Supporting Information

A $K_3ScSi_2O_7$: Eu^{2+} based phosphor with broad-band NIR emission and robust thermal stability for NIR pc-LEDs

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Experimental Section

KSSO: xEu^{2+} ($0 \leq x \leq 0.05$) samples are prepared by solid-state reaction. The stoichiometric mixtures of K_2CO_3 (99.99%, Aladdin), Sc_2O_3 (99.99%, Aladdin), SiO_2 (99.99%, Aladdin), Li_2CO_3 (99.99%, Aladdin, added as flux) and Eu_2O_3 (99.99%, Gansu Rare Earth) were thoroughly grounded. Then the mixture was put into alumina crucibles and sintered at 1050 ^oC for 6 hours in a reducing atmosphere (N_2:H_2 = 50:5). Finally, the cooled samples were ground into powers for further characterization.

The XRD patterns of samples are measured by an X-ray diffractometer (XRD, Bruker D2 PHASER) with Cu Kα radiation (λ = 1.5405 Å). The scanning rate is 2^o min^{-1} and the 2θ ranges from 10° to 80°. Diffuse reflectance spectra (DRS) of the sample was recorded using an ultraviolet/visible spectrophotometer ranging from 250 to 700 nm; $BaSO_4$ was used as a reference. The sample's morphology was performed with a scanning electron microscope (SEM, Hitachi-4800) and the high-resolution transmission electron microscopy (HRTEM) was examined with a FEI TecnaiF30 transmission electron microscope (TEM) operated at 300 kV. The elemental compositions are measured by TEM with an energy dispersive spectrometer system. X-ray photoelectron spectroscopy (XPS) measurement was carried out with a PHI-5702 electron spectrometer. The photoluminescence (PL) and photoluminescence excitation (PLE) spectra were collected using a fluorescence spectrophotometer (FLS-920T) with a 450 W Xe light source. The PL decay curves were obtained using an FLS-920T fluorescence spectrophotometer. The light source is an F900 nanosecond flash hydrogen lamp. The temperature-dependent PL curves were tested between 25 °C and 200 °C, using a heating apparatus (TAP-02) combining with the PL equipment. The photoelectric properties of the NIR pc-LED were obtained with an EVERFINE HAAS 2000 photoelectric measuring system.

