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Supplementary Information

A novel ratiometric optical fiber X-ray sensor based on the $NaGdF_4$: Tb/ $CaAl_2O_4$: Eu/Nd composites

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Chemicals and materials

$Gd(CH_3CO_2)_3·xH_2O$ (99.9%), $Tb(CH_3CO_2)_3·xH_2O$ (99.9%), $Ce(CH_3CO_2)_3·xH_2O$ (99.9%) $Ba(CH_3CO_2)_2$ (99.9%), $Dy(CH_3CO_2)_3$ (99.9%), $Lu(CH_3CO_2)_3$ (99.9%), $Li(CH_3CO_2)$ (99.9%), NH_4F and NaOH were purchased from Aladdin (Shanghai, China). oleic acid (OA, 90%), and 1-octadecence (ODE, 90%) were purchased from Sigma-Aldrich (Shanghai, China).ethanol (≥99.5%), cyclohexane (≥99.5%),methanol (≥99.7%) were purchased from Sinopharm Chemical Reagent Co. (Shanghai, China). Purple long afterglow luminescent powder $CaAl_2O_4$: Eu/Nd was purchased from the Foshan Xiucai Chemicals Co., Ltd. Toluene was purchased from the Hangzhou Gaojing Fine Chemical Industry Co., Ltd. Polymethyl methacrylate (PMMA) were purchased from Cool Chemical Technology (Beijing) Co., Ltd. All the chemical reagents were used as received without further purification.

Preparation of composite scintillator film

In a typical synthesis of $NaGdF_4$: 15Tb, 0.65 mmol $Gd(C_2H_3O_2)_3·xH_2O$ and 0.15 mmol $Tb(CH_3CO_2)_3 · xH_2O$ were mixed with 8 mL OA in a 50 mL three-neck round-bottom flask. The resulting mixture was then heated at 150°C for 30 min to remove the water solvent, followed by the injection of ODE (12 mL), The mixture was stirred at

150^{o}C for another 30 min before cooling down to 80^{o}C.Subsequently, a methanol solution (10 mL) of NH_4F (3 mmol) and NaOH (2 mmol) was added. The reaction mixture was then heated at 90^{o}C for 1h to remove the methanol. The resulting solution was heated to 280^{o}C under N_2 flow with vigorous stirring for 90 min and then cooled down to room temperature. The as-prepared nanoparticles were precipitated by addition of ethanol, collected by centrifugation at 9000 rpm for 5 min, and washed with cyclohexane and ethanol three times. The $BaLuF_5$: 15Tb NPs, $LiLuF_4$: 15Tb NPs and $NaLuF_4$: 15Tb/15Gd NPs were prepared via the similar procedures.

First, the PMMA toluene solution was prepared by dissolving PMMA into toluene via stirring until the solution became uniform and transparent. After that, $CaAl_2O_4$: Eu/Nd and $NaGdF_4$: 15Tb involved toluene suspension was added into1 mL PMMA toluene solution, which was stirred for more than 2h until the solution became uniform paste like without agglomeration. Finally, the mixed liquid was evenly dropped into a mold of 30 mm*30 mm*1 mm and then volatilized at room temperature for 12 h until the film was formed.

Structural and optical characterization

The X-ray diffraction (XRD) analysis was carried out with a powder diffractometer (Bruker D8 Advance) with a Cu-K_α (λ=1.5405 Å) radiation. The morphology and the size of the products were characterized by a field emission transmission electron microscopy (TEM, FEI, Tecnai G2 F20) and a field emission scanning electron microscopy (SEM, Hitachi, SU8010). XEOL spectra were measured by a portable fiber spectrometer (Zolix, China) with an X-ray tube (target material: W, voltage 50 kV, tube current 200 μA) and a photon counter (DCS210PC-9S).

