Supplementary Information

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

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Materials

All non-doped and Eu$^{2+}$-doped (2%) samples were directly synthesized by high-temperature reaction of Sr$_2$Eu$_x$SiO$_4$ ($x = 0, 0.04$) with Li$X$ ($X = H, F$). 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$_2$SiO$_4$. LiH was synthesized by heating Li metal with H$_2$ gas in a stainless steel vessel. To prepare Sr$_2$LiSiO$_4$H, Sr$_2$SiO$_4$ 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 Sr$_2$LiSiO$_4$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$_2$O$_3$(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 N$_2$/H$_2$ = 95: 5 gas flow to obtain the precursor with divalent Eu.

For the neutron diffraction measurement, the deuterated and $^7$Li-enriched sample Sr$_2$$^7$LiSiO$_4$D was synthesized using D$_2$ gas (4N) and 99.9% $^7$Li-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 Cu K$_\alpha$ radiation at room temperature.
Figure S1. XRD patterns of (a) Sr$_2$LiSiO$_4$H:Eu$^{2+}$ (impurity phase: 1.36 wt.% Li$_2$SrSiO$_4$, GOF = 1.32, $R_{wp} = 5.60$). (b) Sr$_2$LiSiO$_4$F:Eu$^{2+}$ (impurity phase: 5.16 wt.% Sr$_2$SiO$_4$, GOF = 1.84, $R_{wp} = 9.32$)

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 Sr$_2$LiSiO$_4$F and Sr$_2$LiSiO$_4$H. The $(F(R)hv)^{1/2}$ data of Sr$_2$LiSiO$_4$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 Sr$_2$LiSiO$_4$H:Eu$^{2+}$ and Sr$_2$LiSiO$_4$F: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:

$$M = N g_J \mu_B B_J(x)$$

where $N$ is the number of atoms, $B_J(x)$ is Brillouin function $^1$:

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

and $x$ is given by $x = gJ \mu_B/k_BT$ 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 $^8S_{7/2}$ 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 Sr$_2$LiSiO$_4$H: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 Sr$_2$LiSiO$_4$F: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 Sr$_2$LiSiO$_4$H:Eu$^{2+}$ and Sr$_2$LiSiO$_4$F:Eu$^{2+}$ sample.
**Figure S3.** $M$-$T$ curve and $M$-$H$ curve (insert) of (a) $\text{Sr}_2\text{LiSiO}_4\text{H}:\text{Eu}^{2+}$ and (b) $\text{Sr}_2\text{LiSiO}_4\text{F}:\text{Eu}^{2+}$ fitted by Brillouin function with $J = 7/2$.

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

The TOF-NPD data of the $^7\text{Li}$-enriched $\text{Sr}_2\text{LiSiO}_4\text{D}$ 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.

**Table S1.** Summary of the Rietveld refinement analysis of $\text{Sr}_2\text{LiSiO}_4\text{D}$

| Mass ratio (wt.%) | $R_{wp}$  | $R_p$ | $R_{wp}/R_p$ | $R_B$ | $R_F$ |
|------------------|-----------|-------|--------------|-------|-------|
| $\text{Sr}_2\text{LiSiO}_4\text{D}$ | 2.0935% | 1.7904% | 3.441258 | 1.0152% | 1.0715% |
| $\text{SrLi}_2\text{SiO}_4$ | 97.44(2) | |
| $\text{SrO}$ | 2.12(2) | 0.44(1) | |
| $\text{Sr}_2\text{LiSiO}_4\text{D}$ | 1.0152% | 1.0715% |
| $\text{SrLi}_2\text{SiO}_4$ | 4.2738% | 1.4514% |
| $\text{SrO}$ | 1.9159% | 1.1176% |

$R_{wp}$, 2.0935%; $R_p$, 1.7904%; $R_{wp}/R_p$, 0.6084%; $R_B$, 1.0152%; $R_F$, 1.0715%.
**Phase 1: Sr₂LiSiO₄D**
Crystal system: monoclinic
Space group: \( P2_1/m \) (11)
Lattice parameters: \( a = 6.5820(5) \, \text{Å}, b = 5.4197(4) \, \text{Å}, c = 6.9475(5) \, \text{Å}, \beta = 112.5628(2) \, ^\circ \)

