig. 3b)–c) are derived to be ~1.67, and ~1.70 eV, respectively. During TL-readout, the activation energies required to liberate holes from Tb4+ (1.67 eV) and from Pr4+ (1.70 eV) are about 0.7 eV smaller than that to liberate electrons from Eu4+ (~2.34 eV). Therefore, the holes liberate from Tb4+ and Pr4+ to
recombine with the electrons captured at Eu$^{3+}$ to generate the TL glow peaks T$_{Bh}$ and Pr$_h$, with characteristic red 4f-4f emission of Eu$^{3+}$. Columns 6 and 8 of Table 1 show that the experimentally determined average hole trap depth for both Tb$^{3+}$ and Pr$^{3+}$ is $\sim$1.80 eV in LiLu$_{0.25}$Si$_{1-y}$Ge$_y$O$_4$, and $\sim$1.52 eV in LiY$_{1-x}$SiO$_4$, respectively. It is about 0.33, and 0.61 eV smaller compared with the ones estimated from the VRBE scheme (2.22 eV for Tb$^{3+}$ and 2.04 eV for Pr$^{3+}$) in Ref. [1a]. Similar deviation about 0.6 eV appeared in YPO$_4$ [13], and about 0.3 eV emerged in GdAlO$_3$ [2]. It may suggest there are errors and uncertainties in VRBE scheme construction. However, holes generated in the valence band tend to create a V$_h$ centre by bonding with two neighbouring oxygen anions [61–63]. Bonding means that the hole state moves up in a VRBE diagram [2,13,64]. The $\sim$0.33, and $\sim$0.61 eV energy differences in LiLu$_{0.25}$Si$_{1-y}$Ge$_y$O$_4$ and LiY$_{1-x}$SiO$_4$ could also be largely attributed to the binding energies of the V$_h$ centres. Upon thermal stimulation during TL-readout, holes are liberated from Tb$^{3+}$ or Pr$^{4+}$ to form a V$_h$ centre, which then migrates to recombine with electrons trapped at Eu$^{2+}$ to generate characteristic 4f-4f emission of Eu$^{3+}$ in LiLu$_{0.25}$Si$_{1-y}$Ge$_y$O$_4$ or LiY$_{1-x}$SiO$_4$.

The VRBE scheme in Fig. 1a) was constructed with the method outlined in Ref. [60] where the ground state of Pr$^{3+}$ is 0.18 eV below that of Tb$^{3+}$. One then expects that the Pr$_h$ TL glow peak appears at about 60–70 K lower temperature than the Tb$_h$ TL glow peak. In Refs. [65,66] experimental evidence was presented that the ground state of Pr$^{3+}$ and Tb$^{3+}$ should be at similar energy and also slightly compound dependent. This is now further confirmed in this work. The Pr$^{3+}$ TL glow peak appears at only about 10 K lower temperature than that of Tb$^{3+}$ in LiLu$_{0.75}$Y$_{0.25}$Si$_{0.9}$O$_{2.1}$, and 0.011n (Ln = Tb or Pr) in Fig. 4a)-b) and YPO$_4$0.01Eu$^{3+}$,0.01Ln$^{3+}$ in Ref. [13]. Columns 6 and 8 of Table 1 show that the experimentally derived hole trap depth of Tb$^{3+}$ is almost the same as that of Pr$^{3+}$ in LiLu$_{0.25}$Y$_{0.75}$Si$_{0.75}$O$_{4}$.

Fig. 1a) illustrates that Bi$^{3+}$ acts as a $\sim$1.90 eV deep hole trap, while Eu$^{2+}$ and Bi$^{3+}$ act as $\sim$2.34 and $\sim$1.81 ± 0.5 eV deep electron traps in LiLu$_{0.25}$Si$_{1-y}$Ge$_y$O$_4$. The TLEM plots in Fig. 3d-e) for LiLu$_{0.25}$Y$_{0.75}$Si$_{0.75}$O$_{4}$,0.01Eu$^{3+}$,0.01Bi$^{3+}$ and LiLu$_{0.25}$Y$_{0.75}$Si$_{0.75}$O$_{4}$,0.01Bi$^{3+}$,0.01Sm$^{3+}$ share the same Bi$_h$ TL peak near 532–535 K. A slightly higher Bi$_h$ TL peak near 553 K emerges in LiLu$_{0.25}$Si$_{1-y}$Ge$_y$O$_4$ (Fig. 4c). Bi$_h$ hole trap depth in LiLu$_{0.25}$Si$_{1-y}$Ge$_y$O$_4$ is determined to be 1.62 eV in Table 1, which is $\sim$0.3 eV smaller than that predicted by the Bi$^{3+}$ 1S$_0$ ground state level based on Bi$^{3+}$ D-band in the VRBE diagram in Fig. 1a). Like the Tb$^{3+}$ and Pr$^{4+}$ hole detrapping processes discussed above, the $\sim$0.3 eV energy difference may be due to the errors and uncertainties in VRBE diagram construction, but also could be largely attributed to the binding energy of the V$_h$ centre. Note that the Bi$^{3+}$ hole trap depth (1.90 eV) is less deep than the predicted electron trap depth of Eu$^{3+}$ ($\sim$2.34 eV) in Fig. 1a). During TL-readout, a hole is therefore released from Tb$^{3+}$ or Pr$^{4+}$ to form a V$_h$ centre, which then migrates to recombine with the electrons captured at Eu$^{2+}$ to generate characteristic 4f-4f emission of Eu$^{3+}$ in LiLu$_{0.25}$Si$_{1-y}$Ge$_y$O$_4$ or LiY$_{1-x}$SiO$_4$.

