Supplementary Information

X-ray-Irradiation-induced Photoluminescence and Photochromic $LiNbO_3$ Phosphors for Anti-Counterfeiting and X-ray Imaging

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This file includes Figure S1 to S20 and Table S1 to S8.

Figure S1 to S20 and Table S1 to S8

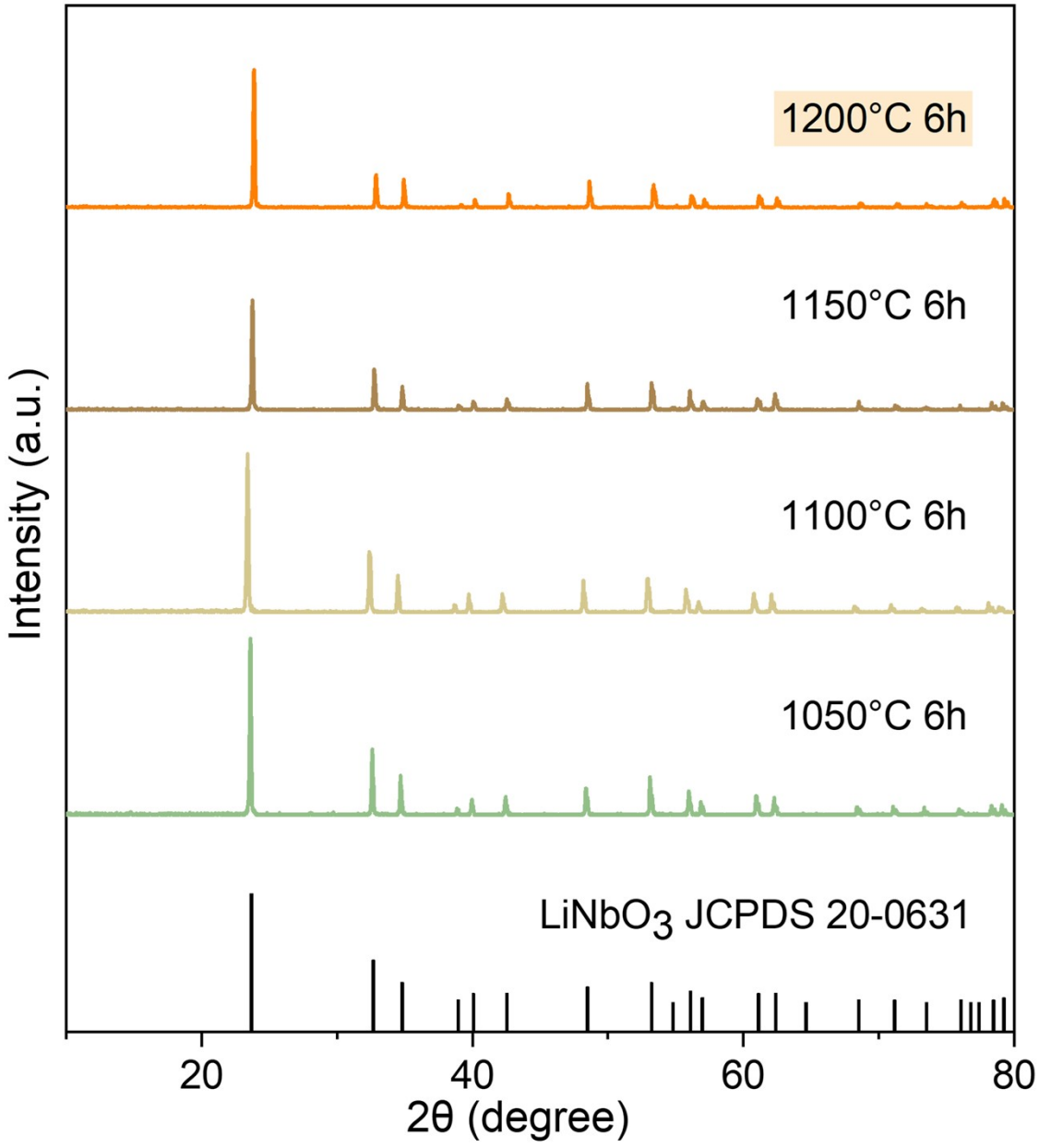

Fig. S1 The XRD patterns (JCPDS: 20-0631) of this series of $LiNbO_3$ substrates sintered at different temperatures (1050 °C, 1100 °C, 1150 °C and 1200 °C) for 6h.

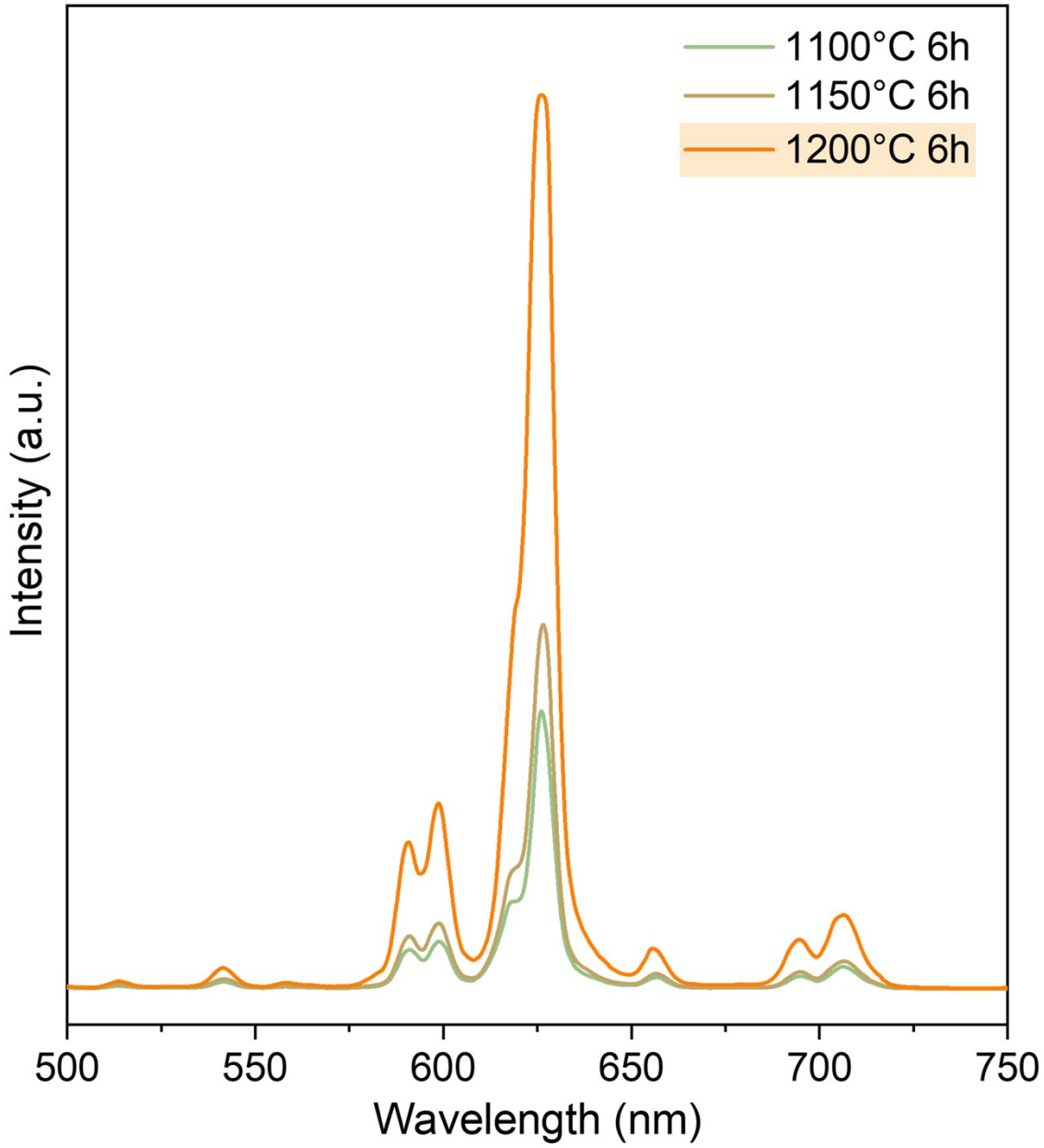

Fig. S2 The emission spectra of LNO: $0.01Eu^{3+}$ phosphors sintered at different temperatures (1100 °C, 1150 °C, and 1200 °C).