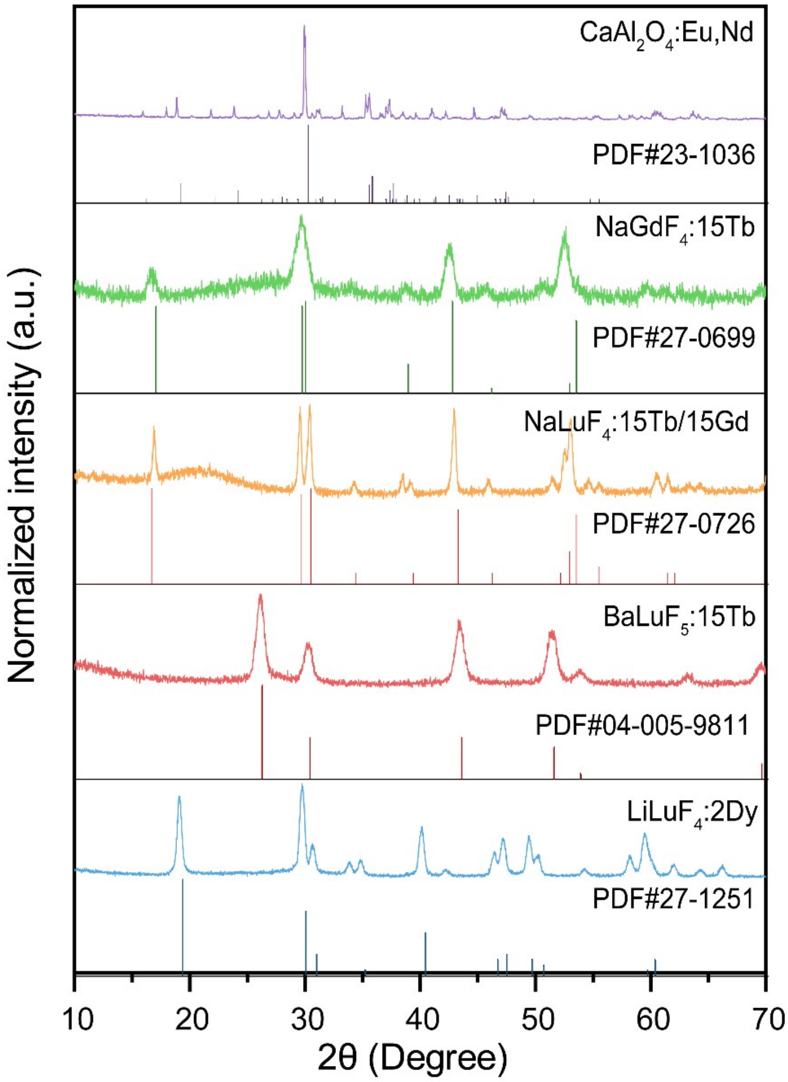

Fig. S1 XRD patterns of the studied materials.

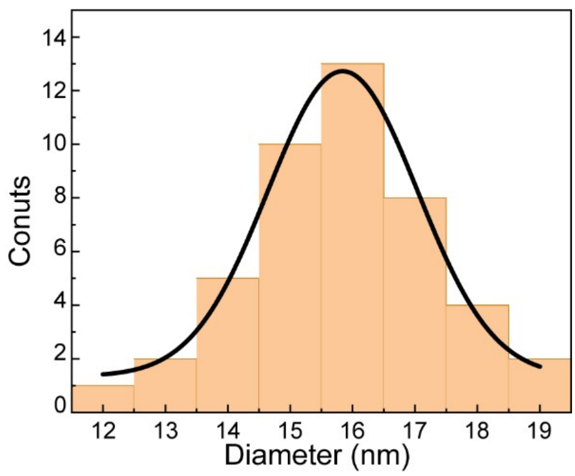

Fig. S2 Histograms of size distributions of the as-prepared $NaGdF_4$: 15Tb NPs.

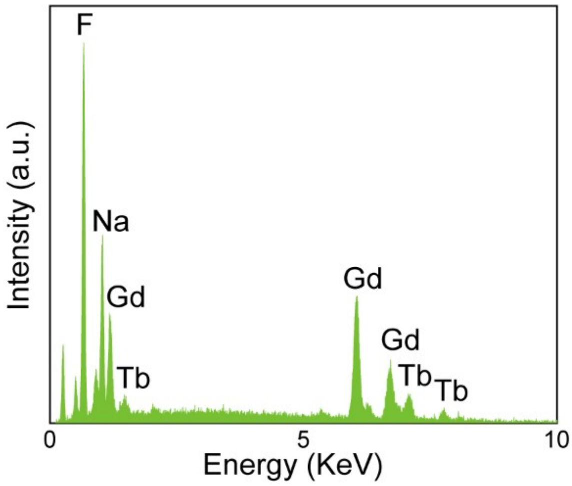

Fig. S3 EDX spectra of the $NaGdF_4$: 15Tb NPs.

