

Supplementary Information

**Nephelauxetic effect of hydride ligand in $\text{Sr}_2\text{LiSiO}_4\text{H}$ as a host
material for rare-earth-activated phosphors**

Tong Wu,^a Asako Ishikawa,^a Takashi Honda,^b Hiromu Tamatsukuri,^b Kazutaka Ikeda,^b Toshiya Otomo^b and Satoru Matsuishi^{*a}

^aMaterials Research Center for Element Strategy, Tokyo Institute of Technology, 4259 Nagatsuta-cho, Midori-ku, Yokohama 226-8503, Japan.

^bInstitute of Materials Structure Science, High Energy Accelerator Research Organization, Tsukuba 305-0801, Japan

*Corresponding author. E-mail address: matsuishi@mces.titech.ac.jp

Materials

All non-doped and Eu^{2+} -doped (2%) samples were directly synthesized by high-temperature reaction of $\text{Sr}_{2-x}\text{Eu}_x\text{SiO}_4$ ($x = 0, 0.04$) with LiX ($X = \text{H}, \text{F}$). Specifically, to prepare the non-doped samples, SrCO_3 (99.9%, Kojundo Chemical Laboratory co., ltd, Japan) and SiO_2 (99.9%, Kojundo Chemical Laboratory co., ltd, Japan) were thoroughly mixed in alumina mortar in air at a stoichiometric ratio of 2:1. The mixture was then heated in an alumina boat in a tube furnace with N_2 gas flow at 1300 °C for 6 h to obtain the precursor Sr_2SiO_4 . LiH was synthesized by heating Li metal with H_2 gas in a stainless steel vessel. To prepare $\text{Sr}_2\text{LiSiO}_4\text{H}$, Sr_2SiO_4 was thoroughly mixed with LiH (1:1.05) in an Ar-filled glove box and pressed into pellet. The pellet was then placed in a vessel and heated at 700 °C for 5 h under 0.9 MPa H_2 pressure. To prepare $\text{Sr}_2\text{LiSiO}_4\text{F}$, the precursor was mixed with LiF (99.9%, Kojundo, Japan) at a mole ratio of 1:1.05 in ambient environment and pressed into pellet. The pellet was sintered at 900 °C for 12 h under N_2 gas flow.

To prepare the Eu-doped samples, the same procedure was used except that the precursor contained Eu. Specifically, SrCO_3 (99.9%, Kojundo Chemical Laboratory co., ltd, Japan), Eu_2O_3 (99.9%, Kojundo Chemical Laboratory co., ltd, Japan), and SiO_2 (99.9%, Kojundo Chemical Laboratory co., ltd, Japan) were thoroughly mixed in alumina mortar in air at a stoichiometric ratio of 1.96:0.04:1. The mixture was then sintered in an alumina boat placed inside a tube furnace at 1200 °C for 6 h under $\text{N}_2/\text{H}_2 = 95:5$ gas flow to obtain the precursor with divalent Eu.

For the neutron diffraction measurement, the deuterated and ^7Li -enriched sample $\text{Sr}_2^7\text{LiSiO}_4\text{D}$ was synthesized using D_2 gas (4N) and 99.9% ^7Li -enriched Li metal ingot.

Thermal desorption spectroscopy (TDS)

To determine the hydrogen content, TDS was performed (TDS, TDS1400, ESCO, Japan) under vacuum ($<10^{-7}$ Pa). The temperature was increased from room temperature to 1476 K at a heating rate of 60 K/min.

Powder x-ray diffraction (XRD)

XRD patterns of the samples were recorded on a D8 Advance diffractometer (Bruker, Germany) with $\text{Cu K}\alpha$ radiation at room temperature.