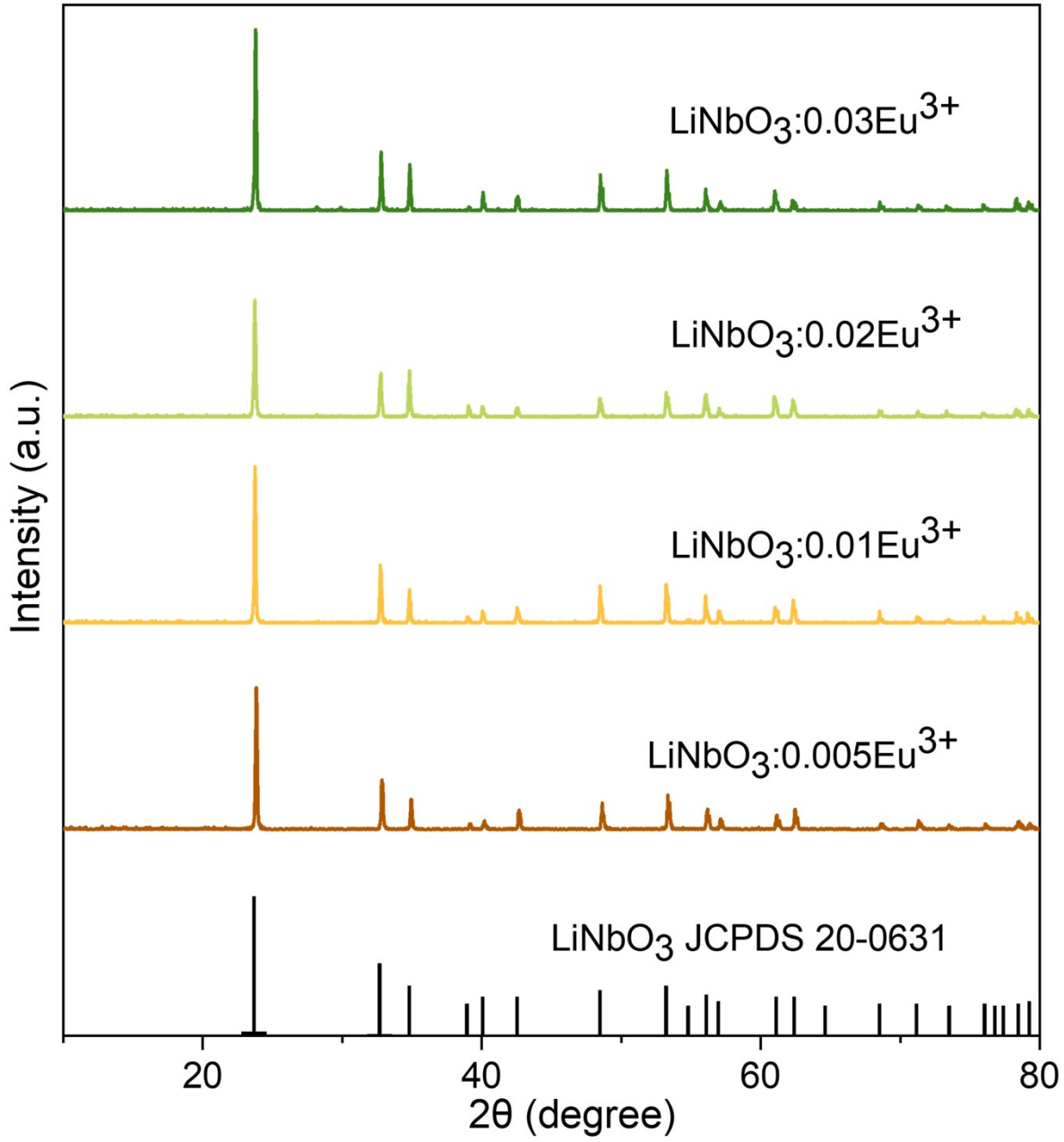

Fig. S3 Under the same sintering condition (1200℃, 6h), the XRD patterns (JCPDS: 20-0631) of the series of LNO: xEu^{3+}(x=0.005, 0.01, 0.02, 0.03) phosphors.

Table S1 The refinement results of pure LNO and LNO: $0.01Eu^{3+}$.

Compound	**LNO**	**LNO: $0.01Eu^{3+}$**
Crystal System	Trigonal	Trigonal
Space Group	R 3 C	R 3 C
Lattice Parameters	a=b= 5.151778 Å c= 13.864429 Å α = β = 90° γ =120°	a=b= 5.154160 Å c= 13.863468 Å α = β = 90° γ =120°
Unit Cell Volume	318.674 $Å^3$	318.947 $Å^3$
R_p R_{wp} χ^2	6.1% 3.2% 1.434	5.3% 2.9% 1.468

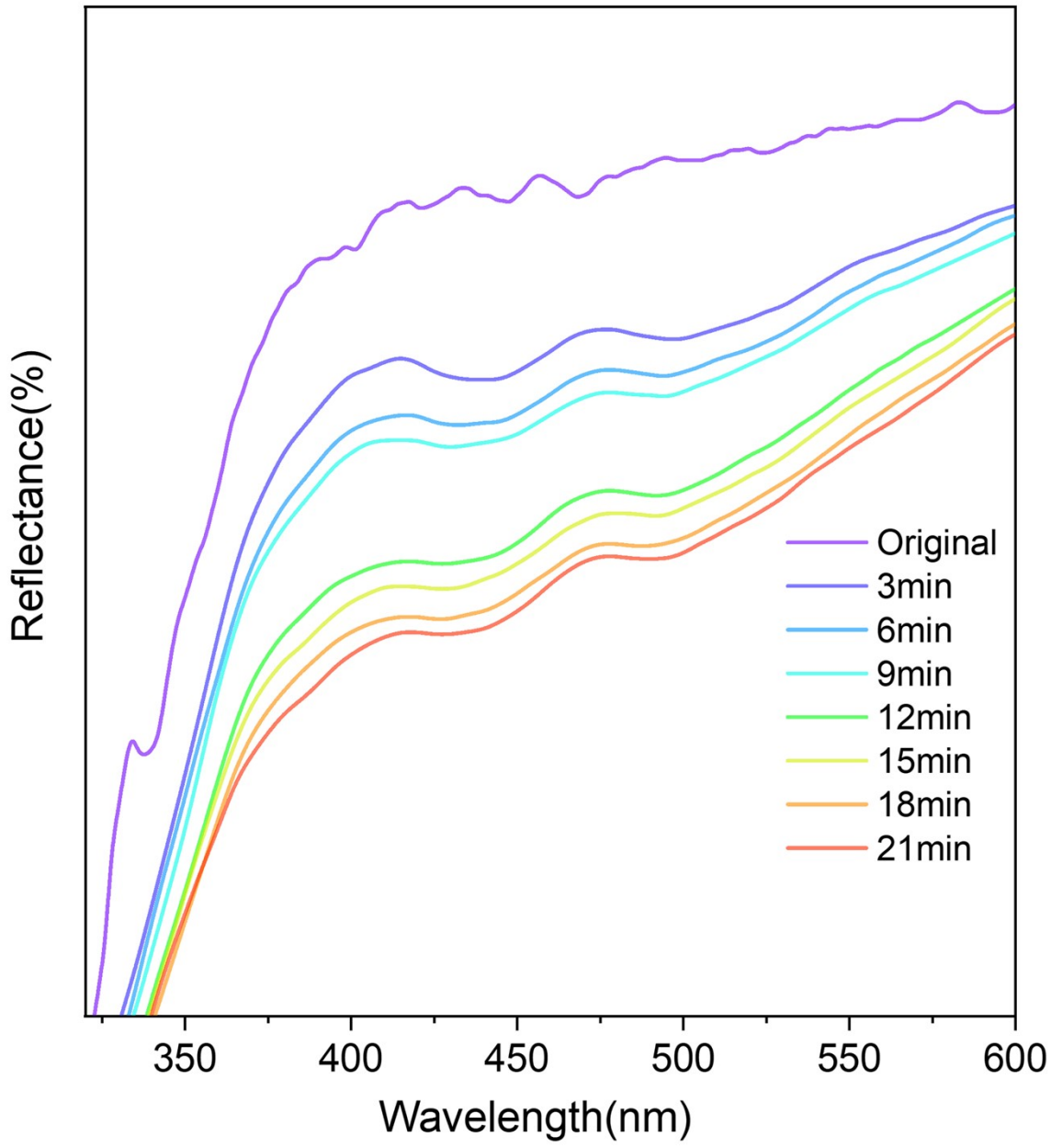

Fig. S4 The diffuse reflectance spectrum of LNO: $0.01Eu^{3+}$ phosphor after direct irradiation of 3.46×10^{-3} $Gy \cdot s^{-1}$ X-ray at different times (3 min, 6 min, 9 min, 12 min, 15 min, 18 min, 21 min).

Table S2 ΔAbs of LNO: 0.01Eu^{3+} under different doses of X-ray.