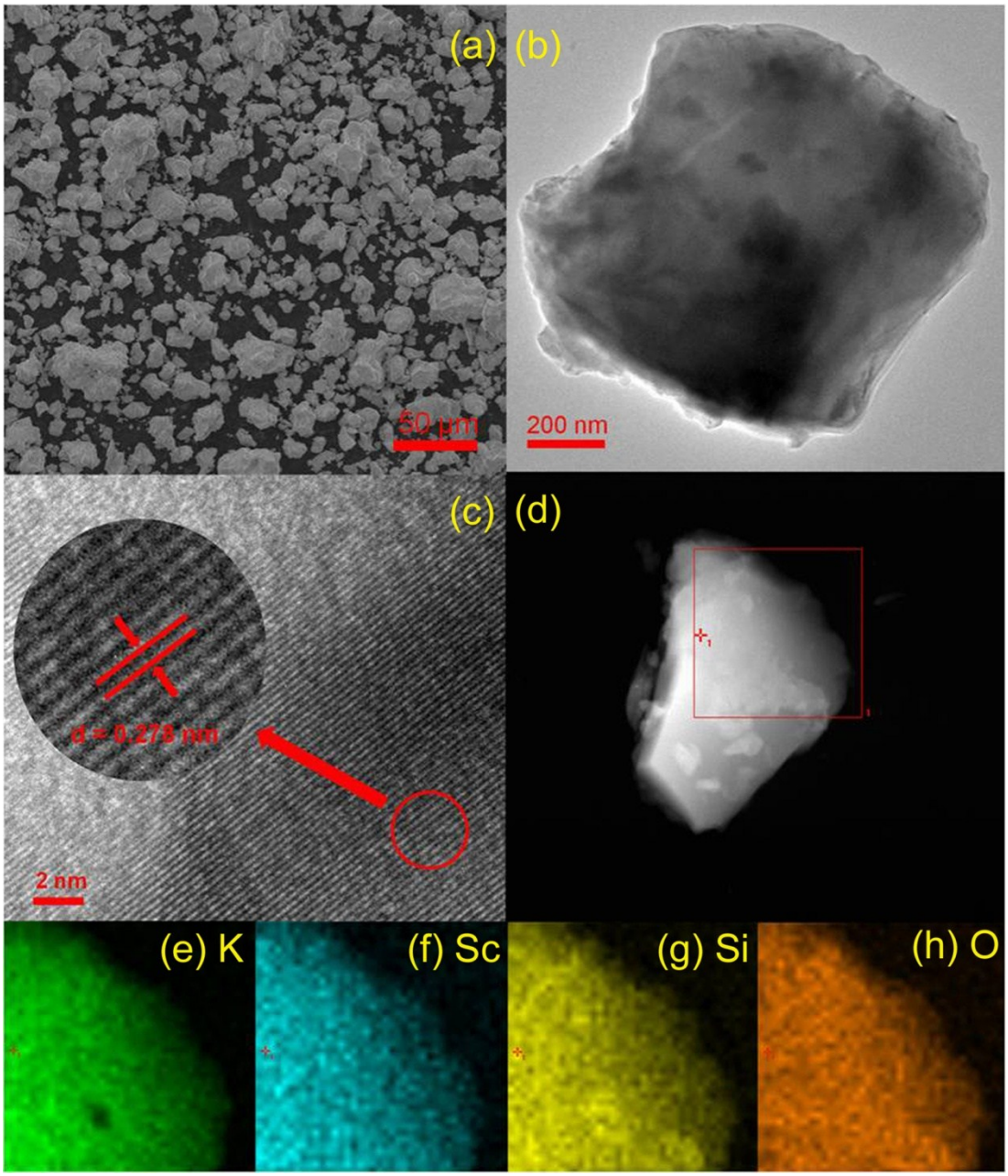

Fig. S1 (a) SEM image, (b) TEM image, (c) HRTEM image and (d–h) EDS mapping of KSSO. The SEM image implies that the sample has good dispersion with an irregular shape and the particle size ranges from 10 to 40 μm. The TEM image indicates that the particle size is about 800–900 nm and from the HRTEM image, it can be noticed that there is an apparent interplanar spacing of 0.278 nm, which belongs to the (110) plane. The mapping images certify that the sample has a chemical composition of K, Sc, Si and O elements with a homogeneous distribution in the single-particle.

