

Supporting Information

Title: Phosphate-based phosphor for urban mining of lanthanides: a case study of samarium

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The Supporting information include:

1. Experimental section
2. Supplementary tables
3. Supplementary Figures

1. Experimental Section

Materials and synthesis of the phosphor.

The $\text{NaBa}_{1-x}\text{PO}_4: x\text{Sm}^{3+}$ ($x=0.1, 0.5, 1, 3, 5, 7$ mol%) phosphor was synthesized by conventional solid-state reaction method. The raw materials of BaCO_3 (Aladdin, 99.99%), $(\text{NH}_4)\text{H}_2\text{PO}_4$ (Macklin, AR), Na_2CO_3 (purity 99.99%) and Sm_2O_3 (Aladdin, 99.99%). The starting materials in stoichiometric amounts were mixed thoroughly in a corundum crucible. Firstly, the mixture was heated up to 400 °C and kept at this temperature for 3 h. The powder obtained from pretreatment was ground again and heated at 1200 °C for 3 h under an air atmosphere. Finally, the NBP: Sm^{3+} samples were obtained. The phosphor is thoroughly mixed with the epoxy resin 1:1 by weight, and the resulting phosphor-epoxy mixture is coated onto the diode chip (CDX-3WGH40B).

The Sm^{3+} recycling.

Typically, 1.0 g of Sm^{3+} ion doped NBP at a concentration of 5 mol% is dispersed in 30 mL of distilled water. A small amount of the phosphoric acid was added to adjust the pH to 2~3 and the dispersion became transparent completely (solution A). After adjusting the pH to 9 using 0.1 M NaOH solution, the white precipitation was obtained. The precipitation was collected using centrifugation and drying, and it commixed with a proper amount of sodium carbonate and ammonium biphosphate. The mixture was calcined at 1200 °C for 2 hours and an optical glass sample was obtained after cooling down naturally to room temperature.

Characterizations of the materials.

Powder X-ray diffractometer operating at 36 kV and 20 mA and equipped with a Cu-K α ($\lambda = 1.54178 \text{ \AA}$) radiation rotating anode for recording the powder X-ray diffraction (XRD) patterns of NaBa_{1-x}PO₄: xSm³⁺ (x=0.1, 0.5, 1, 3, 5, 7 mol%) was collected in 10° to 90° range at a scanning step of 0.01° and a scanning rate of 10 °/min. The morphology and elemental distribution of the samples were characterized using a Hithit-S4800 scanning electron microscope (SEM) and an energy dispersive X-ray spectrometer (EDS). The fluorescence spectrophotometer (FLS-980, Edinburgh instruments) with a 450 W Xenon lamp was employed to study excitation, the steady-state fluorescence spectra, including the excitation spectra (PLE), emission spectra (PL), and fluorescence lifetime. The temperature-dependent PL spectrum of the sample within the temperature range of 25-250 °C was determined using an Edinburgh Model FLS 980 spectrofluorometer equipped with a thermal accessory. Ultraviolet-visible diffuse reflection spectra (DRS) were tested by a spectrophotometer (Shimadzu, UV-3600 plus with BaSO₄ white powder as reference). After nitric acid treatment, inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7700s (ICP-MS)) was used to study how many ions were dissolved in the phosphor.

2. Supplementary Tables.

Table S1. A table of abbreviations

Acronyms	Full name
wLEDs	warm light emitting diodes
NBP	NaBaPO ₄
UV	ultraviolet
ICP-MS	inductively coupled plasma mass spectrometry
GS	Sm ³⁺ was successfully doped into the glass
XRD	X-ray diffraction
EDS	energy dispersive spectroscopy

Table S2. ICP-MS result of acid treated NBP:Sm³⁺

Sample	Concentration of Sm ³⁺ (mg/L)	Sm ³⁺ percentage (%)
Original NBP:0.05Sm ³⁺ dispersion with phosphoric acid	4.172	100.0
Residual solution without precipitate	0.101	2.4