Samples	X-ray dose (Gy·s^{-1})	ΔAbs (%)
LNO: 0.01Eu^{3+}	2.87×10^{-6}	2.1
	1.97×10^{-5}	2.8
	3.94×10^{-4}	6.0
	8.63×10^{-4}	11.1
	3.09×10^{-3}	13.2
	3.46×10^{-3}	18.7

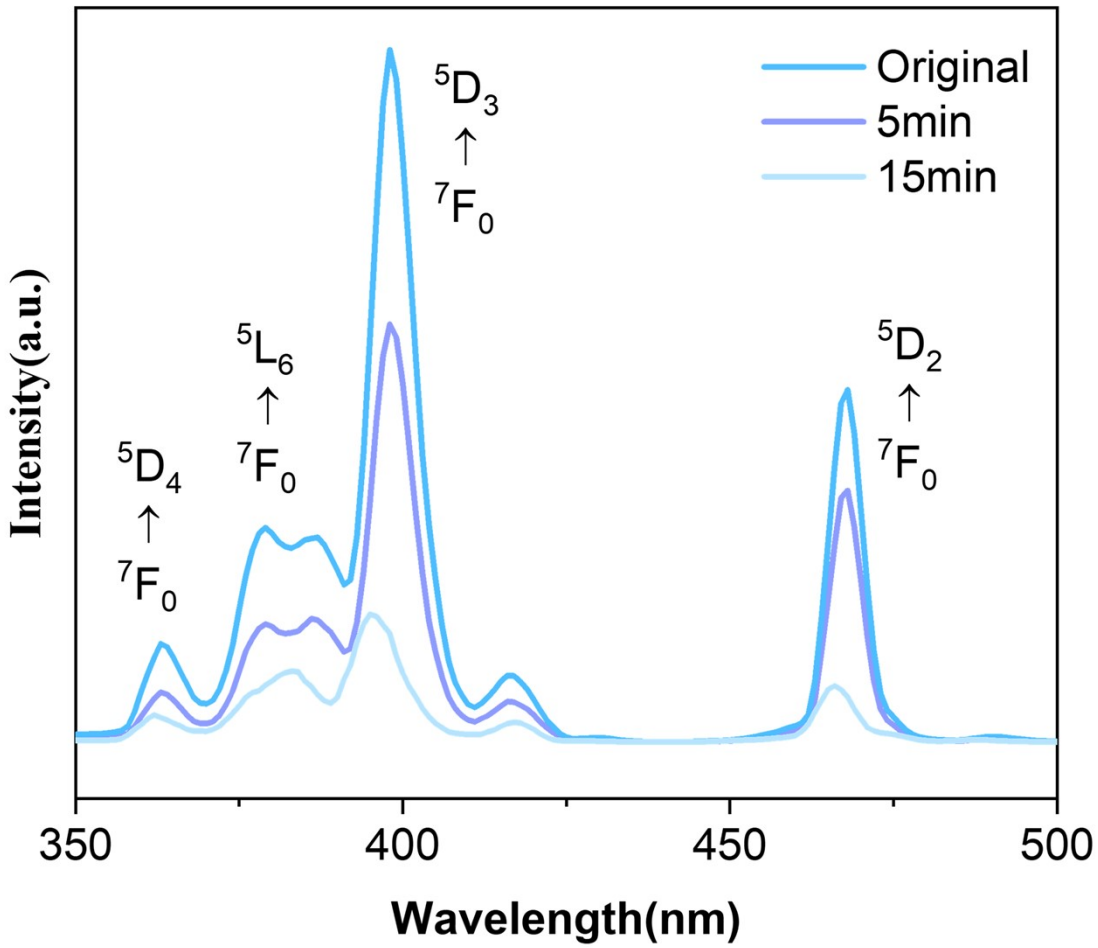

Fig. S5 PL excitation spectra (λem =626 nm) of LNO: $0.01Eu^{3+}$ phosphor. The intensity of the excitation peak decreases as the X-ray irradiation time increases (3.46×10^{-3} Gy·s^{-1}).

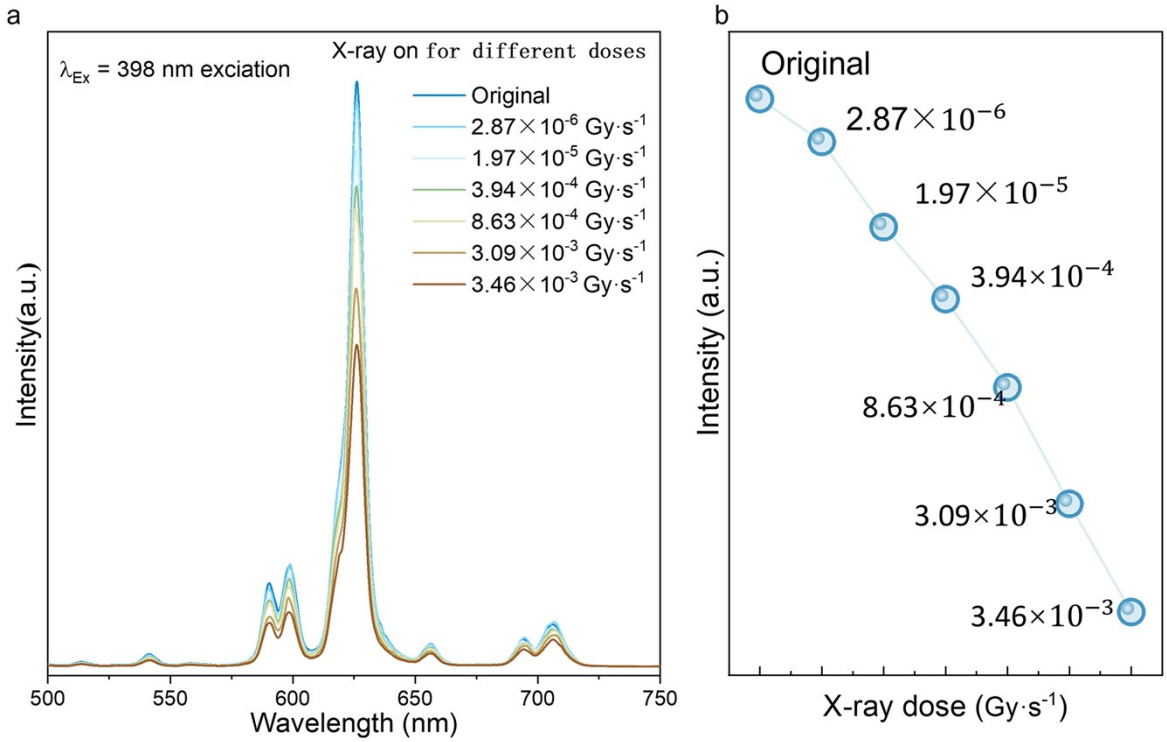

Fig. S6 (a) Directly X-ray-induced photoluminescence emission spectra of LNO: $0.01Eu^{3+}$ sample under different doses (15 min irradiation time, 2.87×10^{-6} Gy·s^{-1}, 1.97×10^{-5} Gy·s^{-1}, 3.94×10^{-4} Gy·s^{-1}, 8.63×10^{-4} Gy·s^{-1}, 3.09×10^{-3} Gy·s^{-1}, and 3.46×10^{-3} Gy·s^{-1}). **(b)** Under different doses of X-ray irradiation for 15 min, the corresponding emission intensity change of LNO: $0.01Eu^{3+}$ at 626 nm.

