NUV-pumped luminescence of thermally stable samarium-activated alkali metal borophosphate phosphor

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Abstract: Exploring outstanding rare-earth activated inorganic phosphors with good thermostability has always been a research focus for high-power white light-emitting diodes (LEDs). In this study, we report a Sm^{3+} -activated $\text{KNa}_4\text{B}_2\text{P}_3\text{O}_{13}$ (KNBP) powder phase. Its particle morphology, photoluminescence properties, concentration quenching mechanism, thermal quenching mechanism, and chromatic properties are demonstrated. Upon the near-ultraviolet (NUV) irradiation of 402 nm, the powder phase exhibits orange–red visible luminescence performance, originating from typical $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{J/2}$ ($J = 5, 7, 9$) transitions of Sm^{3+} . Importantly, the photoluminescence performance has good thermostability, low correlated color temperature (CCT), and high color purity (CP), indicating its promising application in the NUV-pumped warm white LEDs.

Keywords: $\text{KNa}_4\text{B}_2\text{P}_3\text{O}_{13}$ (KNBP); Sm^{3+} luminescence; concentration quenching; thermostability

1 Introduction

To support the field of solid-state lighting and display, developing a variety of inorganic phosphors suitable for white light-emitting diodes (LEDs) has increasingly attracted a tremendous attention [1–3]. However, currently phosphor-converted white LEDs technology is facing the urgent challenge. The increase of operating-temperature generally gives rise to the drop of luminescence efficiency of phosphor due to the long-time work of white LEDs. In addition, excellent red phosphor is urgently needed for reducing correlated color temperature and improving color rendering index

of white LEDs. Hence, constructing red phosphor with high thermal stability becomes a research focus in phosphor-converted white LED technology [4,5].

Generally, an LED inorganic phosphor is composed of activator and host material. The activators are doped into a host material to produce luminescence properties. Rare-earth ions, as important activators, can acquire easily various emission light colors (blue, green, yellow, and red) owing to their abundant 4f transition properties [6,7]. To cope with the needs of white LEDs for red phosphors, inorganic aluminates [8,9], phosphates [10,11], borates [12], silicate [13], tungstate [14], vanadate [15], and molybdate [16] activated with rare earth activator samarium (Sm) were reported. The typical near-ultraviolet (NUV) 4f absorption of Sm^{3+} matches well with the emission of NUV LED chips.

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The 4f transitions of Sm^{3+} dominate its visible light emission. The symmetry of the coordination field for Sm^{3+} ions closely affects the luminescence efficiency and emission light color of inorganic phosphors.

Borophosphate materials have been proven to have good optical, physical, and chemical properties correlated with the diversified anionic frameworks, which originate from the various connections of boron–oxygen tetrahedron (BO_4), boron–oxygen triangle (BO_3), and phosphorus–oxygen tetrahedron (PO_4) structural groups [17]. So, the diversified structures of borophosphate materials give a great probability for exhibiting the different emission light colors of Sm^{3+} related to the diversity of its coordination fields. In 2019, Yang *et al.* [18] firstly reported borophosphate $\text{KNa}_4\text{B}_2\text{P}_3\text{O}_{13}$ (KNBP) with the non-centrosymmetric $Pna2_1$ space group and its nonlinear optical properties. The $(\text{B}_2\text{P}_3\text{O}_{13})^{5-}$ anionic framework of the borophosphate is composed of BO_4 and PO_4 tetrahedra. The borophosphate KNBP exhibits a good transmittance in the whole visible light region. Besides, it has the characteristics of stable physicochemical properties, facile preparation, and nontoxicity. The previous investigation indicates that the inorganic KNBP borophosphate could be a prospective host of phosphor materials. However, KNBP-based phosphor doped with Sm^{3+} activators has not been proposed.

In this work, we utilized a facile solid-state synthesis procedure for synthesizing $\text{KNBP}:\text{xSm}^{3+}$ ($x = 0, 0.25, 0.5, 0.75, 1, 2, 3$ mol%) powder phases. The phase identification, morphological characterization, photoluminescence properties, chromatic properties, concentration quenching, and thermal quenching mechanisms were systematically analyzed.

