Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

Alkaline-Earth-Metal-Ion Blending Enhanced Mechanoluminescence of Lanthanide Ion in MZnOS Host for Stress Sensing and Anticounterfeiting

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1. Experimental Section

1.1 Materials and reagents

All reagents are of analytical grade and used as received. $CaCO_3$ (AR, 99%, Aladdin), ZnS (99.99% metals basis, Aladdin), $SrCO_3$ (AR, 99%, Aladdin), REF_3 (RE=Er^{3+}, Dy^{3+}, Sm^{3+}, Yb^{3+}) (99% metals basis, Aladdin), $LiNO_3$ (99% metals basis, Aladdin).

1.2 Apparatus and optical measurements

PL spectra are recorded on an FLS920 fluorescence spectrometer (Edinburgh Instruments, U.K.). SEM spectrum are carried out on high resolution field emission scanning electron microscope (JSM-7800F, SU8010). EDX measurements are carried out on a multifunctional imaging electron spectrometer (Bruker Nano GmbH Berlin, Germany). XRD patterns are recorded on an X-ray diffractometer (Bruker AXS D8 Advance, Germany) with Cu Kα radiation (λ=1.5418 Å). ML spectra are acquired by a Pixis400BR CCD (Princeton Instruments) coupled with IsoPlane160 monochromator. TL curves were collected on a YULI instrument (TOSL-3DS) in the temperature range from RT to 575 K at a heating rate of 1 K/s after pre-excitation under 365 nm for about 5 min..

1.3 ML Sample preparation

All the ML samples are prepared via a solid-state reaction at high temperature.[1] After grounding the precursors into powders in an agate mortar, the precursor are calcined powders at 1000 °C for 4 hours under Ar atmosphere (purity, 99.99%). The sintered products were cooled to room temperature in the furnace and grounded into powders to achieve ML samples.

The binary host of (Ca, Sr)ZnOS samples, i.e. $Ca_{1-x}Sr_xZnOS$, were prepared with ZnS, $CaCO_3$, and $SrCO_3$ as precursors and $LiNO_3$ as fluxing agent. The lanthanide-ions activated binary host (Ca, Sr)ZnOS, i.e. $Ca_{0.96-x}Sr_xZnOS:RE_{0.04}$, were prepared with ZnS, $CaCO_3$, $SrCO_3$, REF_3 (RE=Er^{3+}, Dy^{3+}, Sm^{3+}, Yb^{3+}) as precursors and $LiNO_3$ as fluxing agent. Typically, $Ca_{0.66}Sr_{0.30}ZnOS:Er_{0.04}$ is prepared with a precursor molar

ratio Ca:Sr:Zn:Er of 0.66:0.30:1.00:0.04.

Both unary CaZnOS and SrZnOS samples were prepared in a similar way without precursor of either $SrCO_3$ or $CaCO_3$.

The ML samples were mixed with polydimethylsiloxane (PDMS) at a weight ratio of 5:1, and place in the mold at 80 °C for 2 hours to form right circular cylinder composites with a diameter of 10 mm and a thickness of 1 mm for the ML measurement.

Scheme 1 The schematic diagram of synthesis method.

2. Results and discussion

2.1 XRD patterns for typical $Ca_{1-x}Sr_xZnOS$ host and $Ca_{0.96-x}Sr_xZnOS:Er_{0.04}$

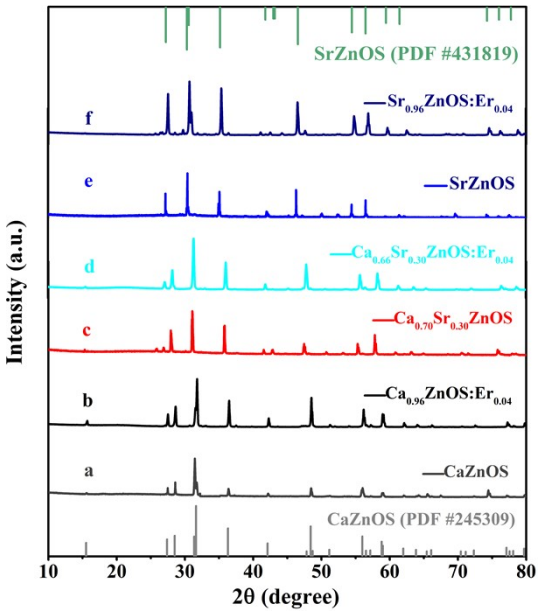

Fig. S1 XRD patterns of $Ca_{1-x}Sr_xZnOS$ (x=0, 0.3, 1) and $Ca_{0.96-x}Sr_xZnOS:Er_{0.04}$ (x=0, 0.3, 0.96).