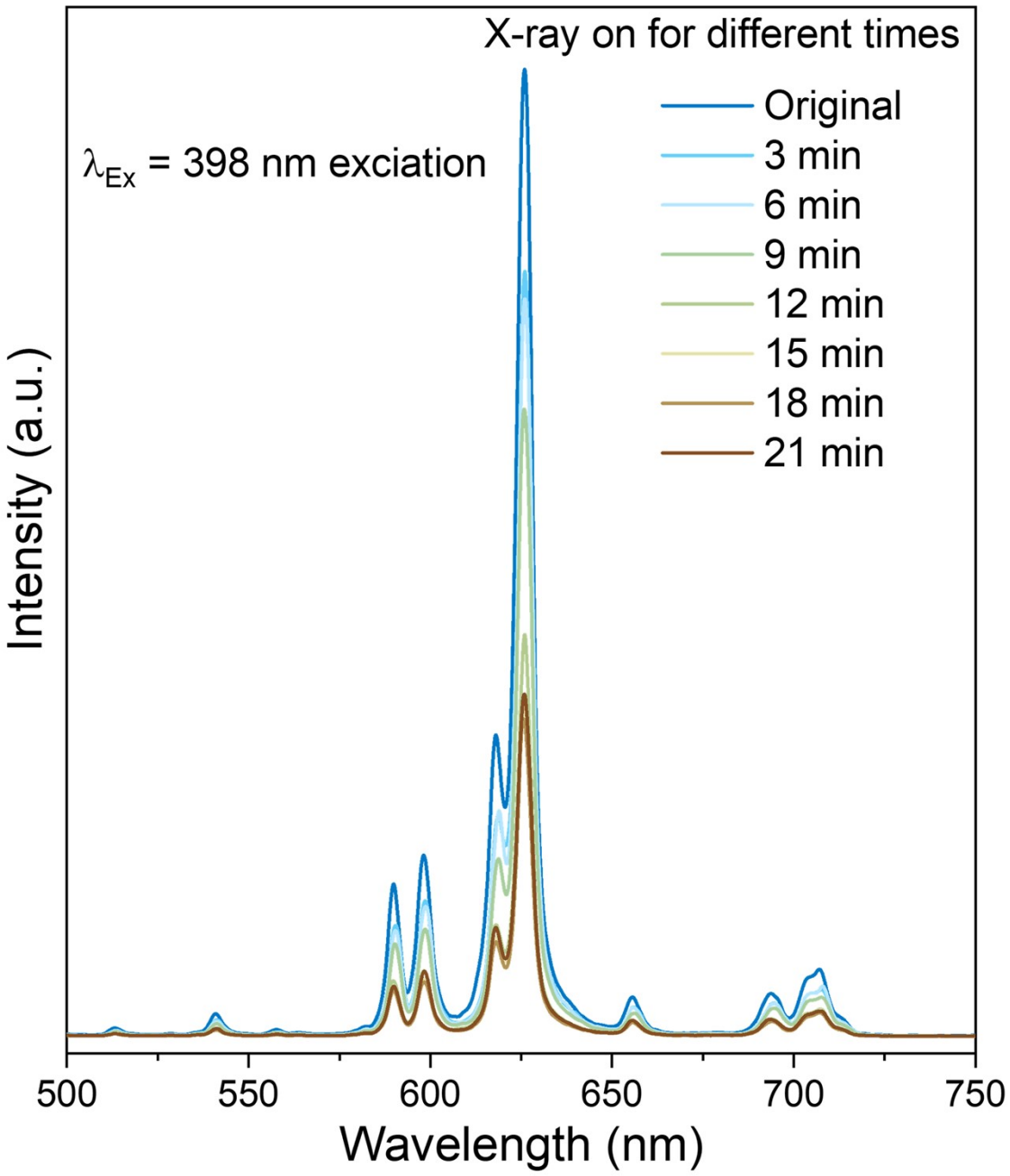

Fig. S7 Photoluminescence emission spectra of LNO: $0.01Eu^{3+}$ phosphor under 398 nm excitation after direct 3.46×10^{-3} $Gy \cdot s^{-1}$ X-ray irradiation for different times (3 min, 6 min, 9 min, 12 min, 15 min, 18 min and 21 min).

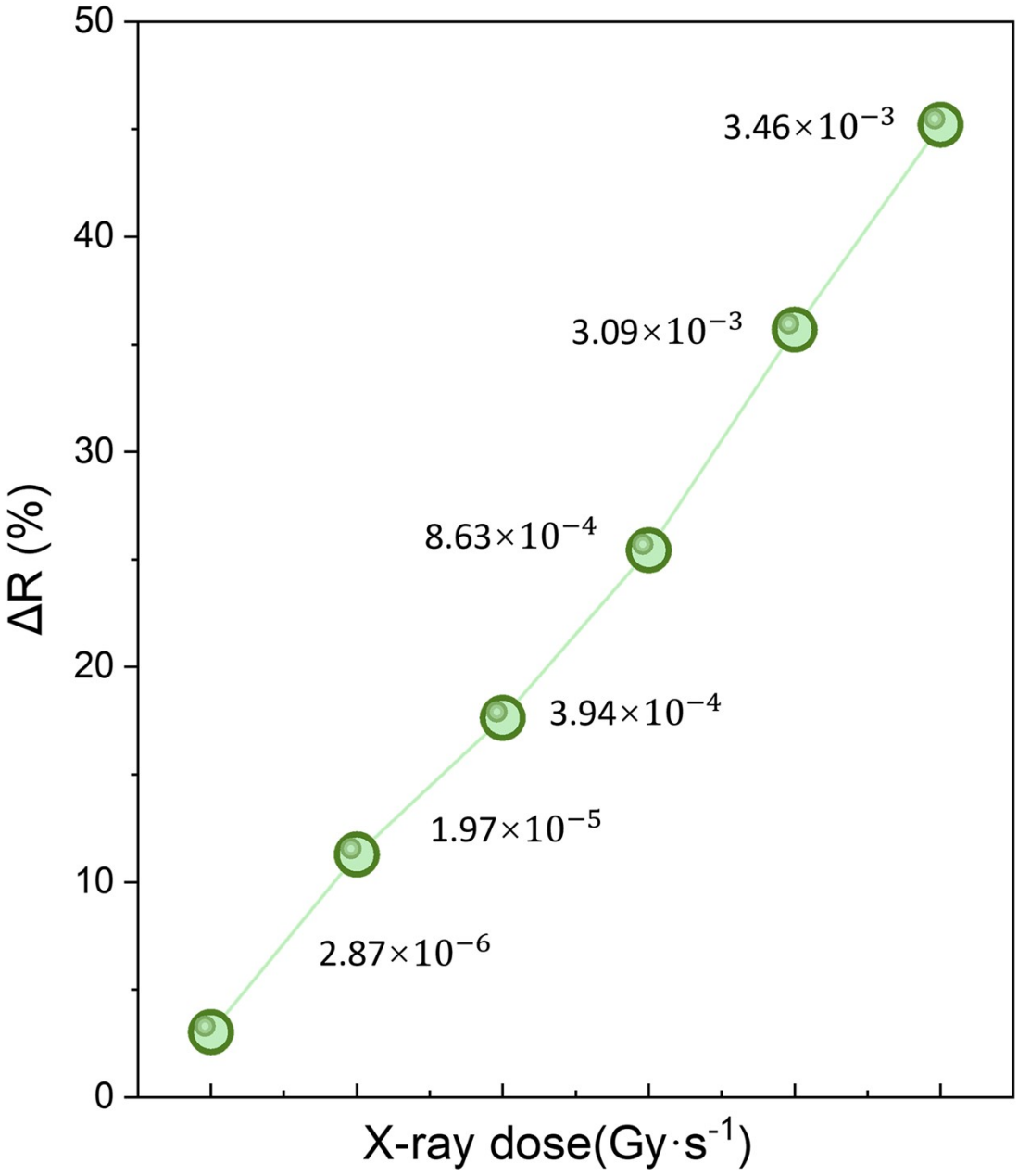

Fig. S8 The luminescence modulation ΔR of LNO: 0.01Eu^{3+} under different doses of X-ray irradiation (2.87 × 10^{-6} Gy·s^{-1}, 1.97 × 10^{-5} Gy·s^{-1}, 3.94 × 10^{-4} Gy·s^{-1}, 8.63 × 10^{-4} Gy·s^{-1}, 3.09 × 10^{-3} Gy·s^{-1}, and 3.46 × 10^{-3} Gy·s^{-1}) for 15 min.

Table S3 ΔR of LNO: 0.01Eu^{3+} under different doses of X-ray.

Samples	X-ray dose ($Gy \cdot s^{-1}$)	ΔR (%)
LNO: 0.01Eu^{3+}	2.87×10^{-6}	3.03
	1.97×10^{-5}	11.28
	3.94×10^{-4}	17.64
	8.63×10^{-4}	25.43
	3.09×10^{-3}	35.68
	3.46×10^{-3}	45.21

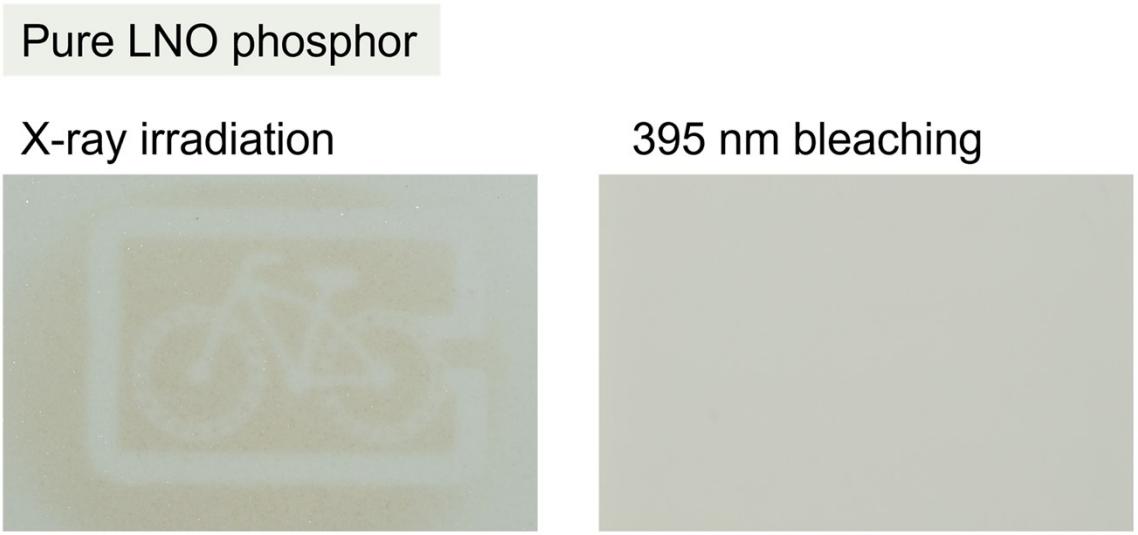

Fig. S9 Photochromic photo of pure LNO phosphor after X-ray irradiation and after bleached by 395 nm UV lamp.