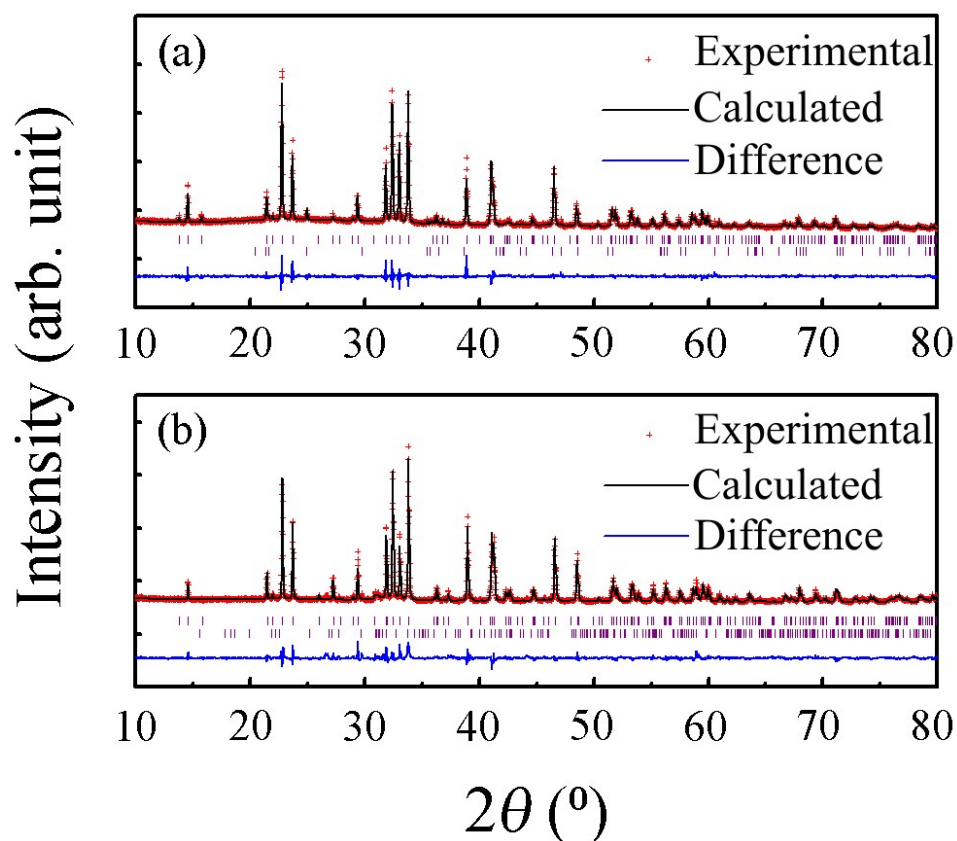


Figure S1. XRD patterns of (a) $\text{Sr}_2\text{LiSiO}_4\text{H}:\text{Eu}^{2+}$ (impurity phase: 1.36 wt.% $\text{Li}_2\text{SrSiO}_4$, GOF = 1.32, $R_{\text{wp}} = 5.60$). (b) $\text{Sr}_2\text{LiSiO}_4\text{F}:\text{Eu}^{2+}$ (impurity phase: 5.16 wt.% Sr_2SiO_4 , GOF = 1.84, $R_{\text{wp}} = 9.32$)

Optical property measurement

Diffuse reflectance spectra of the samples were measured in ambient atmosphere on a U4100 (Hitachi High-Technologies Corp., Japan) spectrophotometer equipped with an integrating sphere and Spectralon SRS-99-010 as a reflection standard. The powder sample was contained in the sample holder with SiO_2 glass window. The photoluminescence spectra of the samples were measured at room temperature on a F-4500 (Hitachi High-Technologies Corp., Japan) fluorescence spectrophotometer.