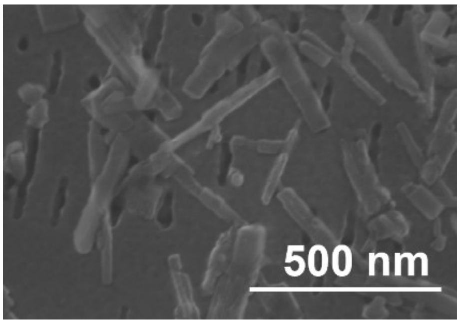

Fig. S4 SEM image of the $CaAl_2O_4$: Eu/Nd phosphor.

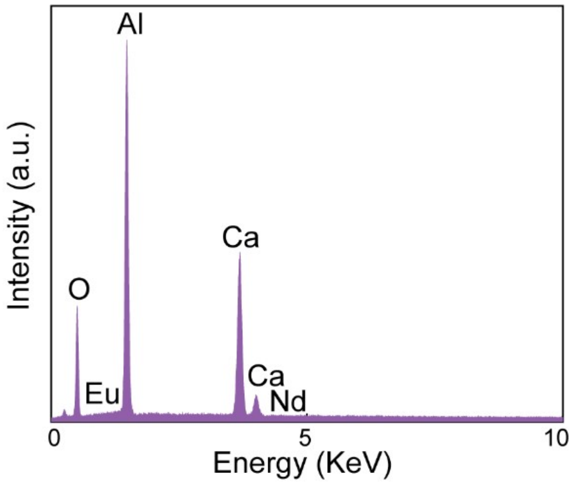

Fig. S5 EDX spectrum of the $CaAl_2O_4$: Eu/Nd phosphor.

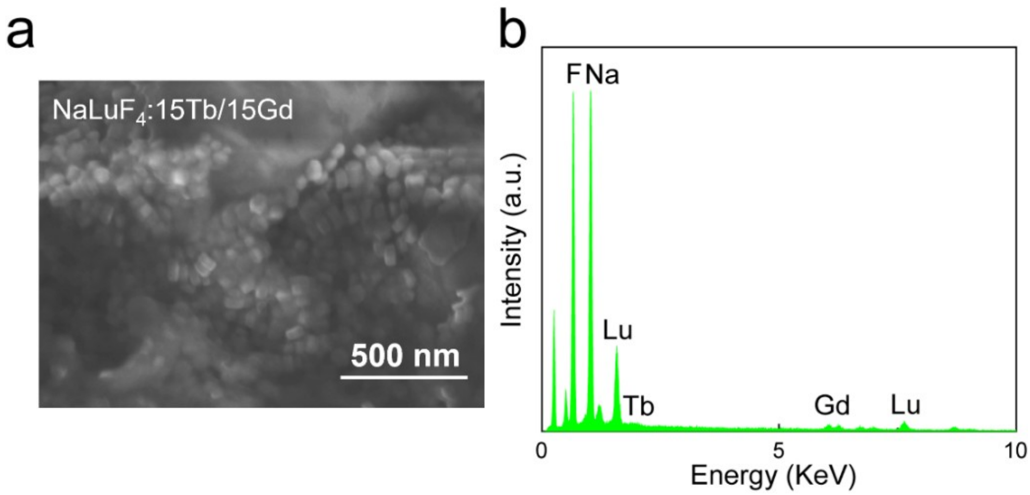

Fig. S6 SEM image (**a**) and EDX spectrum (**b**) of the $NaLuF_4$: 15Tb/15Gd NPs.

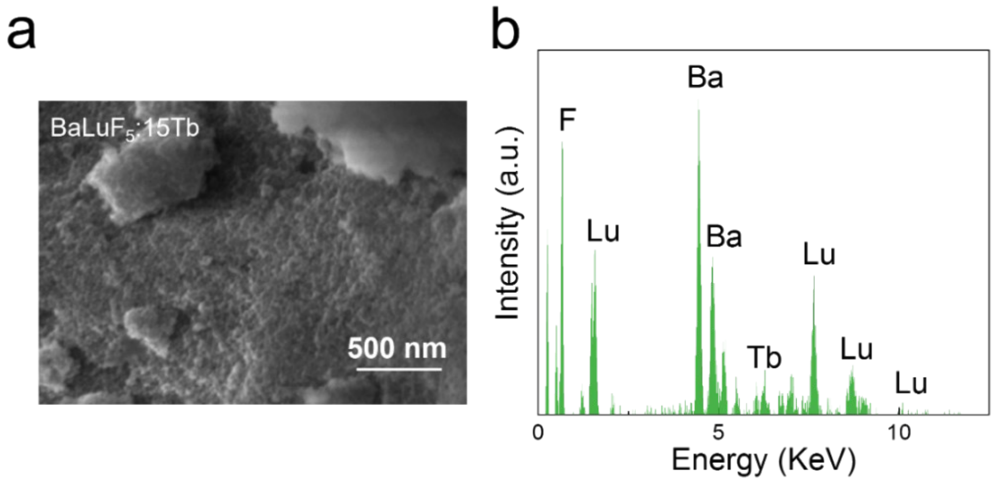

Fig. S7 SEM image (**a**) and EDX spectrum (**b**) of the $BaLuF_5$: 15Tb NPs.