Table S3. Color coordinates of different Sm³⁺ ion concentrations

Phosphors	CIE coordinates		CCT
	x	y	
NBP:0.001Sm ³⁺	0.58	0.41	1674
NBP:0.005Sm ³⁺	0.60	0.40	1622
NBP:0.01Sm ³⁺	0.60	0.40	1624

NBP:0.03Sm ³⁺	0.60	0.40	1623
NBP:0.05Sm ³⁺	0.60	0.40	1627
NBP:0.07Sm ³⁺	0.60	0.40	1631
GS	0.61	0.39	1627

3. Supplementary Figures.

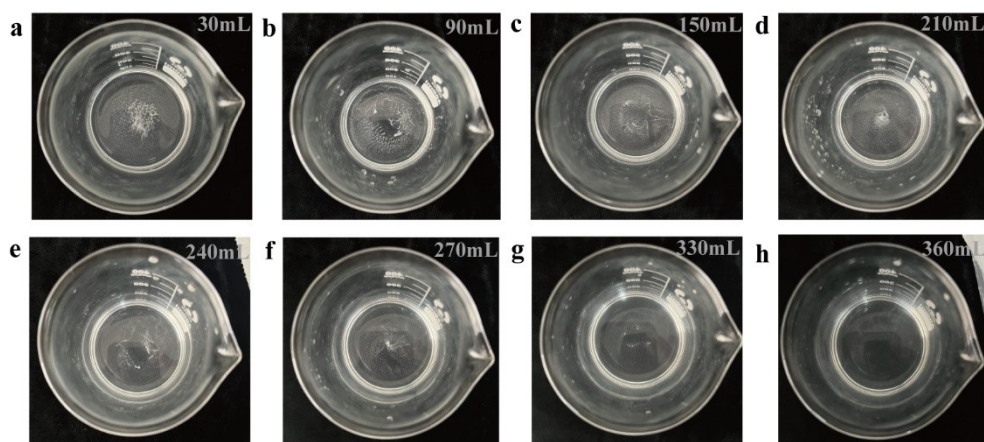


Fig. S1. 50 mg NBP sample dissolved in 30 mL (a), 90 mL (b), 150 mL (c), 210 mL (d), 240 mL (e), 270 mL (f), 330 mL (g) and 360 mL (h).