2 Experimental

2.1 Material synthesis

The reagents used in the experiment were Sm_2O_3 (99.99%), H_3BO_3 (99.9%), $\text{NH}_4\text{H}_2\text{PO}_4$ (99.9%), K_2CO_3 (99.9%), and Na_2CO_3 (99.9%). According to the stoichiometric ratio of the KNBP host, the required reagents were weighed precisely. After mixing and grinding these reagents, the mixture was preheated at 673 K for 5 h in a high-temperature furnace. Then the temperature was increased to 873 K. The heat preservation period was 168 h in Ref. [18]. To optimize the synthesis procedure, we carried out a series of

solid-state reactions with different heat preservation periods (24, 48, 72, 120, and 168 h). The sintering time-dependent X-ray diffraction (XRD) patterns of the KNBP host powder phase are shown in Fig. S1 in the Electronic Supplementary Material (ESM). The pure KNBP powder with good crystallinity can be prepared in only 24 h. Thus, a series of $\text{KNBP}:\text{xSm}^{3+}$ ($x = 0, 0.25, 0.5, 0.75, 1, 2, 3$ mol%) polycrystalline phases were synthesized by the more simplified solid-state synthesis procedure, in comparison to the preparation reported in Ref. [18].

2.2 Characterizations

Powder XRD patterns were recorded via a Rigaku D/Max-3B diffractometer with $\text{Cu K}\alpha$ radiation. A Nicolet iS10 spectrometer was used for recording Fourier transform infrared (FTIR) spectra. The morphology observation was carried out via a scanning electron microscope (SEM, FEI QUANTA200) and a transmission electron microscope (TEM, JEOL 2100F), and the elemental analysis was made by the scanning electron microscope with an energy dispersive spectroscopy (EDS) detector. The UV–Vis diffuse reflectance spectra (DRS) were performed via a SHIMADZU UV2600 spectrophotometer. A Hitachi F7100 spectrophotometer equipped with an integrating sphere was used to measure photoluminescence excitation (PLE), photoluminescence (PL), and internal quantum efficiency (IQE). An Edinburgh FLS920 spectrophotometer with xenon lamp excitation was employed to measure decay lifetime.

3 Results and discussion

3.1 XRD and FTIR analysis

The powder XRD reflections for the prepared $\text{KNBP}:\text{xSm}^{3+}$ ($x = 0, 0.25, 0.5, 0.75, 1, 2, 3$ mol%) phases are displayed in Fig. 1(a). Based on the crystallographic information file (CIF) of the KNBP orthorhombic phase reported in 2019 [18], we have used the Diamond software to simulate its XRD reflection. The XRD patterns for all Sm^{3+} -doped samples have the same peak positions and relative intensities as the simulated one, revealing that all the prepared powder phases are isostructural with the KNBP orthorhombic matrix and belong to the non-centrosymmetric space group $Pna2_1$. There are crystallographically independent four sodium (Na),

one potassium (K), two boron (B), three phosphorus (P), and thirteen oxygen (O) atoms in its asymmetric unit. K, B, and P atoms are connected with eight, four, and four O atoms, respectively. Figure 1(b) shows the 5, 6, and 10-coordinated environments of Na atoms. The coordination number (CN)-dependent radius values for K^+ , Na^+ , B^{3+} , P^{5+} , and Sm^{3+} ions are listed in Table S1 in the ESM [19]. There is a good approximation for the ionic radius values of Na^+ and Sm^{3+} ions. The dopant Sm^{3+} ion prefers to occupy the lattice position of the Na^+ ion, and the structure of the KNBP host is not altered. To discuss the influence of the dopant Sm^{3+} ion on the shift of diffraction peak, the enlarged XRD patterns in the 29° – 30.5° range are shown in Fig. 1(a). The strongest peak at around 29.7° slightly shifts toward a higher 2θ angle with the increase of the dopant Sm^{3+} concentration, supporting the fact that Sm^{3+} ion is doped into the host lattice and substitute Na^+ ion. The main reason for the peak-shift