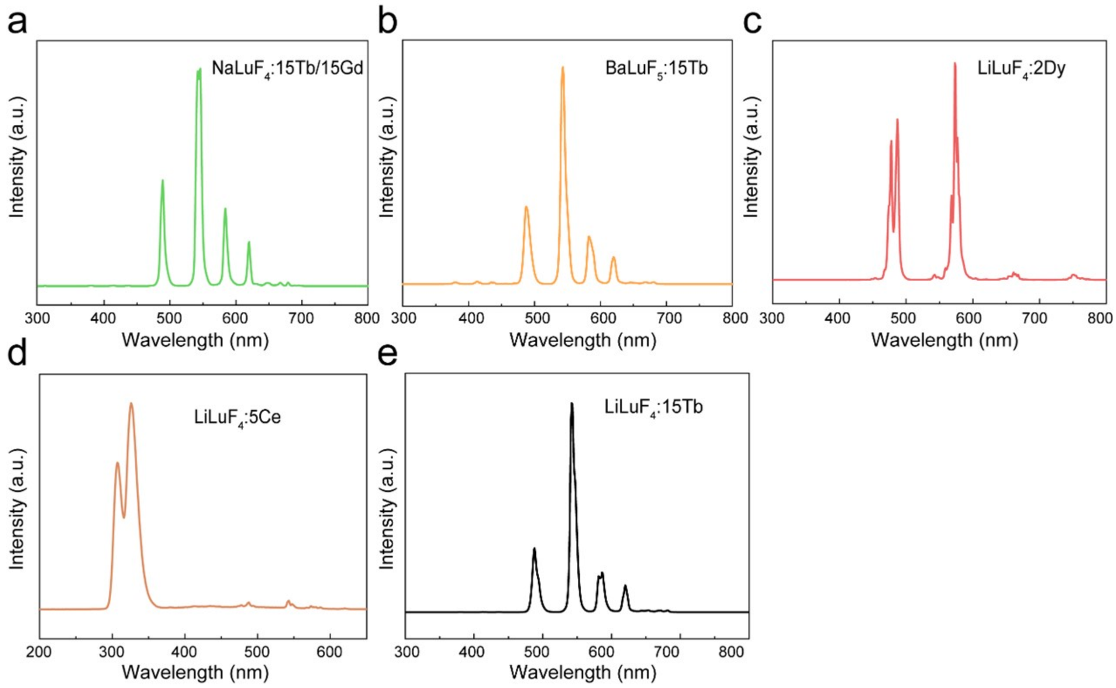

Fig. S8 XEOL spectra of the $NaLuF_4$: 15Tb/15Gd, $BaLuF_5$: 15Tb, $LiLuF_4$: 2Dy, $LiLuF_4$: 5Ce and $LiLuF_4$: 15Tb NPs.

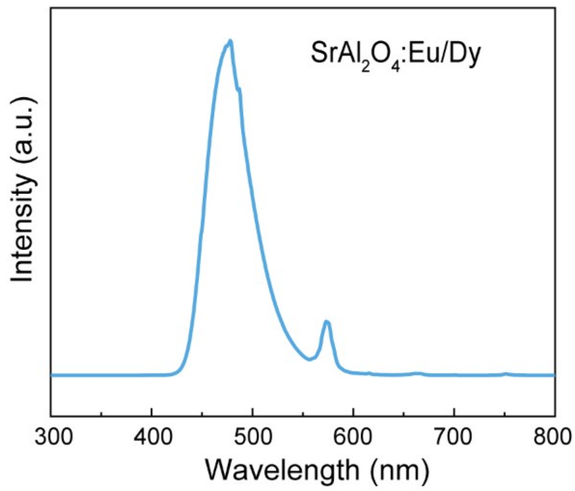

Fig. S9 XEOL spectrum of the $SrAl_2O_4$: Eu/Dy phosphor.