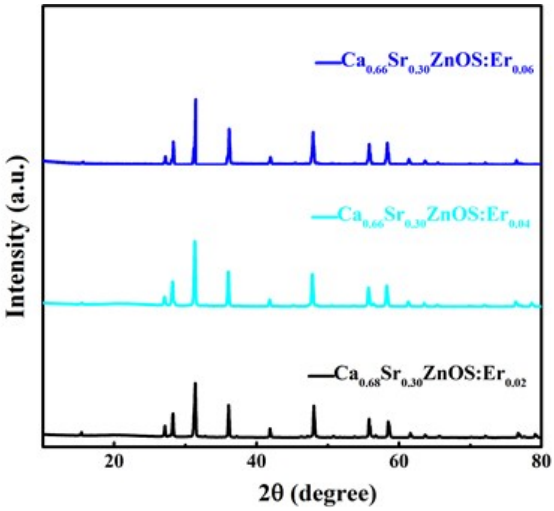

Fig. S2 XRD patterns of $Ca_{0.70-y}Sr_{0.30}ZnOS:Er_y$ (x=0.02, 0.04, 0.06).

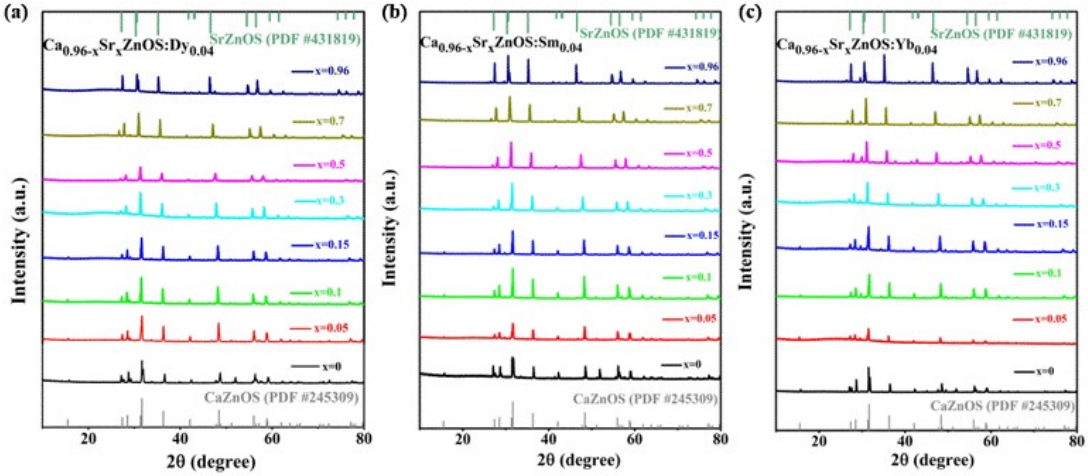

Fig. S3 XRD patterns of $Ca_{0.96-x}Sr_xZnOS:RE_{0.04}$ (RE=Dy^{3+}, Sm^{3+}, Yb^{3+}).

2.2 EDX mapping characterization of $Ca_{0.66}Sr_{0.3}ZnOS:Er_{0.04}$

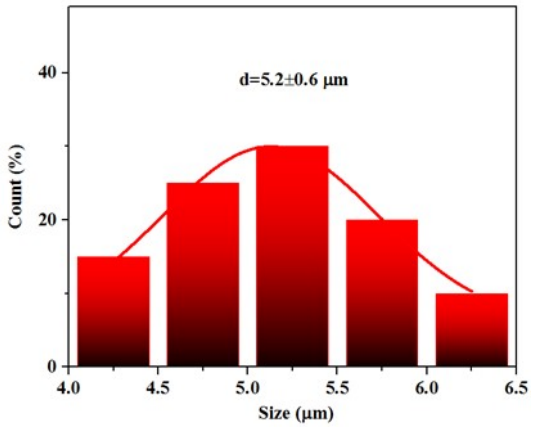

Fig. S4 The size distribution analysis of $Ca_{0.66}Sr_{0.30}ZnOS:Er_{0.04}$.

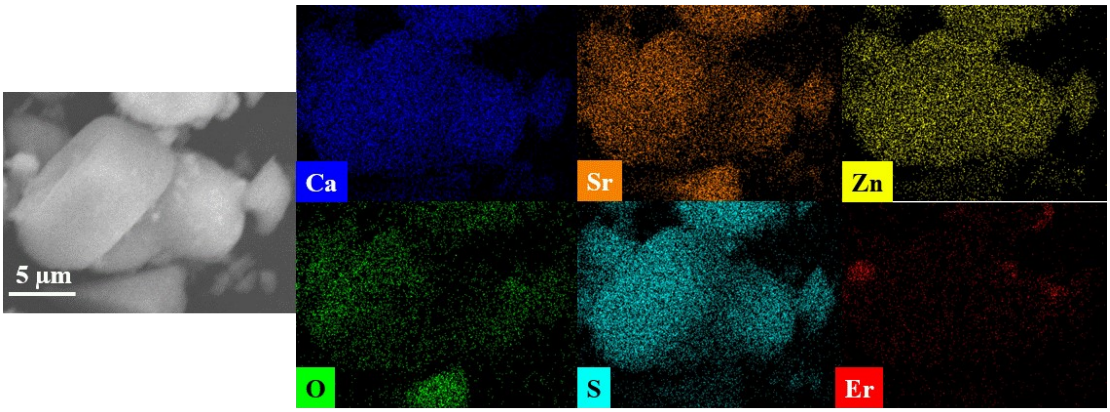

Fig. S5 The EDX mapping diagrams of $Ca_{0.66}Sr_{0.3}ZnOS:Er_{0.04}$.