Table S4 After X-ray irradiation, the degree of self-recovery of pure LNO and LNO: 0.01Eu^{3+} after standing at room temperature for 3 h.

Samples	Δ^{RD_R} **(3h)**	$\Delta^{RD_{PL}}$ **(3h)**
LNO	85.80%	-
LNO: 0.01Eu^{3+}	95.01%	87.11%

Table S5 The fitting parameters and self-recovery time coefficients of the diffuse reflectance spectra of pure LNO and LNO: 0.01Eu^{3+} after X-ray irradiation.

Samples	A_1	A_2	B_1	B_2	**τ**
LNO	-9.3869	-21.4587	12.5108	139.7861	134.9909
LNO: 0.01Eu^{3+}	28.4606	$2.8274*10^{-4}$	52.0418	-20.3005	52.0421

Table S6 The fitting parameters and self-recovery time coefficients of the emission spectra of LNO: 0.01Eu^{3+} after X-ray irradiation.

Samples	A_1	A_2	B_1	B_2	**τ**
LNO: 0.01Eu^{3+}	-8.9763	-30.6519	4.6737	73.1578	71.9001

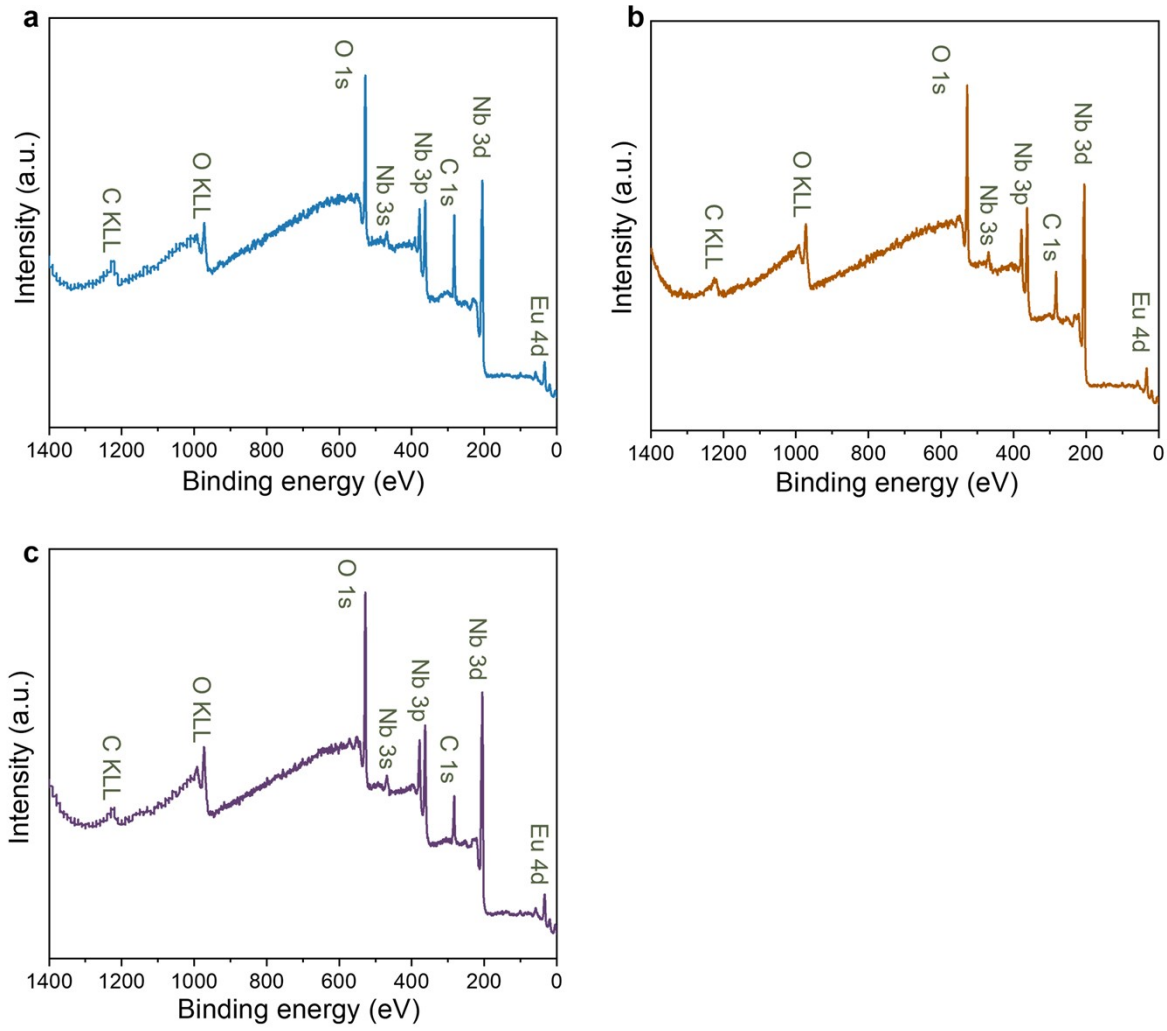

Fig. S10 XPS Spectra of LNO: $0.01Eu^{3+}$ phosphor **(a)** before X-ray Irradiation, **(b)** during photochromism and **(c)** after bleaching.

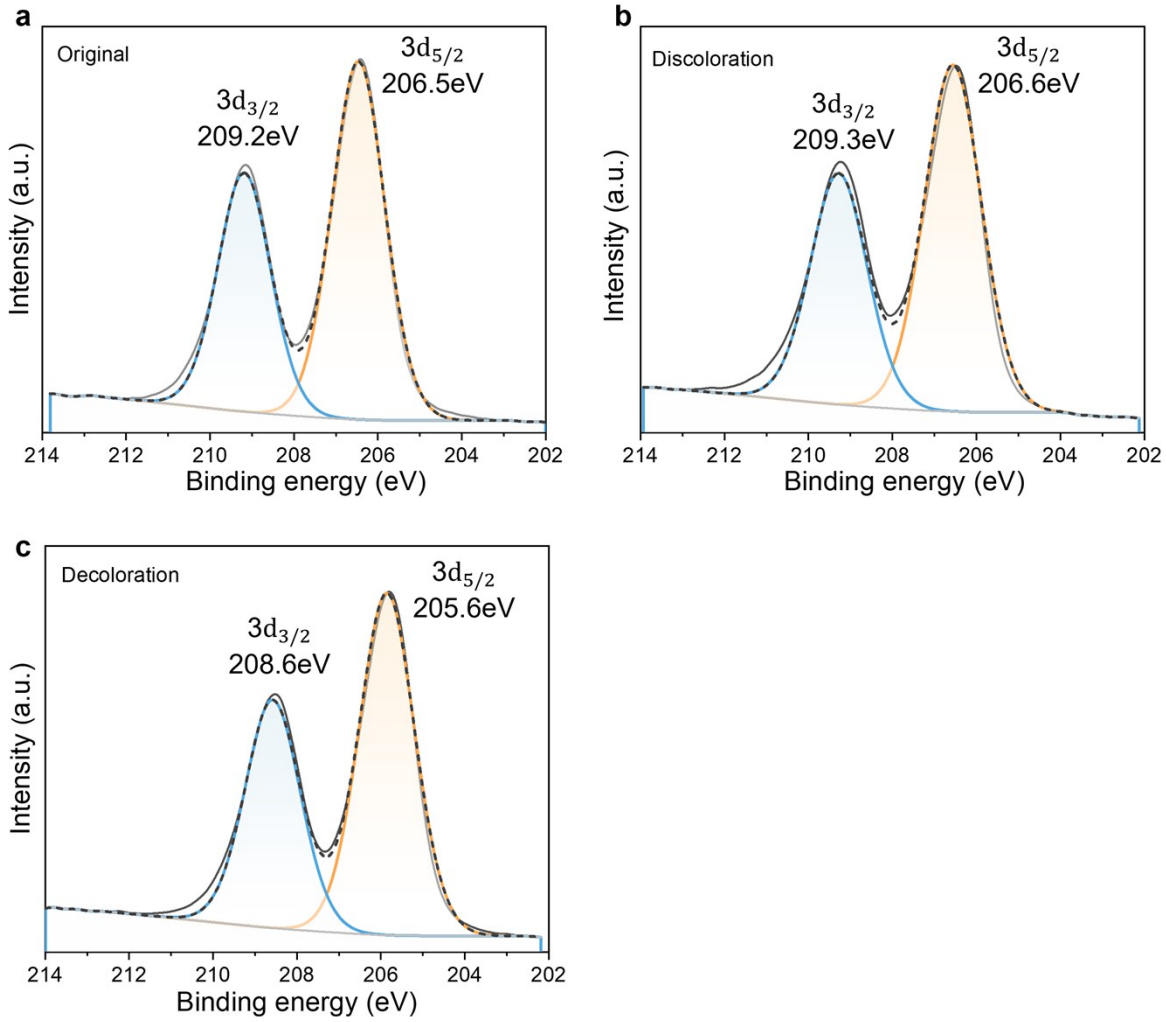

Fig. S11 XPS spectra of Nb in LNO: $0.01Eu^{3+}$ phosphor **(a)** before X-ray irradiation, **(b)** during photochromism and **(c)** after bleaching.