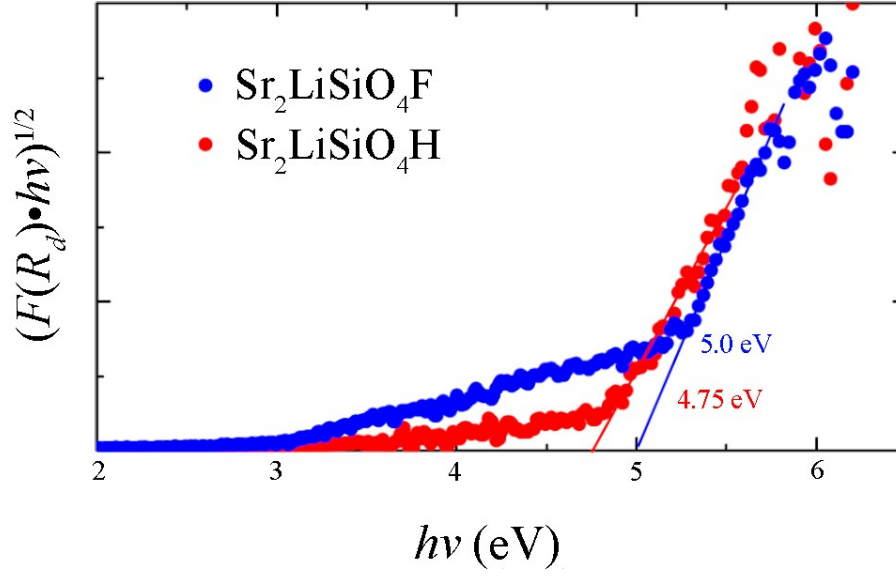


Figure S2. Diffuse reflectance spectra of $\text{Sr}_2\text{LiSiO}_4\text{F}$ and $\text{Sr}_2\text{LiSiO}_4\text{H}$. The $(F(R_d) \cdot hv)^{1/2}$ data of $\text{Sr}_2\text{LiSiO}_4\text{F}$ were multiplied by 10 so that both sets of data are displayed within the same coordinate axis range.

Magnetization measurement

To determine Eu valence state in $\text{Sr}_2\text{LiSiO}_4\text{H}:\text{Eu}^{2+}$ and $\text{Sr}_2\text{LiSiO}_4\text{F}:\text{Eu}^{2+}$, magnetization measurements were performed by using a SQUID vibrating sample magnetometer (Quantum Design MPMS). The Magnetization (M) versus Magnetic field (H) plots were obtained from -70000 Oe to 70000 Oe under the fixed temperature $T = 2.5$ K. The M versus Temperature (T) plots were obtained from 2.5 K to 300 K with fixed magnetic field $H = 1$ T. Both M - H curve and M - T curve were well-fitted by the equation;

$$M = NgJ\mu_B B_J(x),$$

where N is the number of atoms, $B_J(x)$ is Brillouin function¹;

$$B_J(x) = \frac{2J+1}{2J} \coth\left(\frac{2J+1}{2J}x\right) - \frac{1}{2J} \coth\left(\frac{1}{2J}x\right)$$

and x is given by $x = gJ\mu_B/k_B T$ with total angular momentum J , Landé g -factor $g = 2$, Bohr magneton $\mu_B = 9.274 \times 10^{-21}$ and Boltzmann constant $k_B = 1.38065 \times 10^{-16}$. We chose $J = 7/2$ which corresponds to Eu^{2+} with $^8\text{S}_{7/2}$ state. Based on the well-fitted curve, we evaluated the number of Eu^{2+} and compared with nominal concentration of Eu in the samples. For $\text{Sr}_2\text{LiSiO}_4\text{H}:\text{Eu}^{2+}$, the M - H curve gave the number of Eu^{2+} corresponding to 95.2% of nominal Eu content while the M - T curve gave the value of 89.4%. For $\text{Sr}_2\text{LiSiO}_4\text{F}:\text{Eu}^{2+}$, the values of 80.2% and 80.0% were also obtained from M - H and M - T curves, respectively. These results indicate the most of Eu atom form divalent states in both $\text{Sr}_2\text{LiSiO}_4\text{H}:\text{Eu}^{2+}$ and $\text{Sr}_2\text{LiSiO}_4\text{F}:\text{Eu}^{2+}$ sample.