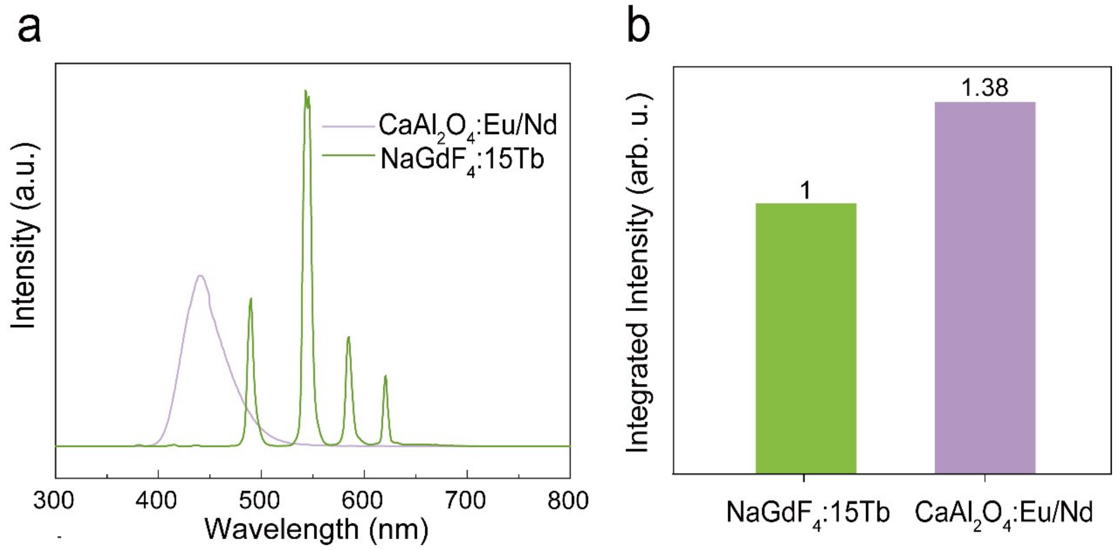

Fig. S10 a The XEOL intensity of $NaGdF_4$: 15Tb NPs and $CaAl_2O_4$: Eu/Nd with the same weight (38mg). **b** Integrated XEOL intensity ratio of $CaAl_2O_4$: Eu/Nd and $NaGdF_4$: 15Tb.

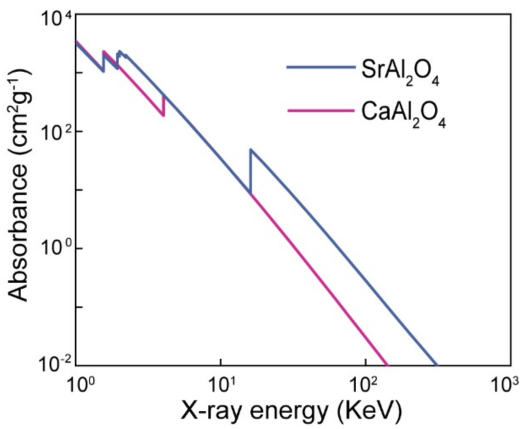

Fig. S11 Absorption spectra of the $SrAl_2O_4$ and $CaAl_2O_4$ as a function of X-ray energy.

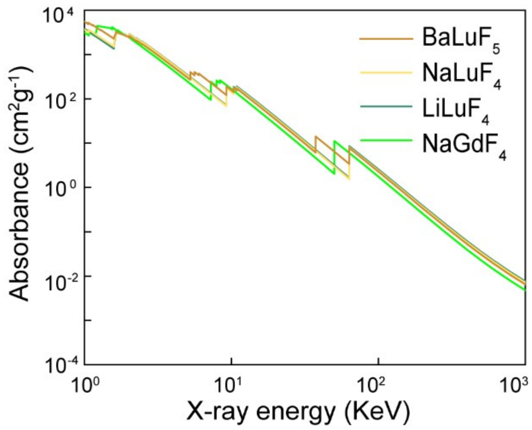

Fig. S12 Absorption spectra of the $BaLuF_5$, $NaLuF_4$, $LiLuF_4$ and $NaGdF_4$ as a function of X-ray energy.