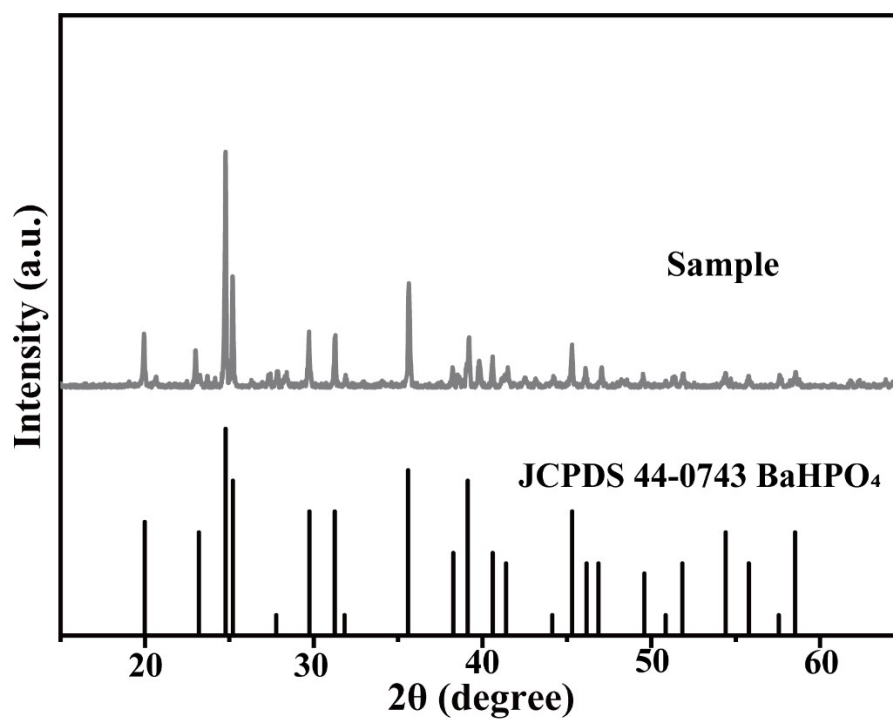


Fig. S2. XRD pattern of precipitation in alkalinity range.

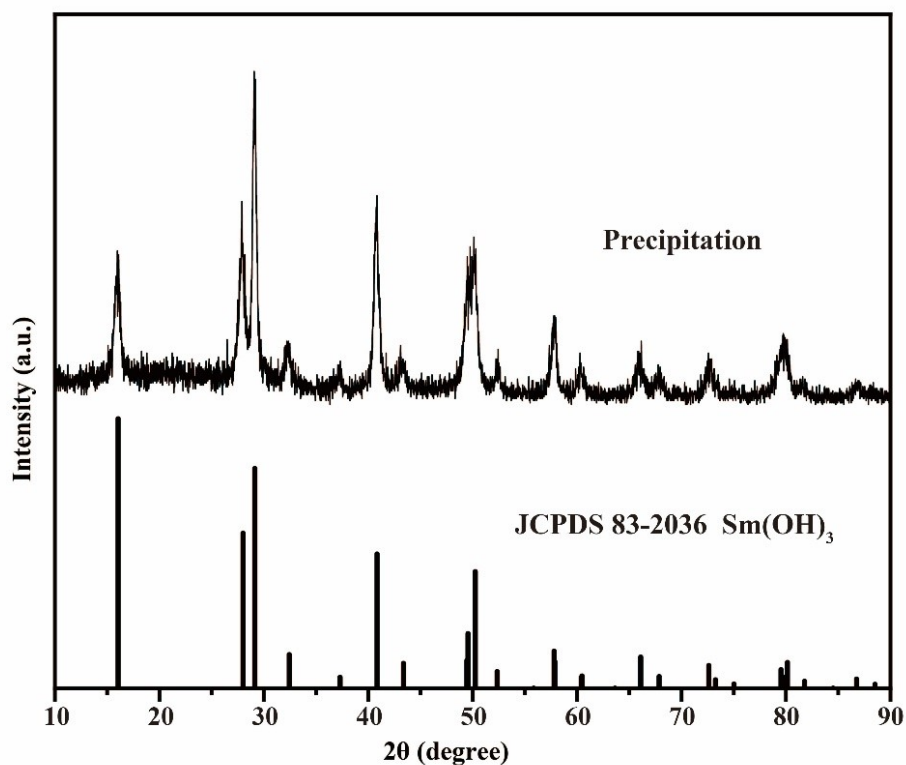


Fig. S3. The XRD pattern precipitated in the form of Sm(OH)₃.

The DRS of NBP host and NBP: xSm³⁺ (x=0.1, 0.5, 1, 3, 5, 7 mol%) range (200-800 nm) is presented in **Fig. S4a**. Both the pure host and the doped samples show strong absorption in the UV region (200-300 nm). Before 250 nm, the DRS shows a sharp drop in reflectance mainly due to the charge transfer (CT) from the 2p orbital of O²⁻ to 3d⁰ orbital of the P⁵⁺ in the PO₄³⁻ groups¹. Obviously, there are six distinct absorption bands between 330-500 nm in the samples doped with Sm³⁺ owing to the typical 4f-4f transitions of Sm³⁺. These absorption bands appear at 342, 361, 374, 403, 438, 474 nm as shown in the inset of **Fig. S4a**, originating from ⁶H_{5/2}→⁴K_{17/2}, ⁴H_{7/2}, ⁴P_{7/2}, ⁴F_{7/2}, ⁴I_{15/2}, and ⁴I_{13/2} transitions, respectively¹. In the range of 550-800 nm, the pure NBP exhibits