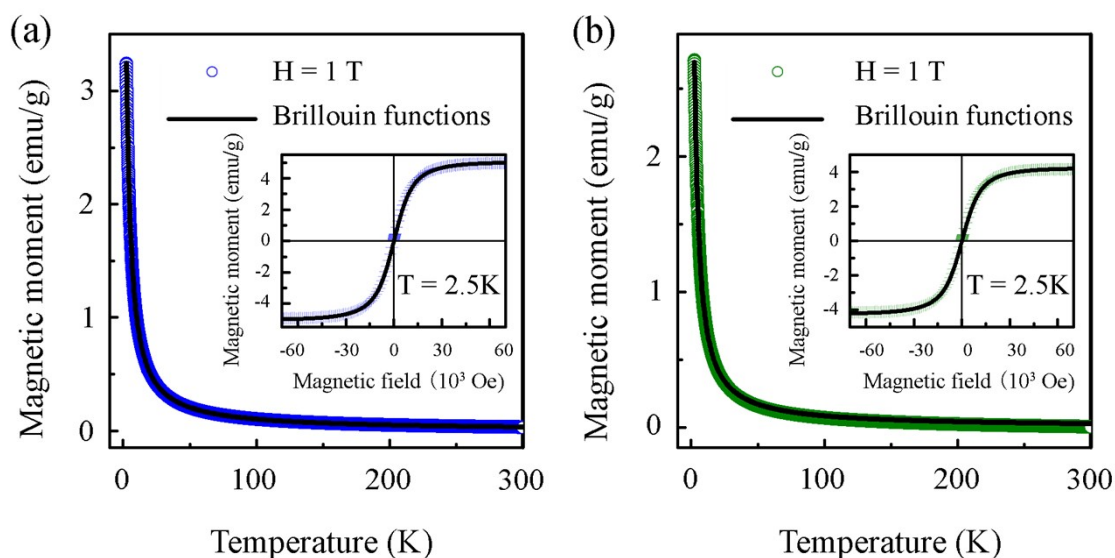


Figure S3. M - T curve and M - H curve (insert) of (a) Sr₂LiSiO₄H:Eu²⁺ and (b) Sr₂LiSiO₄F:Eu²⁺ fitted by Brillouin function with $J = 7/2$.

Time-of-flight neutron powder diffraction (TOF-NPD)

The TOF-NPD data of the ⁷Li-enriched Sr₂LiSiO₄D sample were collected at room temperature in a vanadium–nickel alloy holder with a diameter of 6 mm. Rietveld refinement of the data was performed using the Z-Rietveld code.²

Table S1. Summary of the Rietveld refinement analysis of Sr₂LiSiO₄D

	R_{wp}	2.0935%
	R_p	1.7904%
	R_{wp}/R_e	3.441258
Mass ratio (wt.%)	Sr ₂ LiSiO ₄ D	97.44(2)
	SrLi ₂ SiO ₄	2.12(2)
	SrO	0.44(1)
R_B	Sr ₂ LiSiO ₄ D	1.0152%
	SrLi ₂ SiO ₄	4.2738%
	SrO	1.9159%
R_F	Sr ₂ LiSiO ₄ D	1.0715%
	SrLi ₂ SiO ₄	1.4514%
	SrO	1.1176%

R_{wp} , 2.0935%; R_p , 1.7904%; R_e , 0.6084%; R_B , 1.0152%; R_F , 1.0715%.

Phase 1: Sr₂LiSiO₄D

Crystal system: monoclinic

Space group: *P2₁/m* (11)Lattice parameters: $a = 6.5820(5)$ Å, $b = 5.4197(4)$ Å, $c = 6.9475(5)$ Å, $\beta = 112.5628(2)$ °**Table S2.** Atomic coordinates, occupancy and isotropic displacement parameters of Sr₂LiSiO₄D