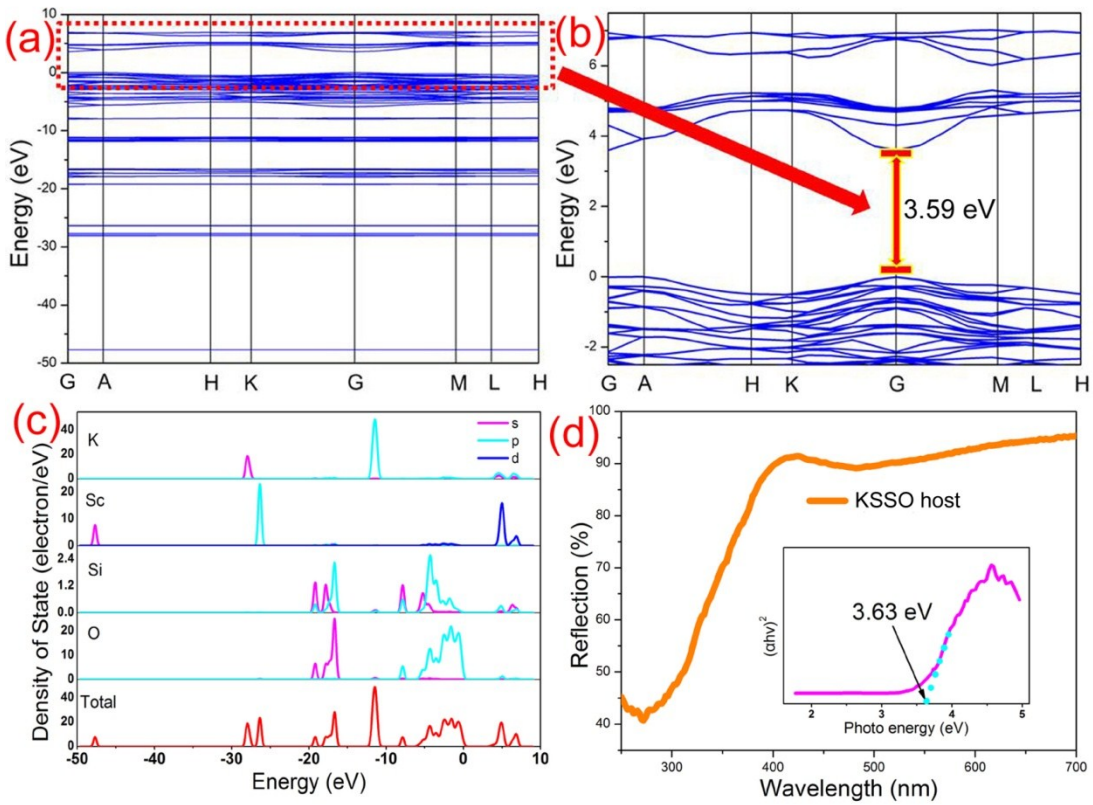

Fig. S2 (a-b) Band structures of KSSO; (c) total and partial densities of the states of KSSO and (d) DRS of the KSSO. The band structure of KSSO was obtained with DFT calculations based on the crystal structure data of Rietveld refinement. Both the valence band maximum and the conduction band minimum located at the G point of the Brillouin zone. Thus the KSSO compound possesses a direct bandgap of about 3.59 eV. The conduction band is mainly composed of Sc 3d states while the valence band is mostly contributed by Si 3s, 3p and O 2s states. By extrapolating the linear portion based on its DRS, the optical bandgap of the KSSO can be obtained, shown in the inset of Figure S2d. And the optical band gap of KSSO host is estimated from the Kubelka–Munk function:1

$$\alpha = [(1 - R)]^2/2R \quad (1)$$

Where R is the reflectance; α is proportional to the extinction coefficient. The optical band gap of NSSO host is estimated to be 3.63 eV, which is approximately the same with calculated bandgap data.

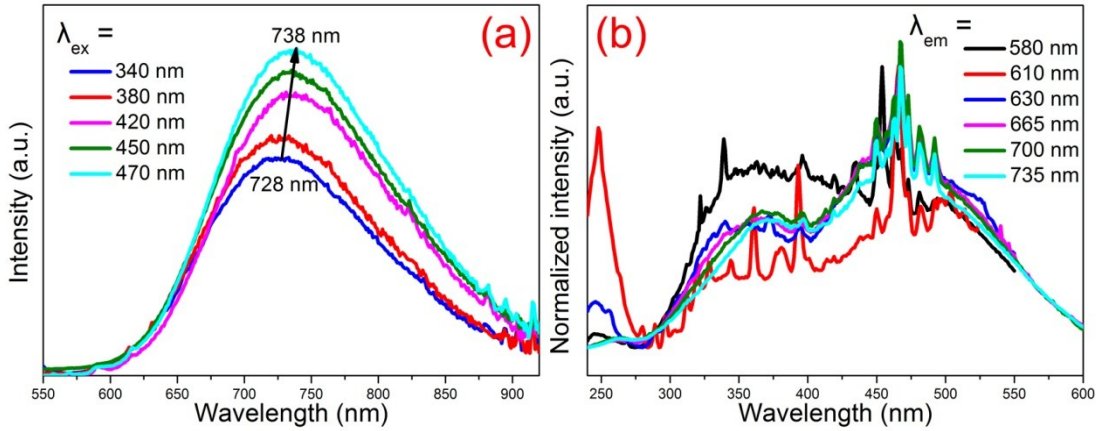

Fig. S3 (a) PL and (b) PLE spectra of KSSO: 0.03Eu^{2+} measured/monitored under different excitation (340-470 nm) and emission (610-735 nm) wavelength.