higher reflectivity. The corresponding band gap can be calculated using Kubelka-Munk(K-M) theory² as following:

$$F(R) = \frac{(1 - R)_2}{2R} = \frac{K}{S} \quad (1)$$

where $F(R)$ is the Kubelka-Munk function, R is the reflectance, K is absorption coefficients, and S is the scattering coefficient. According to the formula proposed by Tauc et al³, the associated energy bandgap (E_g) of NBP can be calculated by Equation (2):

$$[F(R)hv]^n = A (hv - E_g) \quad (2)$$

where A is a constant, h Planck's constant, ν the frequency of light, $h\nu$ incident photon energy. The value of n is 2 and 1/2 depending on the direct and indirect band gaps of the material, respectively. In this work, the n value is 2⁴. Using $[F(R)hv]^2$ and $h\nu$ as the coordinates to plot, the result is shown in the inset of **Fig. S4b**. Take the intersection of the tangent and the X axis, the optical band gap of NBP can be obtained as 5.73 eV.

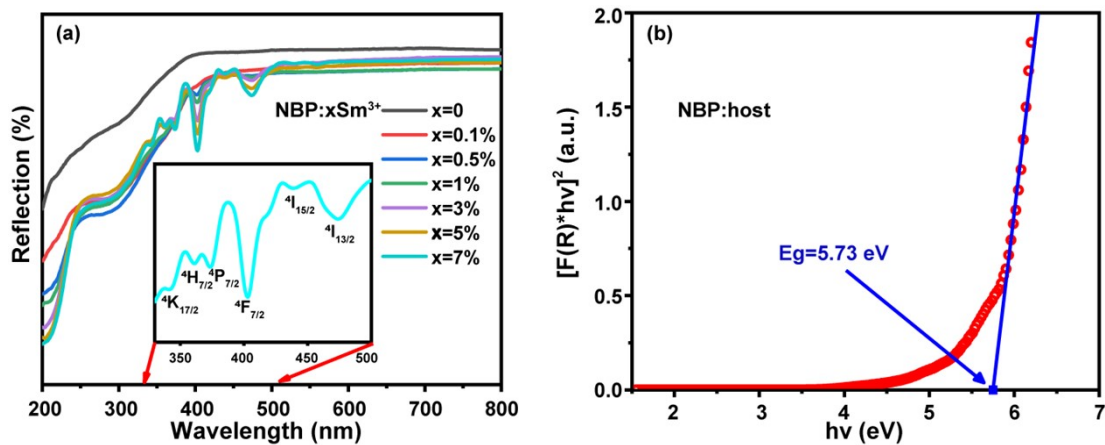


Fig. S4. (a) UV-vis diffuse reflection spectra of NBP: $x\text{Sm}^{3+}$ ($x=0.1, 0.5, 1, 3, 5, 7$ mol%) (The inset shows reflection curve in the wavelength region from 330 to 500 nm). (b) Absorption spectrum of NBP calculated by the Kubelka-Munk equation.