phenomenon is that the radius of the dopant Sm^{3+} ion is slightly smaller than that of the substituted Na^+ ion (Table S1 in the ESM). However, increasing the dopant concentration of Sm^{3+} ions to 3 mol% gives rise to a weak diffraction peak at $2\theta = 31.7^\circ$, corresponding to a small amount of impurity phase KBO_2 (JCPDS 03-0729) due to the non-equivalent replacement of Sm^{3+} for Na^+ and the solid solubility limitation, which also resulted in the appearance of the second phase in $Ba_3(VO_4)_2:Sm^{3+}$ and $LiNaB_5P_2O_{14}:Eu^{3+}$ phosphors reported recently [15,20]. Besides, to verify the purity of the as-synthesized samples, the XRD data of the KNBP phase and KNBP:0.75% Sm^{3+} powder was refined by the Rietveld method, as shown in Fig. 2. Here, the basis refinement was derived from the KNBP initial structure parameters (orthorhombic system with space group $Pna2_1$). The refinement results of profile residual factor (R_p) and weighted profile R -factor (R_{wp}) are reliable and reasonable owing to $R_p = 7.42\%$, $R_{wp} =$

Fig. 1 (a) Powder XRD patterns of the prepared KNBP: xSm^{3+} ($x = 0, 0.25, 0.5, 0.75, 1, 2, 3$ mol%) phases and (b) coordination environments for Na atoms.

Fig. 2 Rietveld refinements of XRD patterns of the (a) KNBP phase and (b) KNBP:0.75% Sm^{3+} powder.

10.99% for the KNBP phase and $R_p = 7.21\%$, $R_{wp} = 9.55\%$ for the KNBP:0.75%Sm³⁺ powder, indicating that the samples have good phase purity.

Figure 3 displays the FTIR curves of the KNBP:*x*Sm³⁺ (*x* = 0, 0.25, 0.5, 0.75, 1, 2, 3 mol%) powders. All the FTIR spectra with dopant Sm³⁺ ions keep the same shapes and locations of vibration peaks as that of the pure KNBP phase. These absorption vibrations are caused by BO₄ and PO₄ tetrahedra [21,22], which are basic structural groups in the KNBP matrix. The vibrations at 1193 and 1148 cm⁻¹ result from the asymmetric stretching mode of the PO₄ group. The vibrations at 1093 and 918 cm⁻¹ originate from the symmetric stretching mode of the BO₄ group. The vibration at 986 cm⁻¹ arises from the P–O–P asymmetric stretching. The vibrations at 869 and 821 cm⁻¹ are ascribed to the B–O–P asymmetric stretching. The vibrations at 750 and 674 cm⁻¹ correspond to the symmetric stretching of B–O–P and P–O–P. The vibrations at 622 and 591 cm⁻¹ belong to the asymmetric bending of the BO₄ group. The vibration at 542 cm⁻¹ is assigned to the asymmetric bending of the PO₄ group. The symmetric bending of the BO₄ and PO₄ groups result in the vibrations at 521 and 468 cm⁻¹. The investigation confirms that the doping of Sm³⁺ ions does not destroy the BO₄ and PO₄ structural units.

3.2 Particle morphology and elemental analysis

Particle morphology and size of a phosphor is closely related to photoluminescence performance. The comparative investigation on the particle morphologies of the KNBP host and KNBP:0.75%Sm³⁺ powder was carried out (Figs. 4(a) and 4(b)). Both powder samples

Fig. 3 FTIR spectra of KNBP:*x*Sm³⁺ (*x* = 0, 0.25, 0.5, 0.75, 1, 2, 3 mol%) powders.

consist of block-like micron particles with irregular shape and inhomogeneous size. During the high-temperature sintering process, adjacent small-sized particles have aggregated to attain micron bulks. The aggregation of the KNBP:0.75%Sm³⁺ particles (Fig. 4(b)) is more serious than that of the KNBP particles (Fig. 4(a)). The TEM image of the KNBP:0.75%Sm³⁺ powder (Fig. 4(c)) shows single particle with a micron-level size. The inset of Fig. 4(c) shows the corresponding high-resolution TEM (HRTEM) image. The lattice fringe with 0.424 nm corresponds to the (112) crystal plane of the host phase. The clear lattice fringe verifies that the sample has good crystallization and stability under high energy electron beam. Figure 4(d) depicts the measured EDS profile of the KNBP:0.75%Sm³⁺ sample, which manifests the presence of the elements Sm, K, Na, B, P, and O. The elemental distribution map for the KNBP:0.75%Sm³⁺ sample is shown in Fig. 4(e), confirming the uniform distribution of these chemical components.