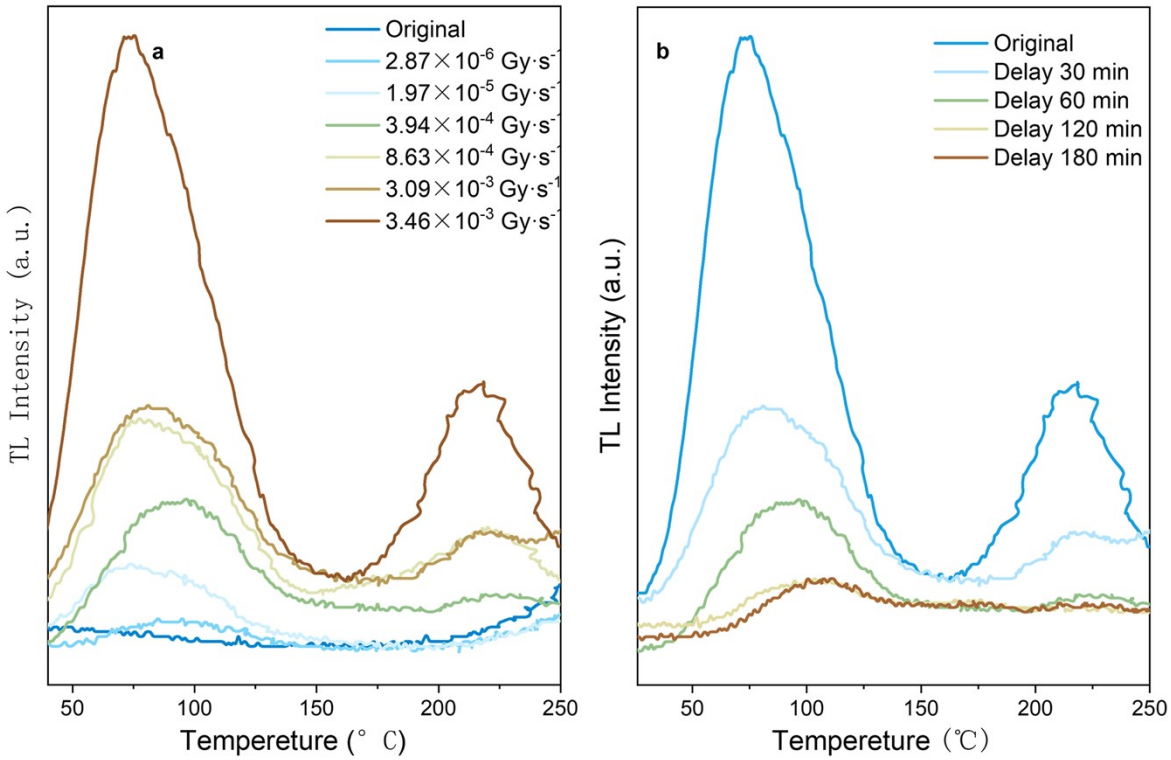

Fig. S12 (a) Thermoluminescence spectra and intensity changes of LNO:0.01Eu^{3+} phosphors under different X-ray irradiation doses for 15 minutes (2.87 × 10^{-6} Gy·s^{-1}, 1.97 × 10^{-5} Gy·s^{-1}, 3.94 × 10^{-4} Gy·s^{-1}, 8.63 × 10^{-4} Gy·s^{-1}, 3.09 × 10^{-3} Gy·s^{-1} and 3.46 × 10^{-3} Gy·s^{-1}). (b) Thermoluminescence spectra of LNO:0.01Eu^{3+} phosphors when standing at room temperature for different times after irradiated at a dose of 3.46 × 10^{-3} Gy·s^{-1} for 15 minutes.

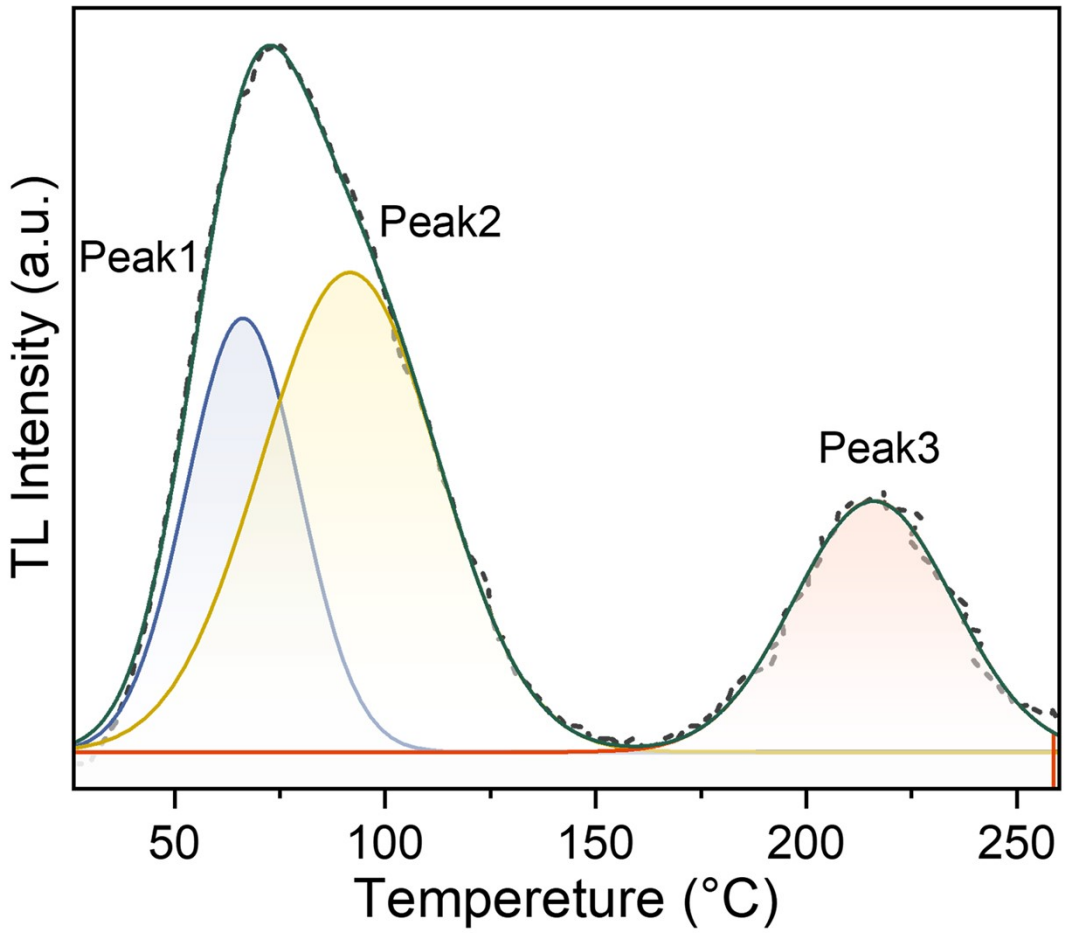

Fig.S13 The fitting thermoluminescence spectra of LNO: $0.01Eu^{3+}$ phosphors after X-ray irradiation.

Table S7 The fitting method of the thermoluminescence spectrum of LNO: $0.01Eu^{3+}$, the peak position and the percentage of the peak area.