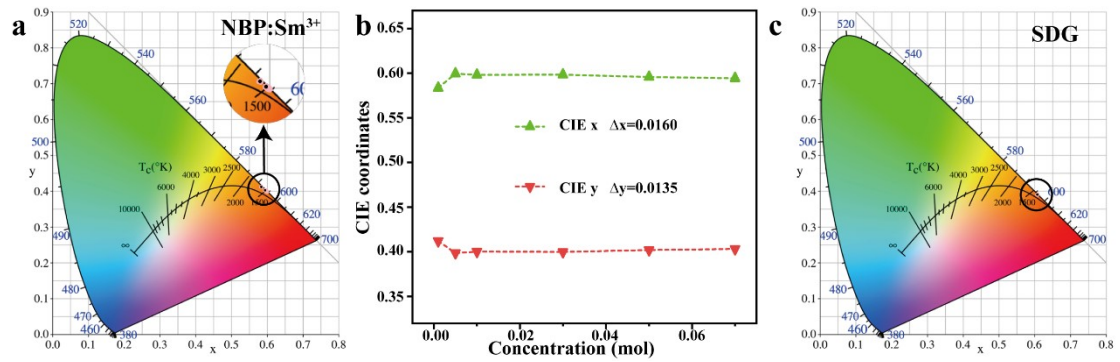


Fig. S5. (a) CIE chromaticity diagram of NBP: $x\text{Sm}^{3+}$ ($x=0.1, 0.5, 1, 3, 5, 7$ mol%) phosphors. (b) Deviation of the x and y of the NBP: $x\text{Sm}^{3+}$ ($x=0.1, 0.5, 1, 3, 5, 7$ mol%). (c) CIE chromaticity diagram of GS.

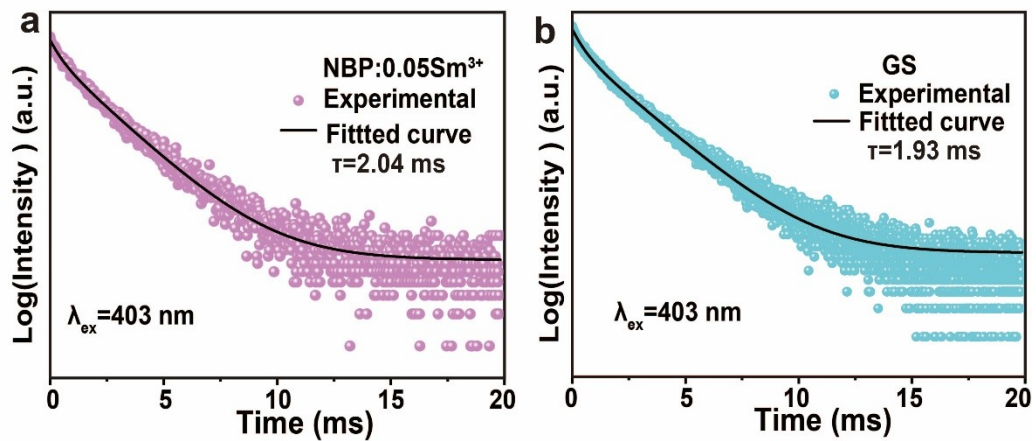


Fig. S6. (a) Decay curves of NBP:0.05 Sm^{3+} (b) Decay curves for the GS.