3.3 Diffuse reflection, excitation, and emission

The measured DRS curves of the KNBP:*x*Sm³⁺ (*x* = 0, 0.25, 0.5, 0.75, 1, 2, 3 mol%) powder phases at room temperature are presented in Fig. 5. The KNBP matrix has no absorption in the visible (Vis) region, which keeps consistent with the diffuse reflection data reported by Yang *et al.* [18]. The observed ultraviolet (UV) absorption mainly comes from the charge transitions of BO₄ and PO₄ groups [18]. Differently, as depicted in the inset of Fig. 5, all the DRS curves with dopant Sm³⁺ ions clearly show UV–Vis absorptions in the 330–510 nm range owing to the typical 4f–4f transitions of Sm³⁺. A series of absorptions appear at 344, 361, 374, 402, 438, and 476 nm, deriving from the ⁶H_{5/2}→⁴H_{9/2}, ⁴D_{3/2}, ⁴D_{1/2}, ⁴F_{7/2}, ⁴G_{9/2}, and ⁴G_{7/2} transitions, respectively [23]. Among these absorptions, the ⁶H_{5/2}→⁴F_{7/2} (402 nm) transition is the strongest.

The PLE curve of the KNBP:0.75%Sm³⁺ powder recorded at the monitoring wavelength of 598 nm is depicted in Fig. 6(a). We can observe excitation peaks at 344 (⁶H_{5/2}→⁴H_{9/2}), 361 (⁶H_{5/2}→⁴D_{3/2}), 374 (⁶H_{5/2}→⁴D_{1/2}), 402 (⁶H_{5/2}→⁴F_{7/2}), 415 (⁶H_{5/2}→⁶P_{5/2}), 438 (⁶H_{5/2}→⁴G_{9/2}), and 469 nm (⁶H_{5/2}→⁴I_{13/2}) [24]. The strongest transition appears at 402 nm (⁶H_{5/2}→⁴F_{7/2}), which keeps consistent with the obtained diffuse reflectance result in Fig. 5. The comparison of photoluminescence under various excitations was investigated. Figure 6(b) illustrates the PL curves of the KNBP:0.75%Sm³⁺

Fig. 4 (a) SEM image (scale bar = 300 μm) of the KNBP phase; (b) SEM image (scale bar = 300 μm); (c) TEM image (scale bar = 1 μm), the inset shows the HRTEM image; (d) EDS spectrum; and (e) elemental mappings of the KNBP:0.75% Sm^{3+} powder.

Fig. 5 DRS curves of the prepared KNBP: $x\text{Sm}^{3+}$ ($x = 0, 0.25, 0.5, 0.75, 1, 2, 3$ mol%) powder phases (the inset shows the enlarged curve in the 330–510 nm range).

powder upon excitations at 344, 361, 374, 402, 415, and 469 nm. All the PL curves are mainly composed of three typical 4f–4f transitions of Sm^{3+} , which are located at 645 nm ($^4\text{G}_{5/2} \rightarrow ^6\text{H}_{9/2}$), 598 nm ($^4\text{G}_{5/2} \rightarrow ^6\text{H}_{7/2}$), and 562 nm ($^4\text{G}_{5/2} \rightarrow ^6\text{H}_{5/2}$) [16]. The dominant $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{7/2}$ (598 nm) transition belongs to visible orange–red light. Differently, the integrated emission intensity obtained by 402 nm excitation is higher than others, indicating that an NUV LED chip is suitable for NUV-pumped photoluminescence of the sample. As a rule, the purely magnetic dipole transition (MDT) and purely electric dipole transition (EDT) are known as $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{5/2}$ and $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{9/2}$ transition in the same order. The combination of MDT and EDT results in the $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{7/2}$ transition. The asymmetry of the local coordination of Sm^{3+} can be used to analyze the EDT/MDT intensity ratio. The

Fig. 6 (a) PLE and (b) PL curves of the KNBP:0.75%Sm³⁺ powder.

asymmetric coordination of Sm³⁺ corresponds to the intensity ratio of EDT/MDT > 1. In this case, the coordination environment of Na⁺ is distorted (Fig. 1(b)). The local coordination of Sm³⁺ has a slight asymmetry due to the substitution of Sm³⁺ for Na⁺. Hence, the MDT intensity is slightly less than the EDT one (Fig. 6(b)) [15].