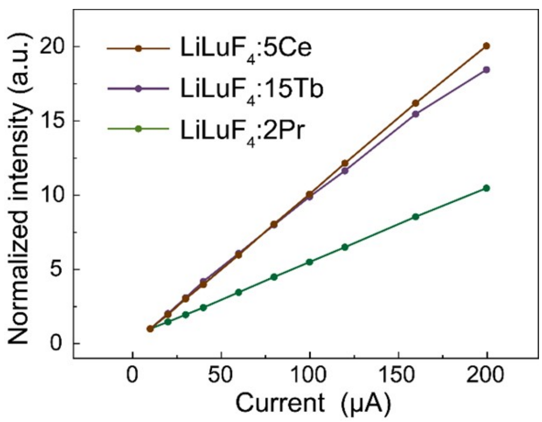

Fig. S13 X-ray current dependent XEOL intensity variations for the $LiLuF_4$: 5Ce, $LiLuF_4$: 15Tb and $LiLuF_4$: 2Pr NPs.

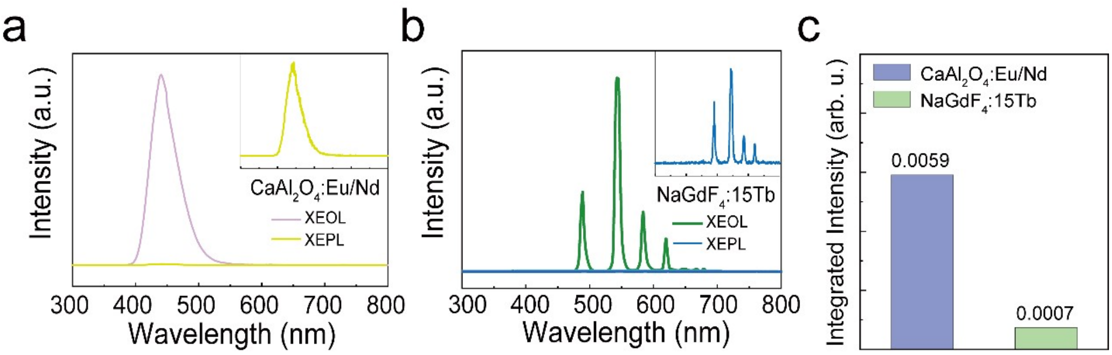

Fig. S14 a Compared XEOL and XEPL spectrum of the $CaAl_2O_4$: Eu/Nd. **b** Compared XEOL and XEPL spectrum of the $NaGdF_4$: 15Tb. **c** Integrated XEPL/XEOL intensity ratio of $CaAl_2O_4$: Eu/Nd and $NaGdF_4$: 15Tb.

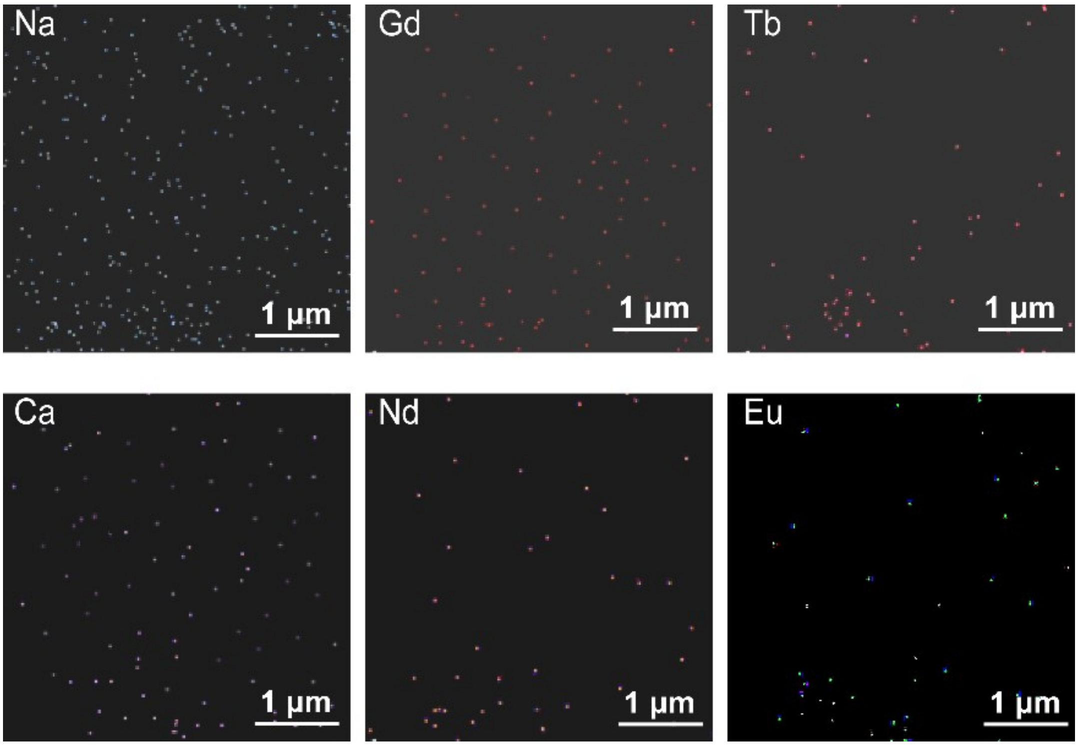

Fig. S15 EDX-mapping results of the $NaGdF_4$: $15Tb/CaAl_2O_4$: Eu/Nd composite scintillator film.