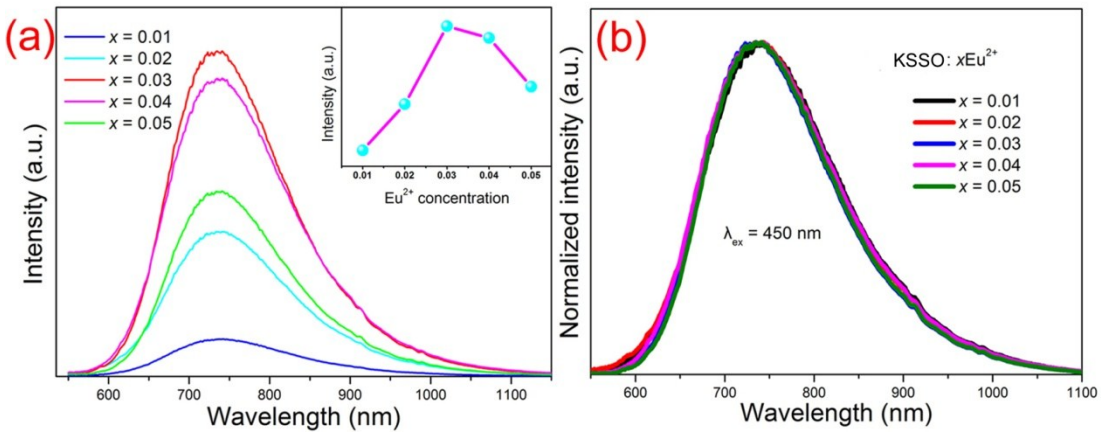

Fig. S4 (a) Non-normalized and (b) normalized PL spectra of KSSO: xEu^{2+} ($0.01 \leqq x \leqq 0.05$) excited by 450 nm, the inset represents the emission intensity as a function of x.