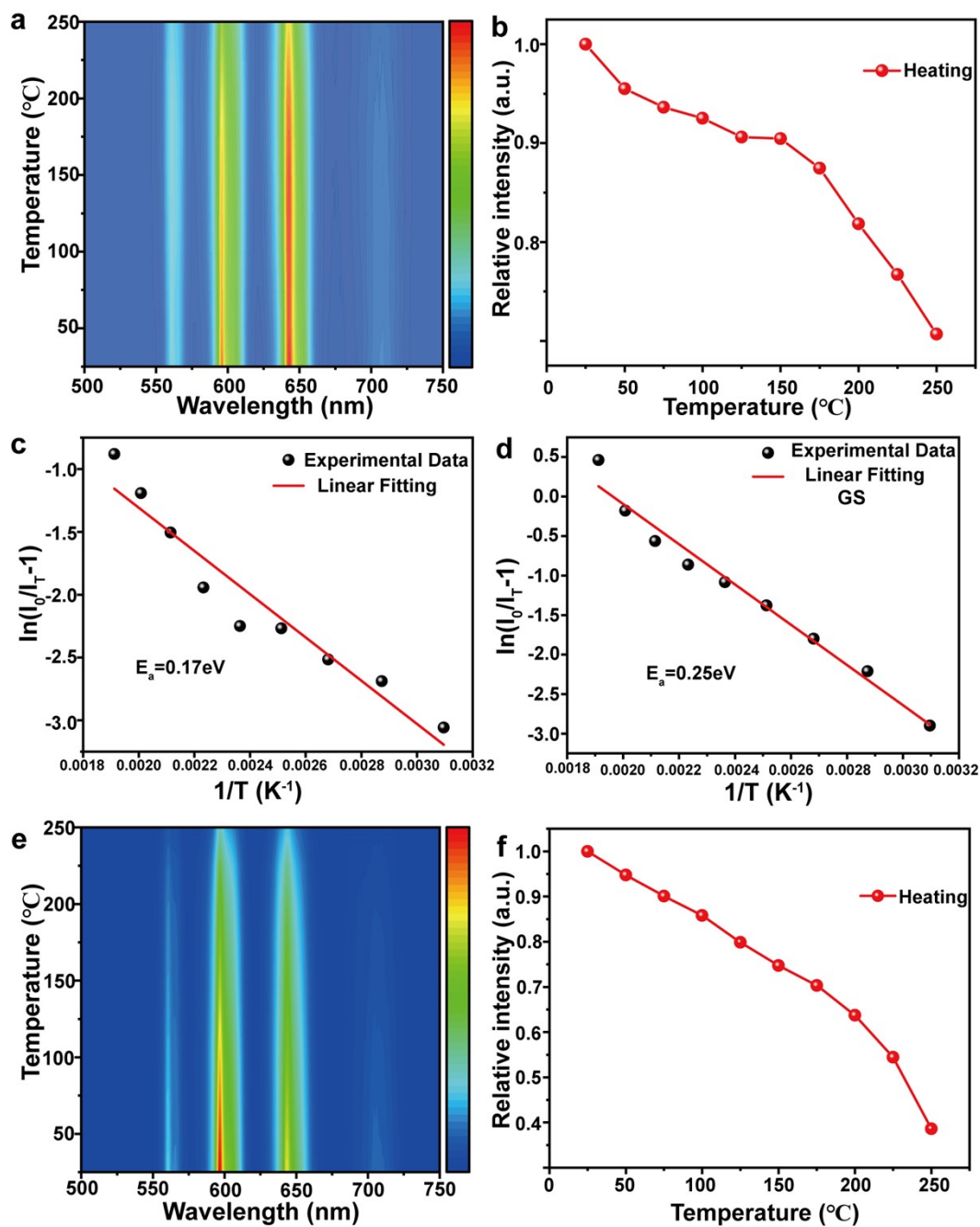


Fig. S7. (a) Temperature-dependent PL curves of NBP: 0.01Sm³⁺ samples under 403 nm excitation. (b) The temperature dependence of the NBP: 0.01Sm³⁺ relative emission intensity. (c) Plot of $\ln(I_0/I_T - 1)$ versus $1/kT$ of the NBP: 0.01Sm³⁺ phosphor. (d) Plot of $\ln(I_0/I_T - 1)$ versus $1/kT$ of the GS samples. (e) Temperature-dependent PL curves of GS samples under 403 nm excitation. (f) Temperature dependence of GS relative emission intensity.

Notes and references

1. M. K. Pradhan and S. Dash, *J. Rare Earths*, 2022, **40**, 1837-1848.
2. L. Yao, Q. Shao, S. Han, C. Liang, J. He and J. Jiang, *Chem. Mat.*, 2020, **32**, 2430-2439.
3. H. Sun, Q. Zhu and J.-G. Li, *Ceram. Int.*, 2022, **48**, 9640-9650.
4. A. Balakrishna, V. Kumar, A. Kumar and O. M. Ntwaeaborwa, *J. Alloy. Compd.*, 2016, **686**, 533-539.