3. 4 Sm³⁺ concentration-dependent photoluminescence

Figure 7(a) shows the PL spectra for the KNBP:xSm³⁺ ($x = 0.25, 0.5, 0.75, 1, 2, 3$ mol%) powder samples upon 402 nm NUV excitation. The Sm³⁺ doping concentration closely affects emission intensity. Figure 7(b) illustrates the Sm³⁺ concentration-dependent emission intensity. As the Sm³⁺ concentration increases from 0.25 to 0.75 mol%, the PL intensity increases. Subsequently, the non-radiative energy transfer among Sm³⁺ ions occurs with the further increase of the Sm³⁺ concentration, leading to the decrease of the emission intensity. The Sm³⁺ concentration of 0.75 mol% is determined to be the optimization for concentration quenching. As a rule, the critical energy transfer distance

(R_c) for concentration quenching is greater than 5 Å, meaning that the multipole–multipole interaction is the cause of concentration quenching. In order to discuss the mechanism of concentration quenching, the R_c value of Sm³⁺ in the KNBP matrix could be estimated using Eq. (S1) in the ESM. The calculated R_c value of Sm³⁺ is 26.1 Å. Hence, the concentration quenching for KNBP:xSm³⁺ comes from the multipole–multipole interaction. The multipolar energy transfer process was further analyzed via Eqs. (S2) and (S3) in the ESM. The obtained result is illustrated in Fig. 7(c), which stands for the linear correlation of $\log(I/\chi)$ versus $\log(\chi)$. On the basis of the slope $-\theta/3 = -1.73$, the obtained θ value equals 5.19, which is near to 6. The result manifests that the electric dipole–dipole interaction dominates the concentration quenching of the prepared KNBP:xSm³⁺ powder samples.

Figure 8 shows the lifetime for the KNBP:xSm³⁺ ($x = 0.25, 0.5, 0.75, 1, 2, 3$ mol%) powder samples, which were recorded under ${}^6\text{H}_{5/2} \rightarrow {}^4\text{F}_{7/2}$ (402 nm) excitation and ${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_{7/2}$ (598 nm) emission. All decay lifetime curves were fitted using a typical double exponential

Fig. 7 (a) PL curves, (b) Sm³⁺ concentration-dependent PL intensity, and (c) dependence of $\log(I/\chi)$ on $\log(\chi)$ for KNBP:xSm³⁺ ($x = 0.25, 0.5, 0.75, 1, 2, 3$ mol%).

Fig. 8 Decay lifetime curves for KNBP: $x\text{Sm}^{3+}$ ($x = 0.25, 0.5, 0.75, 1, 2, 3$ mol%).

function, which is shown as Eq. (S4) in the ESM. The average decay lifetime (τ_{ave}) was calculated via Eq. (S5) in the ESM. As the Sm^{3+} doping concentration increases, the τ_{ave} value shortens from 1.49 to 1.29 ms. The sample with the optimized doping concentration of 0.75 mol% possesses the τ_{ave} value of 1.43 ms. The downtrend of decay lifetime arises from the increased probability of the non-radiative transitions among dopant Sm^{3+} ions [25,26].

Figure 9(a) shows the CIE chromaticity diagram for the KNBP: $x\text{Sm}^{3+}$ ($x = 0.25, 0.5, 0.75, 1, 2, 3$ mol%) powder samples. The inset of Fig. 9(a) lists the values of color coordinates (x, y), correlated color temperature

(CCT), and color purity (CP), which were calculated using Eqs. (S6)–(S9) in the ESM, respectively. The emission colors of all the samples upon 402 nm NUV irradiation are situated in the orange–red area. The CCT parameters range from 2050 to 2890 K, which are far lower than 5000 K. The low CCT indicates the potential application of the title phosphor in warm white LEDs. Furthermore, the CP values of all the samples are higher than 80%. Figure 9(b) illustrates the comparison of the digital photos of the KNBP:0.75% Sm^{3+} powder under daylight and a 365 nm UV lamp. When the KNBP:0.75% Sm^{3+} white powder was excited by a 365 nm UV lamp, the obtained emission