Peak number	Peak type	Peak center	Peak area percentage
1	Gaussian	66.25℃	28.30%
2	Gaussian	91.63℃	48.97%
3	Gaussian	215.96℃	22.73%

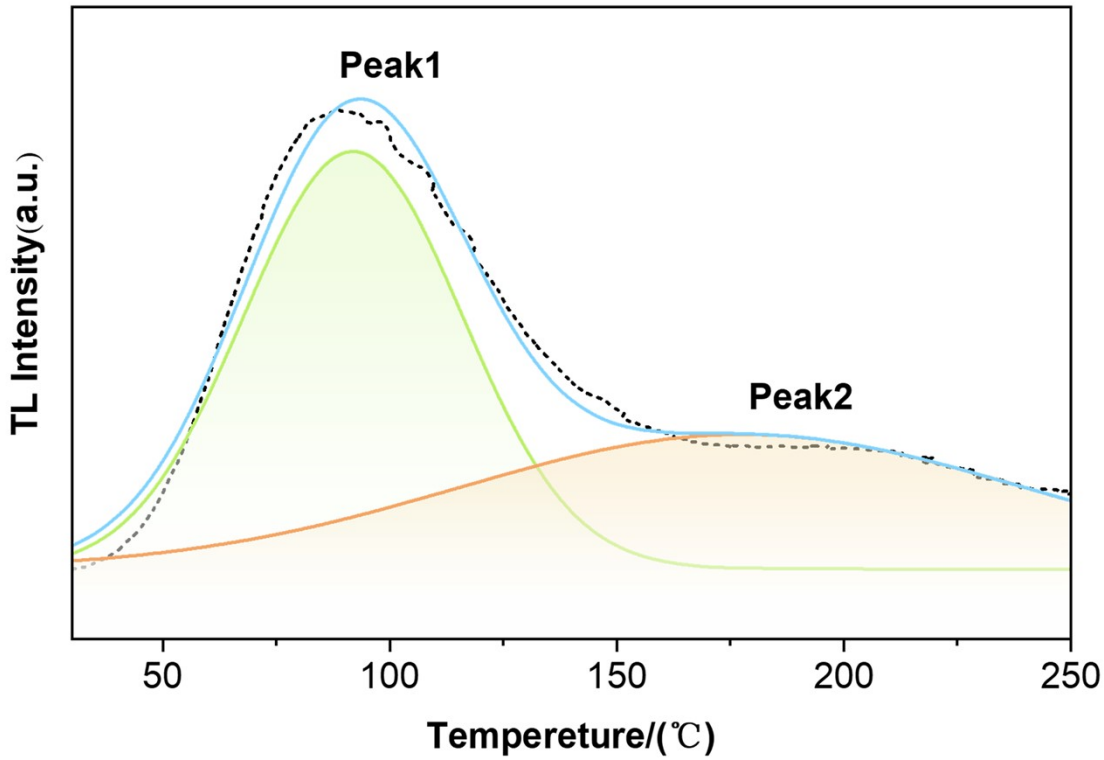

Fig. S14 The fitting thermoluminescence spectra of pure LNO without Eu^{3+} doping after X-ray irradiation.

Table S8 The fitting method of the thermoluminescence spectrum of pure LNO, the peak position and the percentage of the peak area.

Peak number	Peak type	Peak center	Peak area percentage
1	Gaussian	91.94℃	56.99%
2	Gaussian	177.61℃	43.01%

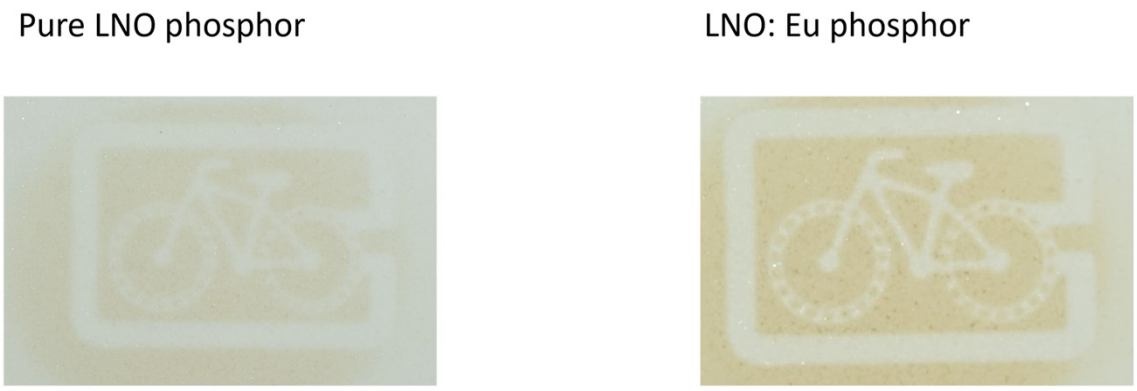

Fig.S15 The photochromic colour change of the pure LNO and LNO: $0.01Eu^{3+}$ phosphors.

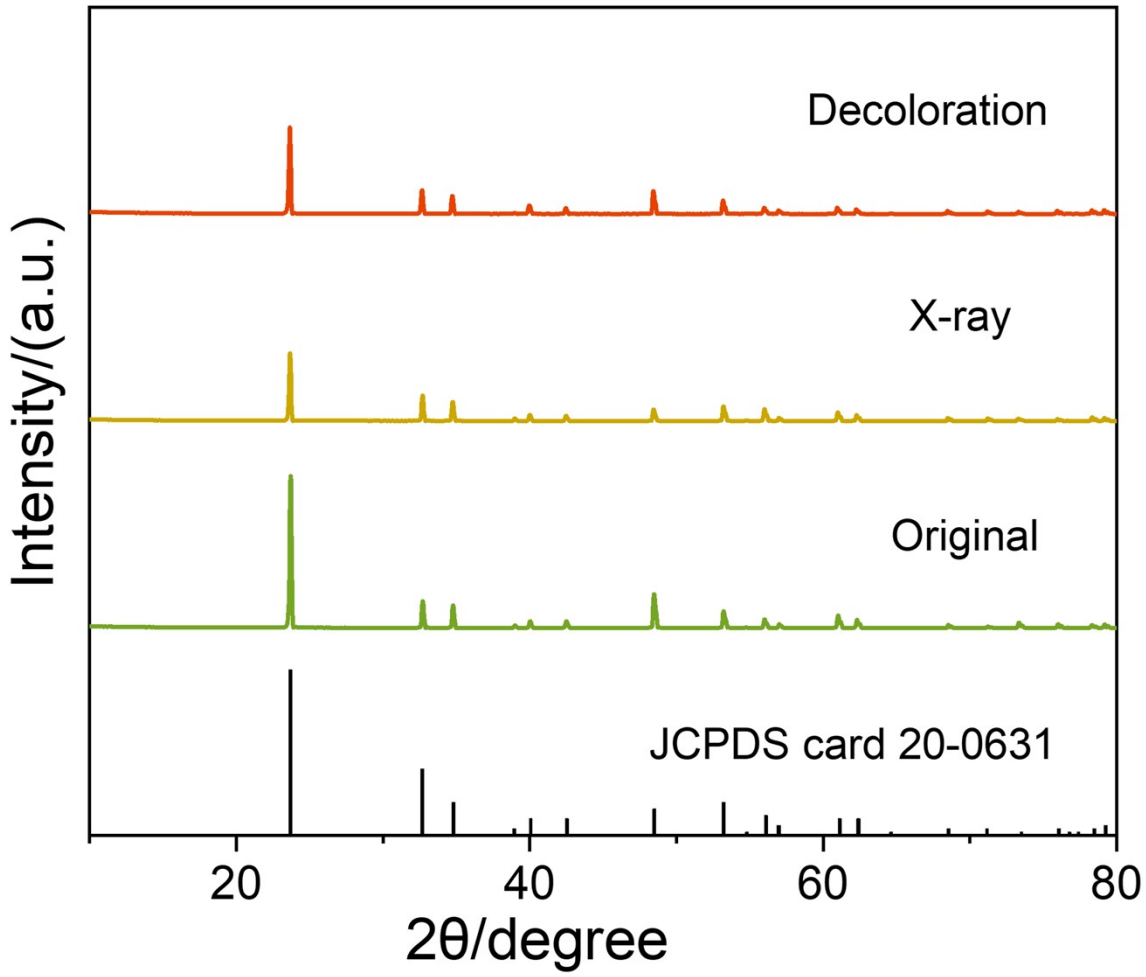

Fig.S16 The XRD spectra of LNO: $0.01Eu^{3+}$ phosphors of the initial state, after X-ray photochromic and decolorization.

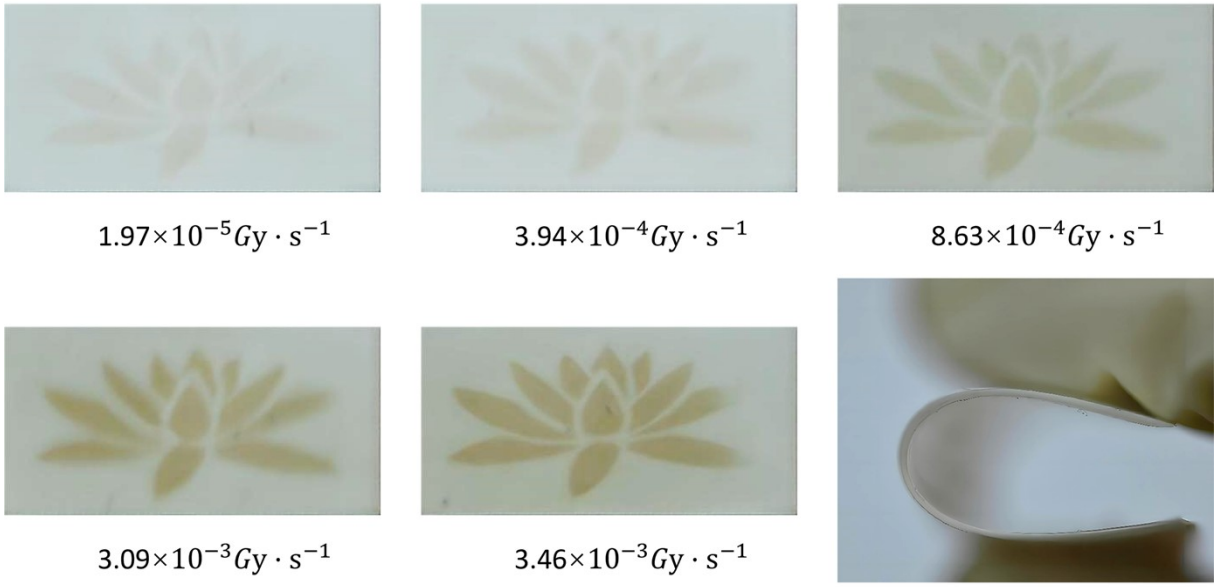

Fig. S17 LNO: $0.01Eu^{3+}$ phosphors have good flexibility after 15 minutes of discoloration photos under different X-ray irradiation doses and LNO:$0.01Eu^{3+}$ embedded film folding.