	Occupancy	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} (10 ⁻² Å ²)
Sr1 2e	1	0.16090(4)	1/4	0.37365(4)	0.936(9)
Sr2 2e	1	0.63362(5)	1/4	0.89818(4)	0.774(10)
Li1 2e	1.000(2)	0.15003(14)	1/4	0.87596(14)	1.116(35)
Si1 2e	1	0.65322(8)	1/4	0.33402(7)	0.547(12)
O1 2e	1	0.40260(6)	1/4	0.15666(6)	0.777(9)
O2 4f	1	0.22628(4)	-0.00820(4)	0.71201(4)	0.889(9)
O3 2e	1	0.65916(6)	1/4	0.56780(4)	1.624(12)
D1 2a	1.000(1)	0	0	0	1.987(14)

Table S3. Isotropic displacement parameters of Sr₂LiSiO₄D (×10⁻² Å²)

	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
Sr1	0.983(19)	1.222(20)	0.603(17)	0	0.530(15)	0
Sr2	1.015(20)	0.688(22)	0.619(21)	0	0.391(17)	0
Li1	0.913(61)	1.593(60)	0.841(57)	0	0.592(48)	0
Si1	0.772(30)	0.564(27)	0.306(27)	0	0.168(22)	0
O1	0.205(24)	1.439(24)	0.685(20)	0	0.015(17)	0
O2	1.251(19)	0.472(14)	0.944(16)	0.485(14)	0.524(15)	-0.008(12)
O3	2.684(24)	1.783(23)	0.405(21)	0	0.973(19)	0
D1	1.687(26)	1.907(25)	2.366(24)	0.035(16)	0.751(20)	0.071(19)

Phase 2: SrLi₂SiO₄

Crystal system: Trigonal

Space group: *P*3₁2₁ (152)Lattice parameters: $a = 5.0238(35)$ Å, $c = 12.4580(12)$ Å**Table S4.** Atomic coordinates, occupancy and isotropic displacement parameters of SrLi₂SiO₄

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}} (\times 10^{-2} \text{ \AA}^2)$
Sr1 6c	0.4118(9)	0	1/3	0.633
Li1 3a	0.0955(22)	0.3909(32)	0.4136(12)	0.633
Si1 3b	0.2997(16)	0	5/6	0.633
O1 6c	0.0386(9)	0.4940(11)	0.0566(3)	0.633
O2 6c	0.2968(8)	0.2396(8)	0.1691(4)	0.633

Phase 3: SrO

Crystal system: Cubic

Space group: *Fm*-3*m* (225)Lattice parameter: $a = 5.1565(45)$ Å**Table S5.** Atomic coordinates, occupancy and isotropic displacement parameters of SrO

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}} (\times 10^{-2} \text{ \AA}^2)$
Sr1 4a	0	0	0	0.633
O1 4b	1/2	1/2	1/2	0.633

Table S6. Interatomic distances in Sr₂LiSiO₄F and Sr₂LiSiO₄D

	Sr ₂ LiSiO ₄ F		Sr ₂ LiSiO ₄ D	
Lattice parameters	$a = 6.5825(9) \text{ \AA}, b = 5.4158(8) \text{ \AA}, c = 6.9266(6) \text{ \AA}, \beta = 112.525(8)^\circ$		$a = 6.5868(2) \text{ \AA}, b = 5.4219(1) \text{ \AA}, c = 6.9498(2) \text{ \AA}, \beta = 112.556(2)^\circ$	
Interatomic distances	Sr1-O1	2.578(9) \AA	Sr1-O1	2.578(5) \AA
	Sr1-O2	2.708(6) \AA	Sr1-O2	2.721(3) \AA
	Sr1-O3	2.911(3) \AA	Sr1-O3	2.9226(10) \AA
	Sr1-F1	2.7401(7) \AA	Sr1-D1	2.7544(3) \AA
	Sr2-O1	2.7341(9) \AA	Sr2-O1	2.73416(15) \AA
	Sr2-O2	2.817(6) \AA	Sr2-O2	2.8259(11) \AA
	Sr2-O3	2.347(8) \AA	Sr2-O3	2.365(3) \AA
	Sr2-F1	2.613 (1) \AA	Sr2-D1	2.6158(3) \AA

The Sr₂LiSiO₄F data were obtained from the literature,³ whereas the Sr₂LiSiO₄D data were obtained from the TOF-NPD measurements.