The TL excitation spectra in Fig. S13c) show that the Ce$^{3+}$ 4f-5d$_1$ excitation band near 350 nm can charge the LiLu$_{0.25}$Y$_{0.75}$Si$_{1-y}$Ge$_y$O$_4$.0.01Bi$^{3+}$ because of the Bi$^{3+}$ hole trap depth through changing the ratio of silicon to germanium. With increasing silicon content, the TL peak shifts from 371 K to 538 K, which is consistent with the decrease of the Bi$^{3+}$ persistent luminescence in Fig. 6b) and the less TL fading in Fig. 6c). With further crystal synthesis optimization, a good storage phosphor may appear like LiLu$_{0.25}$Y$_{0.75}$Si$_{0.75}$O$_{4}$.0.01Bi$^{3+}$ in Fig. 8a) in which the integrated TL intensity between 300 and 800 K is about 4.4 times higher than that of commercial BaFBr(I):Eu$^{2+}$ phosphor after β irradiation.

4.4. Information storage application using Ce$^{3+}$ and Bi$^{3+}$ storage phosphors

The TL emission spectra in Fig. S3) show that the thermally stimulated Ce$^{3+}$ 5d-4f emission which has $\sim$39 ns fluorescence decay time in Fig. 525 appears in the visible region, while the Bi$^{3+}$ A-band emission peaking near 360 nm in Fig. 3e) with $\sim$0.5 μs fluorescence decay time in Fig. S26–S27 emerges largely in the ultraviolet region. Both thermally stimulated Ce$^{3+}$ and Bi$^{3+}$ emissions in LiLu$_{0.25}$Y$_{0.75}$Si$_{0.75}$O$_{4}$ phosphors match well with a traditional photomultiplier tube and are quite intense compared with the commercial BaFBr(I):Eu$^{2+}$ storage phosphor in Fig. 8a). This combined with better TL fading characteristics in Fig. 8c) and the photon stimulation ability of the charge carriers stored during β-ray exposure in Fig. 9 indicates that the developed phosphors have potential application as optically stimulated storage phosphors for information storage as demonstrated in Fig. 10 and S29–S31.

5. Conclusions

The methodology to rational design of storage phosphors with high charge carrier storage capacity for information storage has been explored by studying both the trapping and detrapping processes of electrons and holes in the bismuth and lanthanide-doped LiRE(Si,Ge)O$_4$...
(RE = Y, Lu) family of compounds. For LiLuSiO$_4$:0.01Ln$_3^+$,0.01Tm$_3^+$, the Tm$_3^+$ acts as an electron trap, while the Ln$_3^+$ and Bi$_3^+$ codopants are the hole traps and recombination centres. The electrons are released from Tm$_2^+$ to recombine with holes captured at Ln$_4^+$ and Bi$_4^+$ to generate characteristic Ln$_3^+$ 4f-4f or 5d-4f emission and Bi$_3^+$ A-band emission. The electron trap depth can be controlled by the choice of Tm$_3^+$ or Sm$_3^+$ codopant, and for fixed pair of Bi$_3^+$ and/or Ln$_3^+$ dopants like in LiLu$_{1-x}$Y$_x$SiO$_4$:0.01Ce$_3^+$,0.01Tm$_3^+$ (Ln = Tm or Sm) and LiLu$_{1-x}$Y$_x$SiO$_4$:0.01Bi$_3^+$,0.01Sm$_3^+$ solid solutions, by changing x, resulting in conduction band engineering. The integrated TL intensity of the optimized LiLu$_{0.5}$Y$_{0.5}$SiO$_4$:0.01Ce$_3^+$,0.01Sm$_3^+$ is about 8.5 times higher than that of the commercial BaFBr(II):Eu$_3^+$ storage phosphor based after β irradiation. In LiLu$_4$:0.01Eu$_3^+$,0.01Ln$_3^+$ (Ln = Tb or Pr), LiLu$_{0.25}$Y$_{0.75}$Si$_{1-y}$Ge$_y$O$_4$:0.01Bi$_3^+$, leading to the tailoring of Bi$_3^+$ hole traps and recombination processes in GdAlO$_3$ by valence band engineering, J. Phys. Chem. C 119 (2015) 14047–14055.

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Declaration of interests

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Appendix A. Supplementary data

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