

Reversibly photoresponsive switching in $\text{Bi}_{2.5}\text{Na}_{0.5}\text{Nb}_2\text{O}_9$ -based luminescent ferroelectrics

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Electronic Supporting Information (ESI)

S1 Powder and sample preparation

The Na_2CO_3 (Alfa Aesar, 99.5%), Bi_2O_3 (Alfa Aesar, 99.975%), Nb_2O_5 (Alfa Aesar, 99.5%), Eu_2O_3 (Alfa Aesar, 99.9%) powders as starting materials were weighted and mixed with ethanol, dried, calcined at 900 °C for 4 h in air. After the calcination, these powders were remixed and then dried. Subsequently, the dried powders were granulated with 8 wt% polyvinyl alcohol (PVA) binder, and pressed into disk-shaped pellets with diameter of 10 mm at 100 MPa. The green pellets were heated at 550 °C for 6h to burn off the PVA. Finally, the samples were sintered at 1100 °C for 2 h in air. The sintered pellets were polished to a thickness of 0.5 mm for PL measurements.

S1 Material structure and composition characterization:

X-ray diffraction (XRD, D8 Advanced, Bruker, Germany) and field emission scanning electron microscopy (FESEM, JSM EMP-800, JEOL, Japan) were employed to identify the phase structure and microstructure of the samples, respectively. The inductively coupled plasma atomic emission spectroscopy (ICP-AES) (PROFILE SPEC, Leeman, AMERICA) was used to quantitatively investigate the composition deviation behavior of Na and Bi in NBN host. X-ray photoelectron

spectroscopy (XPS) measurements were performed with a multifunctional imaging electron spectrometer (VG, ESCALAB 250XI, Thermo Scientific, Surrey, U.K.) with Al K α ($h\nu=1486.6$ eV) radiation.

The visible-light coloration was carried out by the visible-light output of a 300 W xenon lamp (PLX-SXE300UV, Beijing Perfect Light Technology Co. Ltd. China) with a AM1.5G filter. The diffuse reflectance spectra were tested by a UV/Vis spectrophotometer (U-4900, HITACHI, Japan). Photoluminescence (PL) and photoluminescence excitation (PLE) spectra were measured using a spectrofluorometer (F-4600, HITACHI, Japan) at room temperature. Reproducibility of the photochromic effect was evaluated by measuring PL intensity changes with irradiation cycles, wherein a xenon lamp equipped with F-4600 was taken into account of not only as photoirradiation sources but also as the exciting light sources. The measured wavelength range is from 500 nm to 700 nm. The scanning rate is 240 nm/min. Finishing a complete PL curve from 500 nm to 700 nm was defined as a cycle, namely, irradiation time of 50 s.

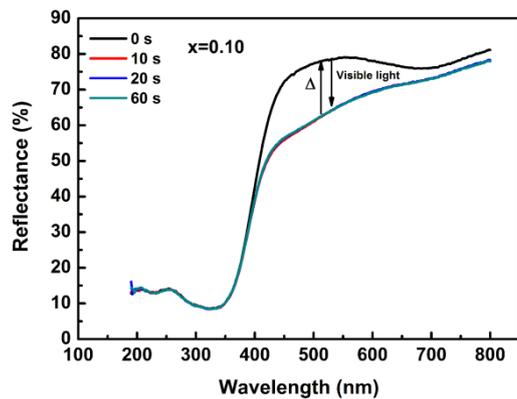


Fig. S1 Reflection spectra for the NBN:0.10Eu by visible light irradiation (0s, 10s, 20s, 60s).

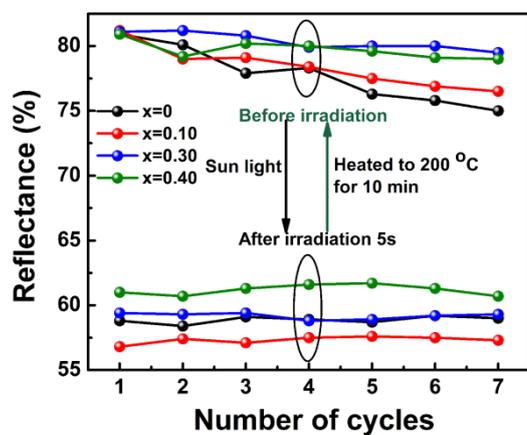


Fig. S2 Reflectance intensity changes of NBN:xEu upon alternating sunlight irradiation and heat treatment at 200 °C for 10 min.