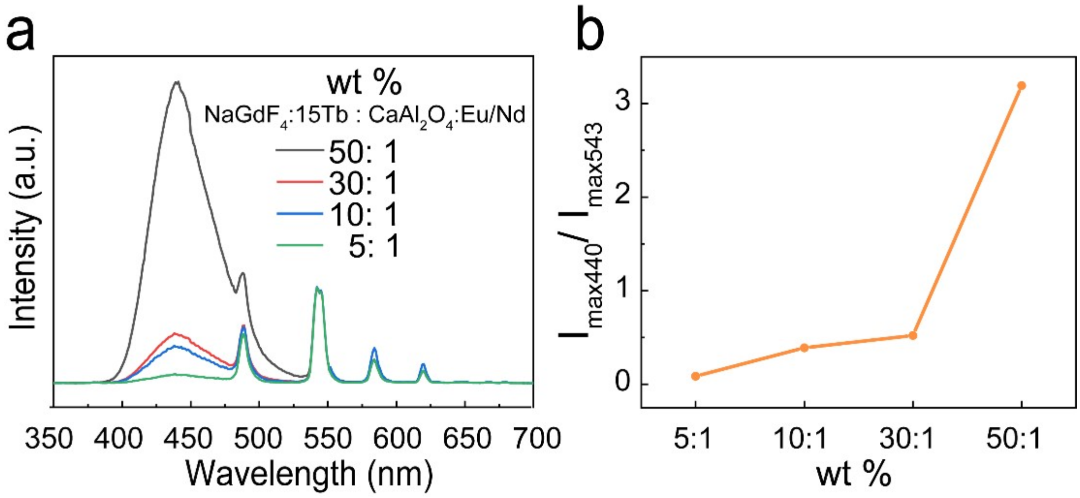

Fig. S16 a XEOL spectra of the composite scintillator film with different compositions. **b** the corresponding XEOL intensity ratio of Eu/Tb.

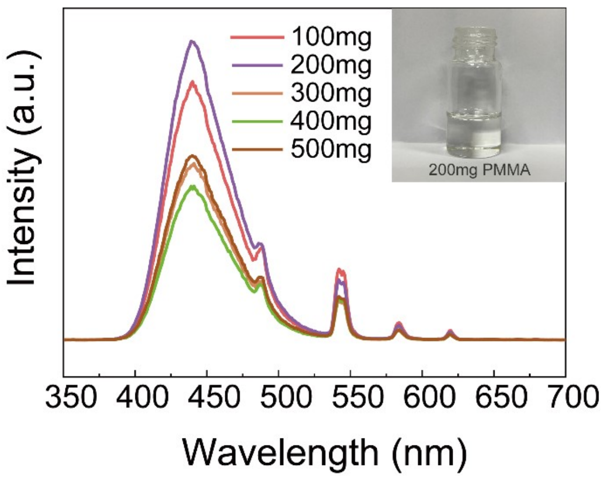

Fig. S17 XEOL spectra of the composite scintillator film with different PMMA contents. Inset is the photograph of $NaGdF_4$: 15Tb and $CaAl_2O_4$: Eu/Nd mixture dissolved PMMA solution.