Fig. 9 (a) CIE chromaticity diagram for KNBP: $x\text{Sm}^{3+}$ ($x = 0.25, 0.5, 0.75, 1, 2, 3$ mol%) (the inset shows the CIE coordinates, CCT, and CP values), (b) comparison on the digital photos of the KNBP:0.75% Sm^{3+} powder under daylight and a 365 nm UV lamp, and (c) the IQE measurement of the KNBP:0.75% Sm^{3+} powder.

color is comparable to the above color coordinate data. Besides, Eq. (S10) in the ESM was employed for assessing the IQE value. Under 402 nm excitation, the IQE value of the KNBP:0.75%Sm³⁺ powder is 26.2%, as depicted in Fig. 9(c).

3.5 Operating temperature-dependent photoluminescence

Figure 10(a) illustrates the correlation between operating temperature and PL intensity for the KNBP:0.75%Sm³⁺ powder upon 402 nm NUV irradiation. As the operating temperature increases to 528 K, there is no obvious change in the positions and peak shapes for the 4f–4f transitions of Sm³⁺. However, the integrated PL intensity slowly drops due to the increased non-radiative transitions stimulated at high temperatures. Figure 10(b) illustrates clearly the normalized emission intensities depending on different temperatures. When the operating temperature rises to 428 K, the loss of the integrated PL intensity is 15% of the initial intensity, which is comparable with the 14% loss of the commercially available phosphor Sr₂Si₅N₈:Eu²⁺ [4]. To further explore the operating temperature-dependent PL performance of the phosphor, the Arrhenius equation (Eq. (S11) in the ESM) was employed for assessing the activation energy (E_a). Figure 10(c) shows the influence of $1/kT$ on $\ln[(I_0/I(T)) - 1]$. The E_a value of the KNBP:0.75%Sm³⁺ powder is around 0.31 eV via fitting the experimental data. The synthesized phosphor has good thermostability comparing with reported inorganic phosphors doped with Sm³⁺, such as SrBi₂Ta₂O₉:Sm³⁺ ($E_a = 0.23$ eV) [27], Ca₁₉Mg₂(PO₄)₁₄:Sm³⁺ ($E_a = 0.13$ eV) [28], and KLaSr₃(PO₄)₃F:Sm³⁺ ($E_a = 0.163$ eV) [29]. Equation (S12) in the ESM was employed for analyzing color stability. The obtained parameter of chromaticity

shift (ΔE) is around 0.029 at 503 K, which is smaller than $\Delta E = 0.044$ at 500 K for commercial red CaAlSiN₃:Eu²⁺ product [30].

4 Conclusions

In conclusion, a new alkali metal borophosphate-based orange-red phosphor KNBP:Sm³⁺ was synthesized via a facile solid-state synthesis procedure. Despite dopant Sm³⁺ occupied the Na⁺ site, the prepared KNBP:*x*Sm³⁺ (*x* = 0, 0.25, 0.5, 0.75, 1, 2, 3 mol%) microparticles keep the orthorhombic structure of the KNBP matrix. The phosphor exhibits the typical 4f–4f transitions of Sm³⁺ at 645 nm (⁴G_{5/2}→⁶H_{9/2}), 598 nm (⁴G_{5/2}→⁶H_{7/2}), and 562 nm (⁴G_{5/2}→⁶H_{5/2}) upon 402 nm NUV irradiation. For the concentration quenching with the optimal 0.75 mol% concentration of Sm³⁺, the electric dipole–dipole interaction plays a dominant role. The operating temperature-dependent photoluminescence reveals that the phosphor has good thermostability with the activation energy of 0.31 eV. The obtained properties confirm that the KNBP:Sm³⁺ phosphor with high CP and low CCT can potentially serve solid-state lighting and display applications.

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Fig. 10 (a) Operating temperature-dependent PL curves excited by a 402 nm light, (b) normalized emission intensities depending on different temperatures, and (c) activation energy of the thermal quenching of the KNBP:0.75%Sm³⁺ powder.

Electronic Supplementary Material

Supplementary material is available in the online version of this article at <https://doi.org/10.1007/s40145-021-0492-z>.

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