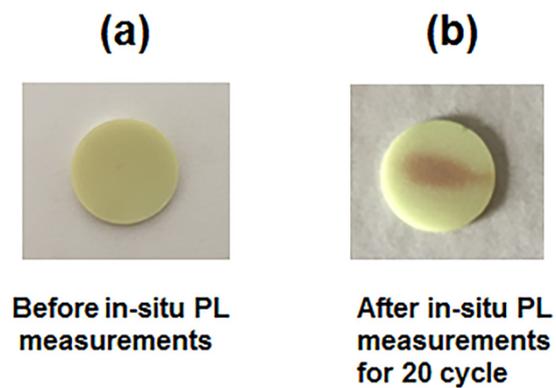


Fig. S3 Photographs of the NBN:0.30Eu sample, a) and b) before and after in-situ PL measurements for 20 cycles.

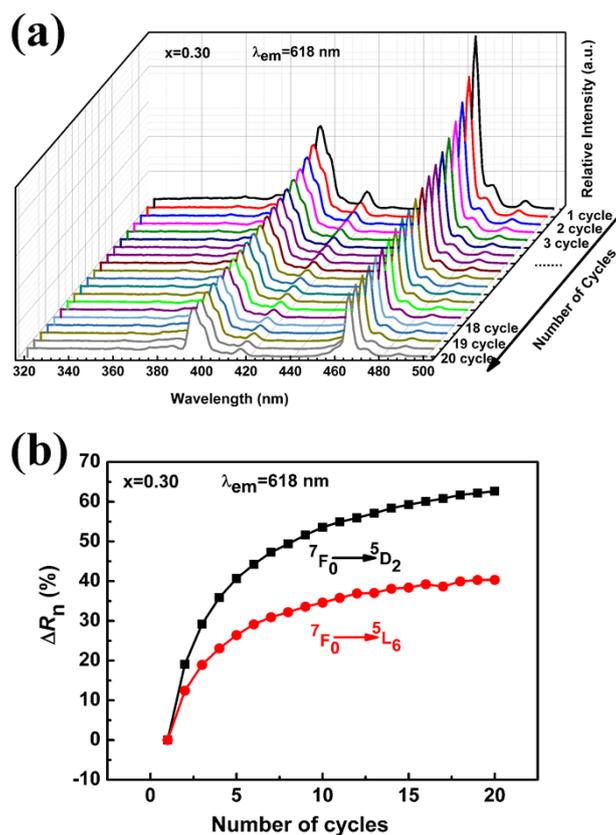


Fig. S4 (a) PLE spectral changes of the NBN:0.30Eu sample monitored at 618 nm different irradiation cycles at room temperature, respectively. (b) The luminescence quenching degree (ΔR_n) as a function of irradiation cycles at 395 nm (${}^7F_0 \rightarrow {}^5L_6$) and 465 nm (${}^7F_0 \rightarrow {}^5D_2$).

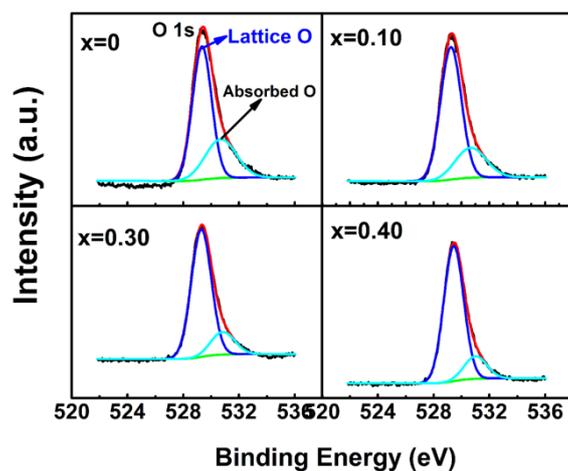


Fig. S5a O 1s XPS spectra for NBN:xEu (x=0, 10, 30, 40) before sunlight irradiation.

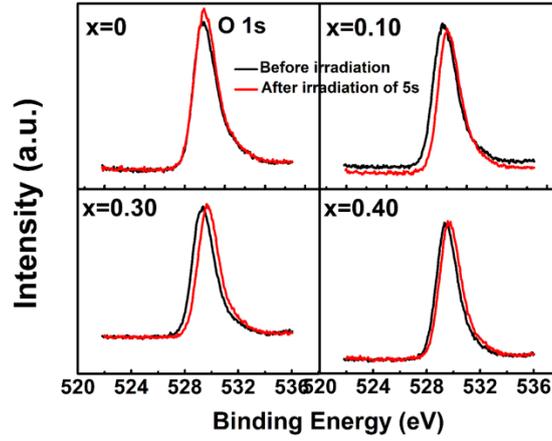


Fig. S5b O 1s XPS spectra for NBN: xEu ($x=0, 10, 30, 40$) before and after sunlight irradiation.