Table S1. Composition of $Ca_{0.66}Sr_{0.3}ZnOS:Er_{0.04}$ determined by EDS

Element	Atom(%)
Ca	17.71
Sr	7.56
Zn	24.26
O	25.23
S	24.29
Er	0.95

2.3 PL lifetime properties of $Ca_{0.66}Sr_{0.3}ZnOS:Er_{0.04}$

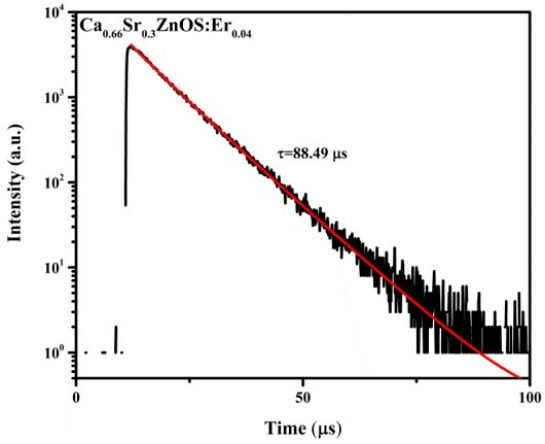

Fig. S6 PL decay curves of $Ca_{0.66}Sr_{0.3}ZnOS:Er_{0.04}$.

Table S2 PL lifetime parameters of $Ca_{0.66}Sr_{0.3}ZnOS:Er_{0.04}$.

τ_1(μs)/(α_1)	τ_2(μs)/(α_2)	τ(μs)	χ^2
65.61/(28.56%)	94.83/(71.44%)	88.49	1.01

2.4 ML repeated properties

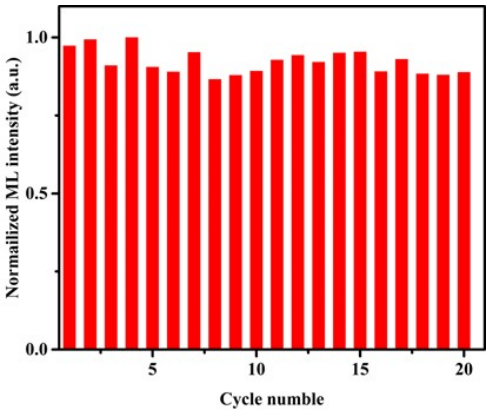

Fig. S7 ML repeatability of $Ca_{0.66}Sr_{0.30}ZnOS:Er_{0.04}$ film upon repetitive mechanical excitation at 25 N.

2.5 CIE Coordinates

Table S3. CIE Coordinates of $Ca_{0.66}Sr_{0.3}ZnOS:RE$ (RE=Er^{3+}, Dy^{3+}, Sm^{3+}).

Samples	x	y
G	0.2947	0.6707
G:O(1:1)	0.4349	0.5031
O	0.4752	0.4409
R	0.6169	0.3573

2.6 ML spectrum for mixture of $Ca_{0.66}Sr_{0.3}ZnOS:Er_{0.04}$ and $Ca_{0.66}Sr_{0.3}ZnOS:Dy_{0.04}$

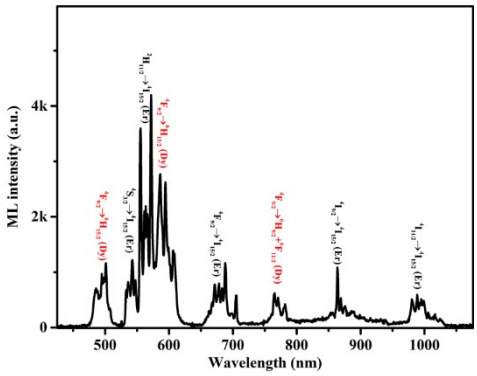

Fig. S8 ML spectrum for the mixture of $Ca_{0.66}Sr_{0.3}ZnOS:Er_{0.04}$ and $Ca_{0.66}Sr_{0.3}ZnOS:Dy_{0.04}$ at 1:1 level.

Notes and references

1. J. Jia, X. Gao and G. Zou, *Adv. Funct. Mater.*, 2022, **32**, 2207881.