DFT calculations

Single-shot G_0W_0 calculations with $3 \times 4 \times 3$ mesh and density functional theory calculations, using the projector-augmented wave method and a Perdew–Burke–Ernzerhof exchange correlation functional implemented in VASP code, were performed to determine the bandgap energies of the host materials.⁴⁻⁷ To investigate the optical energy transitions from Eu 4f to 5d in Sr₂LiSiO₄H and Sr₂LiSiO₄F, constrained density functional theory (cDFT) calculations were performed with a plane-wave cutoff energy of 500 eV as wave function. The $2 \times 2 \times 1$ supercells (Sr₃₁Eu₁Li₁₆Si₁₆O₆₄H₁₆), which were derived from the calculated Eu-free system, contain 144 atoms with one Eu atom substituted on the Sr1 site and Sr2 site. The DFT+U method⁸ was used for localizing the Eu f electrons with $U = 6$ eV for both hydride and fluoride materials.

Table S7. Bond lengths and bond angles of Eu coordination in Sr1 site in the A_0^* state (structure optimized for A_0 state)

Sr ₂ LiSiO ₄ H				Sr ₂ LiSiO ₄ F			
	Bond length (Å)		Bond angle (Å)		Bond length (Å)		Bond angle (Å)
Eu-O1	2.603	O1-Eu-H	62.995	Eu-O1	2.616	O1-Eu-F	62.774
			62.980				62.774
Eu-O2	2.716	O2-Eu-O2	58.296	Eu-O2	2.722	O2-Eu-O2	58.326
	2.724				2.722		
	2.639		64.198		2.619		64.894
	2.639				2.619		
Eu-O3	2.969	O3-Eu-O3	135.065	Eu-O3	2.950	O3-Eu-O3	135.894
	2.969				2.950		
	3.078	O3-Eu-H	112.111		3.077	O3-Eu-F	111.940
			112.113				111.940
Eu-H	2.765	H-Eu-H	58.994	Eu-F	2.810	F-Eu-F	58.427
	2.765				2.810		

In Sr1 substitution, Eu coordinates with one O1, four O2, three O3 atoms and two X ($X = F, H$) atoms.

Table S8. Bond lengths and bond angles of Eu coordination in Sr2 site in the A_0^* state (structure optimized for A_0 state)

Sr ₂ LiSiO ₄ H				Sr ₂ LiSiO ₄ F			
	Bond length (Å)		Bond angle (Å)		Bond length (Å)		Bond angle (Å)
Eu-O1	2.760	O1-Eu-O1	164.213	Eu-O1	2.759	O1-Eu-O1	164.294
	2.760				2.759		
	2.833	O1-Eu-H	120.636 120.654		2.787	O1-Eu-F	120.164 120.164
Eu-O2	2.849	O2-Eu-O2	55.493	Eu-O2	2.857	O2-Eu-O2	55.406
	2.848				2.857		
	2.937	57.405	2.905		57.889		
	2.935		2.905				
Eu-O3	2.362	O3-Eu-H	83.227 83.222	Eu-O3	2.360	O3-Eu-F	82.447 82.447
Eu-H	2.574	H-Eu-H	63.615	Eu-F	2.634	F-Eu-F	62.592
	2.574				2.634		

In Sr2 substitution, Eu coordinates with three O1, four O2, one O3 atoms and two X ($X = F, H$) atoms.