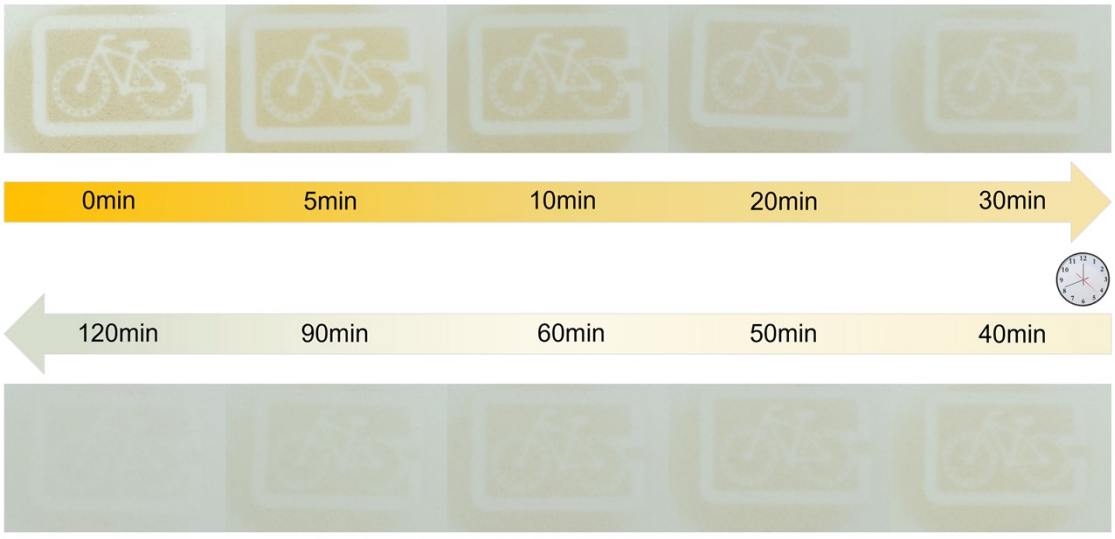

Fig. S18 The contrast pattern of LNO: $0.01Eu^{3+}$ phosphor film self-bleached over time after X-ray irradiation for 15 min. (X-ray dose 3.46×10^{-3} Gy·s^{-1})

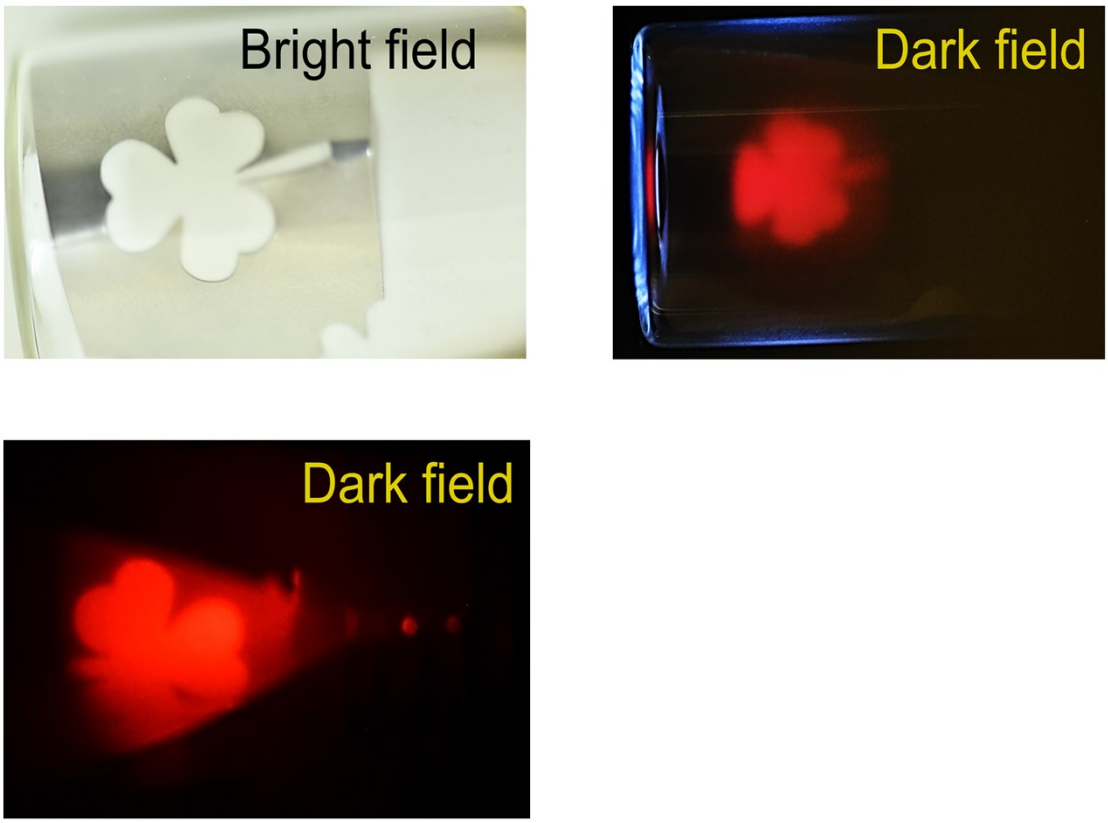

Fig. S19 LNO: 0.01Eu^{3+} phosphor films (X-ray irradiation) in bright and dark fields. (X-ray dose 3.46×10^{-3} $Gy\cdot s^{-1}$)

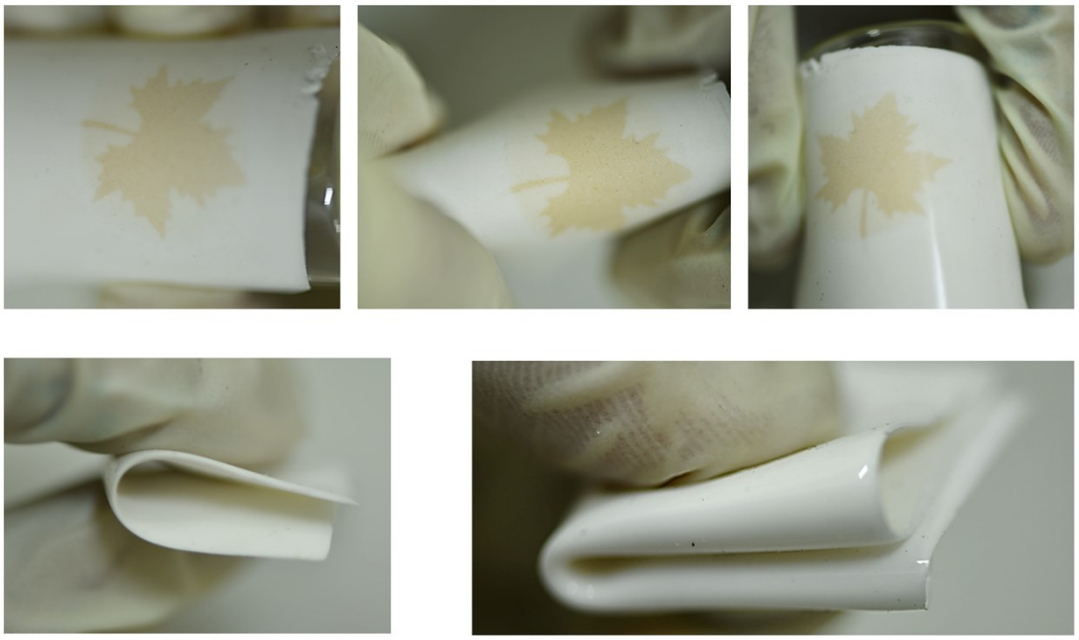

Fig. S20 The bending and folding modes of LNO: $0.01Eu^{3+}$ phosphor film without metal template under bright field. The LNO: $0.01Eu^{3+}$ phosphor film still has good flexibility after multiple folding. (X-ray dose 3.46×10^{-3} $Gy\cdot s^{-1}$ irradiation 15 min)