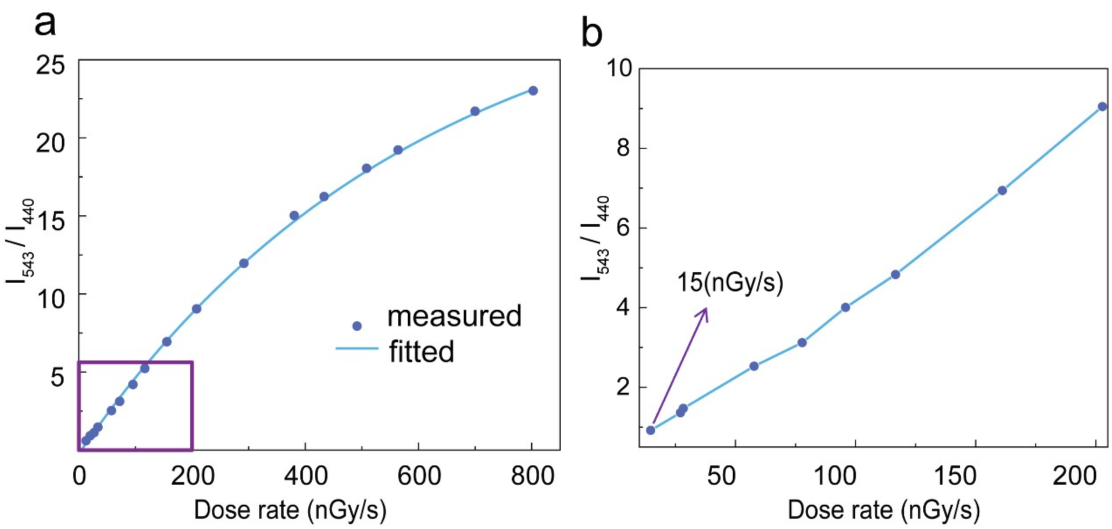

Fig. S18 a Measured and fitted curve of dose rate dependent XEOL intensity ratio of I_{543}/I_{440} in the composite scintillator film. **b** enlarged figure focusing on the low-dose rate range.

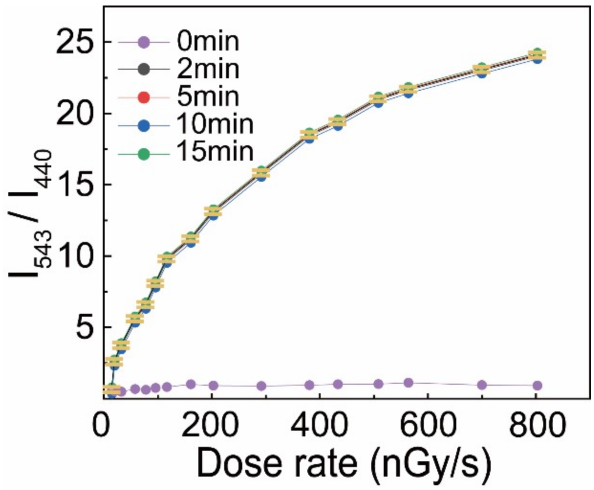

Fig.S19 The relationship between the intensity ratio I_{543}/I_{440} and the dose rate of composite scintillator film under different X-ray irradiation time.

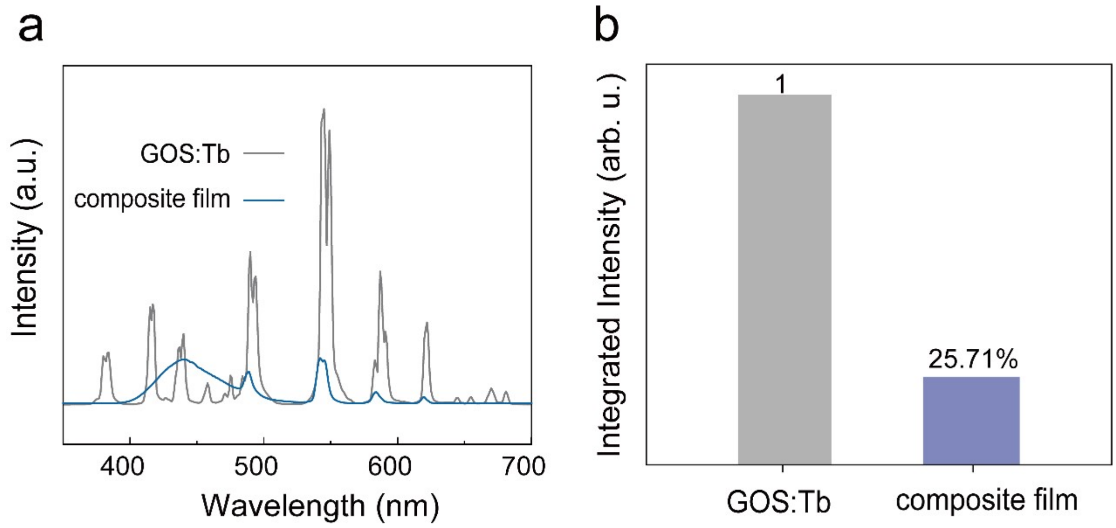

Fig.S20 a The XEOL intensity of GOS: Tb and composite film. **b** Integrated XEOL intensity ratio of composite film and GOS: Tb.