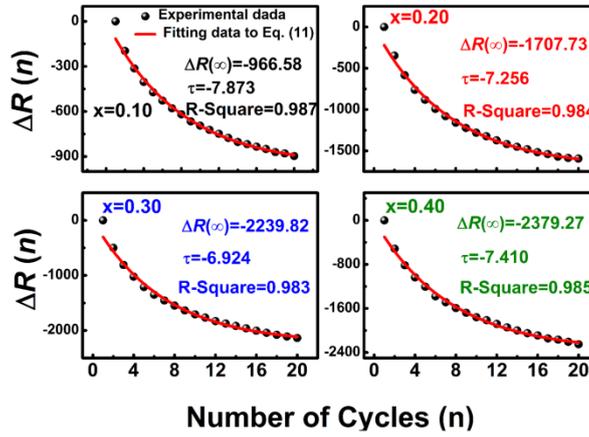


Fig. S6 The $\Delta R(n)$ dependence of different irradiation cycles for NBN: xEu ($x=0, 0.10, 0.20, 0.30$) under 465 nm irradiation. The symbols indicate the experimental data, and the solid lines (red) represent the fitting to the Eq. (5).

The photoinduced dynamic absorption change at different irradiation time (t) follow a universal rule, namely, satisfying the exponential relaxation model, defined as¹⁷

$$\Delta A(t) = A(t+t_0) - A(t_0) \quad (1)$$

$$\Delta A(t) = \Delta A(\infty) [1 - \exp(-t/\tau)] \quad (2)$$

where $\Delta A(t)$ is the absorption difference at irradiation time t , $\Delta A(\infty)$ is the absorption difference at the fully colored state, t_0 is the initial time, τ is the relaxation time constant. According to the Eq. (2), the $\Delta A(t)$ values exhibit the exponential decay trends with increasing irradiation time (t). The exponential decay rule along with irradiation time is equally suitable to luminescence modulation behavior, as observed in Fig. 5, owing to the fact that the photo-generated electrons from Eu ions

partly captured by vacancy related defects get involved the PC, resulting in the decreased emission. By analogy with Eq. (2), we can infer that the luminescence emission intensity difference $\Delta R(t)$ caused by PC also follows the rule, being proportional to the $\Delta A(t)$, as follows:

$$\Delta R(t) \propto \Delta A(t) \quad (3)$$

$$\Delta R(t) = R(t+t_0) - R(t_0) \quad (4)$$

$$\Delta R(t) = \Delta R(\infty) [1 - \exp(-t/\tau)] \quad (5)$$

$$t = 50 \text{ n} \quad (6)$$

where $\Delta R(\infty)$ is the emission intensity difference at the fully colored state, $R(t_0)$ and $R(t+t_0)$ are the initial emission intensity and the relative intensity under different irradiation time or cycle, respectively. The measured wavelength range is from 500 nm to 700 nm, scanning rate is 240 nm/min. A complete PL curve (500-700 nm) was defined as a cycle (n), namely, irradiation time of 50 s. In order to prove the relation in the Eq. (5), the emission intensity difference $\Delta R(t)$ under 452 nm excitation is plotted as a function of irradiation cycles for NBN: xEu (x=0.10, 0.20, 0.30, 0.40) samples, and these data are fitted with the Eq. (5), as shown in Fig. S5. The dependence of the $\Delta R(t)$ on irradiation cycles well fits to the Eq. (11), indicating that the $\Delta R(t)$ values exhibit an exponential decay trend with increasing irradiation cycles, as like the absorption difference $\Delta A(t)$. These results also prove our statements on the luminescence modulation mechanism mentioned above.

¹⁷ T. Saitoh, A. E. Bocquet, T. Mizokawa, H. Namatame, A. Fujimori, M. Abbate, Y. Takeda and M. Takano, Phys. Rev. B 1995, 51(20), 13942.

Table S1 Fitting parameters of the Bi 4f (a) and O 1s (b) XPS spectra of Eu doped NBN samples before and after irradiation

(a) Bi 4f

Samples	Binding energy (eV)					
	Bi 4f (Before irradiation)			Bi 4f (After irradiation)		
	Bi ³⁺ (7/2)	Bi ^{3-x} (7/2)	Bi ^{3-x} /Bi ³⁺	Bi ³⁺ (7/2)	Bi ^{3-x} (7/2)	Bi ^{3-x} /Bi ³⁺
x=0	160.29	158.61	0.99	160.45	158.71	1.18
x=0.10	160.35	158.52	0.818	160.43	158.80	1.03
x=0.30	160.40	158.74	1.01	160.47	158.51	1.39
x=0.40	160.32	158.58	0.68	160.36	158.77	0.80

(b) O 1s

Samples	Binding energy (eV)					
	O 1s (Before irradiation)			O 1s (After irradiation)		
	Lattice O (O ²⁻)	Absorbed O (*Vo)	Vo/O ² -	Lattice O (O ²⁻)	Absorbed O (*Vo)	Vo/O ² -
x=0	529.35	530.69	0.48	529.84	531.03	0.29
x=0.10	529.24	530.65	0.33	529.95	531.29	0.28
x=0.30	529.29	530.83	0.21	529.85	531.06	0.11
x=0.40	529.44	530.99	0.18	530.11	531.45	0.16

*Vo means O vacancy