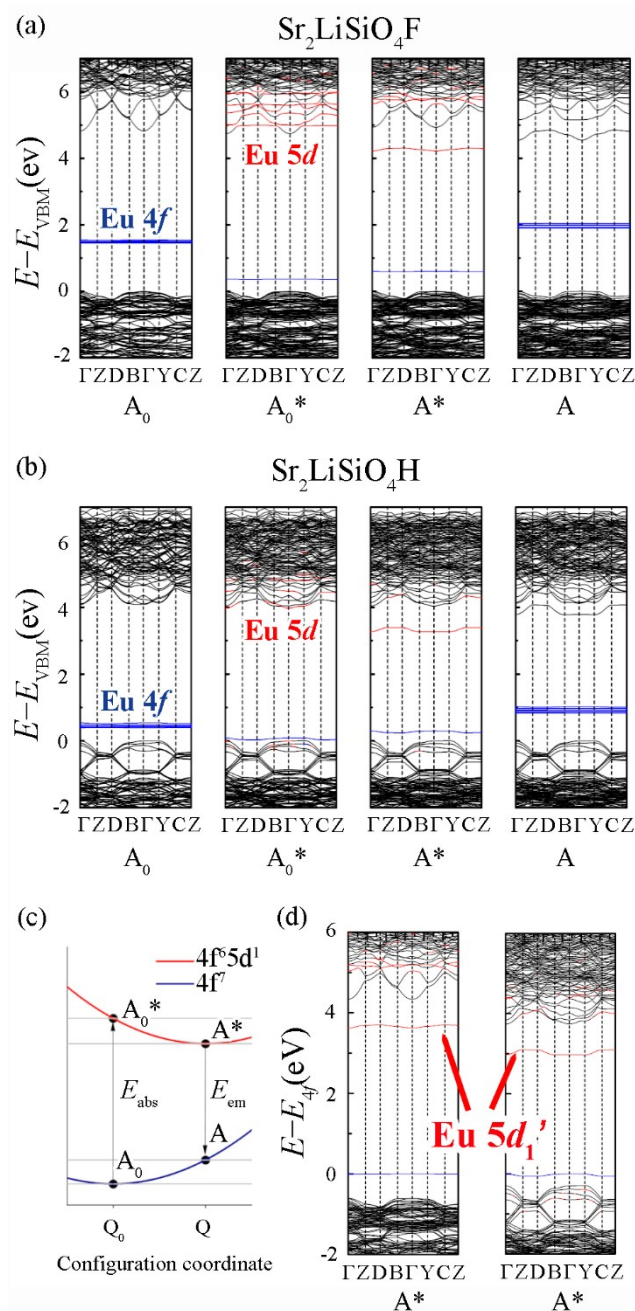


Figure S3. Band structures showing the electronic states (ground state A_0 , excited state A_0^* , excited state after structure relaxation A^* , ground state A) of (a) $\text{Sr}_2\text{LiSiO}_4\text{F}$ and (b) $\text{Sr}_2\text{LiSiO}_4\text{H}$. (c) Configuration coordinate diagram. Band structures showing the A^* states of (d) $\text{Sr}_2\text{LiSiO}_4\text{F}$ (left) and $\text{Sr}_2\text{LiSiO}_4\text{H}$ (right). For better comparison of the Eu $5d$ lowest band in each excited state, the Eu $4f$ energy level was set as 0 eV for both $\text{Sr}_2\text{LiSiO}_4\text{F}$ and $\text{Sr}_2\text{LiSiO}_4\text{H}$.

References

- 1 C. Kittel, *Introduction to Solid State Physics*, 2004.
- 2 R. Oishi, M. Yonemura, Y. Nishimaki, S. Torii, A. Hoshikawa, T. Ishigaki, T. Morishima, K. Mori and T. Kamiyama, *Nucl. Instruments Methods Phys. Res. Sect. A Accel. Spectrometers, Detect. Assoc. Equip.*, 2009, **600**, 94–96.
- 3 A. Akella and D. A. Keszler, *Chem. Mater.*, 1995, **7**, 1299–1302.
- 4 P. E. Blöchl, *Phys. Rev. B*, 1994, **50**, 17953–17979.
- 5 G. Kresse and J. Furthmüller, *Phys. Rev. B - Condens. Matter Mater. Phys.*, 1996, **54**, 11169–11186.
- 6 J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865–3868.
- 7 M. Van Schilfgaarde, T. Kotani and S. Faleev, *Phys. Rev. Lett.*, 2006, **96**, 1–4.
- 8 L. A. I, *J. Phys. Condens. Matter*, 1997, **9**, 767.