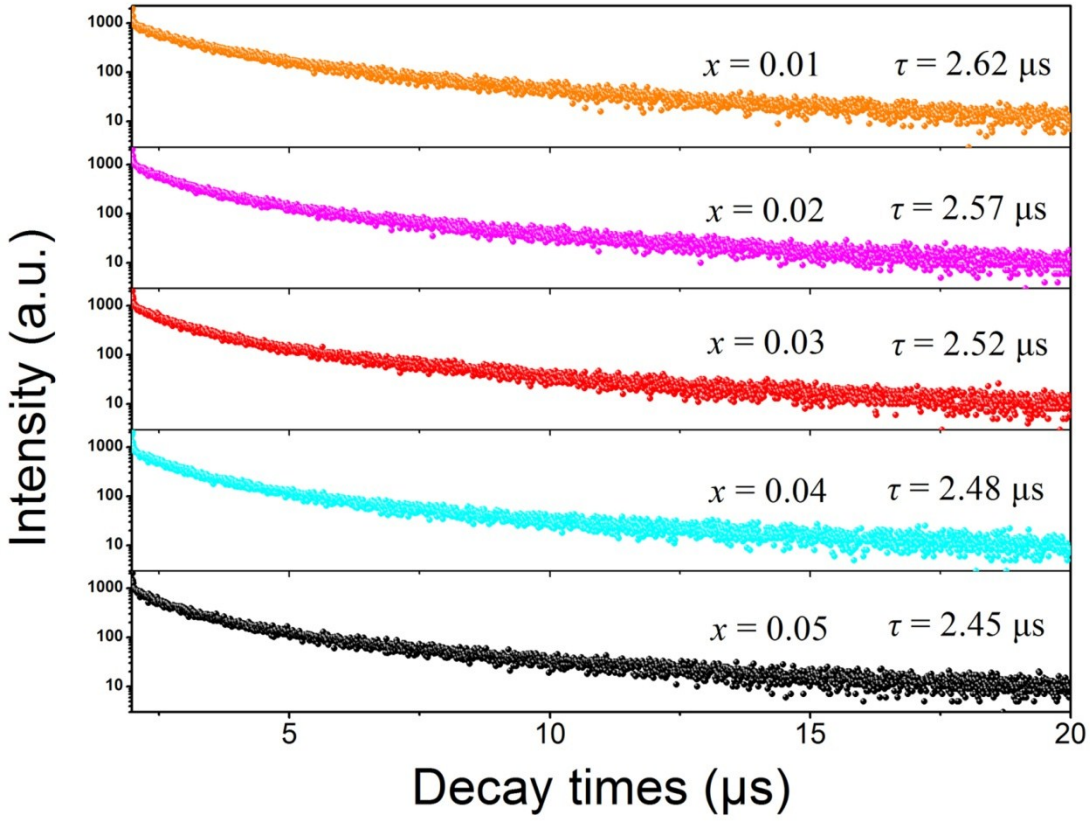

Fig.S5 Decay curves of KSSO: xEu^{2+} ($0.01 \leqq x \leqq 0.05$) phosphor at room temperature.

Table S1. Rietveld refinement and crystallographic data for KSSO.

Formula	$K_3ScSi_2O_7$
crystal system	hexagonal
Space group	$P6_3/mmc$
a/ Å	5.59076(7)
b/ Å	5.59076(7)
c/ Å	13.59232(23)
α	90.0
β	90.0
γ	120.0
Volume/ Å^3	367.931(12)

Z	4
R_{wp}	5.44%
R_p	3.83%
χ^2	1.263

Table S2. Structural data for KSSO.

Atom	*x*	*y*	*z*	U_{iso}	Occ.
K1	1/3	2/3	0.0942(4)	0.0309(7)	1
K2	0	0	1/4	0.0300(2)	1
Sc	0	0	0	0.0159(7)	1
Si	2/3	1/3	0.1322(35)	0.0248(8)	1
O1	0.3596(58)	0.1798(3)	0.0925(15)	0.0307(6)	1
O2	2/3	1/3	1/4	0.0341(1)	1

Table S3. Main bond lengths (Å) of KSSO.

K1-O1	2.846(1)	K2-O1	2.759(5)
Sc-O1	2.147(9)	Si-O1	1.581(5)
Si-O2	1.600(6)		

Table S4. Coordination and emission peaks of Eu^{2+} doped samples.

Phosphor	Occupied site	Coordination	Emission peak (nm)	Ref.
$K_2Al_2B_2O_7$: Eu^{2+}	K1	10	447	2
	K2	9	470	
$K_2ZrSi_3O_9$: Eu^{2+}	K	9	465	3
$KMg_4(PO_4)_3$: Eu^{2+}	K	8	450	4

Table S5. The ionic radii of K^+, Sc^{3+}, Eu^{2+} and Eu^{3+} in the different fold of coordination.

Ion	Coordination	Ionic radii (Å)
K^+	6	1.38
K^+	9	1.55
Sc^{3+}	6	0.745
Eu^{2+}	6	1.17
Eu^{2+}	9	1.3
Eu^{3+}	6	0.947
Eu^{3+}	9	1.12

Table S6. Photoelectric properties of the fabricated NIR pc-LED.

Current (mA)	Voltage (V)	Optical power (mW)	Photoelectric efficiency
20	2.645	1.361	26.655%
40	2.691	2.667	25.793%
60	2.728	3.88	25.026%
80	2.761	5.021	24.269%
100	2.791	6.103	23.549%
150	2.860	8.551	21.994%
300	3.044	14.06	18.209%

References

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