**Table S2.** Atomic coordinates, occupancy and isotropic displacement parameters of Sr₂LiSiO₄D

| Occupancy | \( x \) | \( y \) | \( z \) | \( U_{iso} \) (×10⁻² Å²) |
|-----------|--------|--------|--------|-----------------|
| 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) | 0.899(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)

|       | \( U_{11} \) | \( U_{22} \) | \( U_{33} \) | \( U_{12} \) | \( U_{13} \) | \( U_{23} \) |
|-------|--------------|--------------|--------------|-------------|-------------|-------------|
| 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: SrLi$_2$SiO$_4$
Crystal system: Trigonal
Space group: $P3_1$2$_1$ (152)
Lattice parameters: $a = 5.0238(35)$ Å, $c = 12.4580(12)$ Å

Table S4. Atomic coordinates, occupancy and isotropic displacement parameters of SrLi$_2$SiO$_4$

|     | x    | y    | z    | $U_{iso}$ ($\times 10^{-2}$ Å$^2$) |
|-----|------|------|------|----------------------------------|
| 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: $Fm-3m$ (225)
Lattice parameter: $a = 5.1565(45)$ Å

Table S5. Atomic coordinates, occupancy and isotropic displacement parameters of SrO

|     | x    | y    | z    | $U_{iso}$ ($\times 10^{-2}$ Å$^2$) |
|-----|------|------|------|----------------------------------|
| Sr1 | 4a   | 0    | 0    | 0.633 |
| O1  | 4b   | 1/2  | 1/2  | 0.633 |
Table S6. Interatomic distances in Sr₂LiSiO₄F and Sr₂LiSiO₄D

|                | Sr₂LiSiO₄F                  | Sr₂LiSiO₄D                  |
|----------------|-----------------------------|-----------------------------|
| Lattice parameters | \(a = 6.5825(9) \text{ Å}, b = 5.4158(8) \text{ Å}, c = 6.9266(6) \text{ Å}, \beta = 112.525(8)^\circ\) | \(a = 6.5868(2) \text{ Å}, b = 5.4219(1) \text{ Å}, c = 6.9498(2) \text{ Å}, \beta = 112.556(2)^\circ\) |
| Sr₁-O₁         | 2.578(9) \text{ Å}          | 2.578(5) \text{ Å}          |
| Sr₁-O₂         | 2.708(6) \text{ Å}          | 2.721(3) \text{ Å}          |
| Sr₁-O₃         | 2.911(3) \text{ Å}          | 2.9226(10) \text{ Å}        |
| Sr₁-F₁         | 2.740(1) \text{ Å}          | 2.754(3) \text{ Å}          |
| Sr₂-O₁         | 2.7341(9) \text{ Å}         | 2.73416(15) \text{ Å}       |
| Sr₂-O₂         | 2.817(6) \text{ Å}          | 2.8259(11) \text{ Å}        |
| Sr₂-O₃         | 2.347(8) \text{ Å}          | 2.365(3) \text{ Å}          |
| Sr₂-F₁         | 2.613 (1) \text{ Å}         | 2.6158(3) \text{ Å}         |

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

DFT calculations

Single-shot GoW₀ 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 (Sr₃EuLi₁₆Si₁₆O₆₄H₁₆), 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 method\(^8\) 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 Bond length (Å) | Sr$_2$LiSiO$_4$F Bond length (Å) | Bond angle (Å) | Sr$_2$LiSiO$_4$H Bond angle (Å) | Sr$_2$LiSiO$_4$F Bond angle (Å) |
|------------------|----------------------------------|----------------------------------|----------------|----------------------------------|----------------------------------|
| Eu-O1            | 2.603                            | Eu-O1                            | 2.616          | 62.995                           | 62.774                           |
|                  |                                   |                                 |                |                                  |                                  |
| Eu-O2            | 2.716                            | O2-Eu-O2                         | 58.296         | 2.724                            | 58.326                           |
|                  |                                   |                                 |                |                                  |                                  |
| Eu-O3            | 2.969                            | O3-Eu-O3                         | 135.065        | 2.950                            | 135.894                           |
|                  |                                   |                                 |                |                                  |                                  |
| Eu-H             | 2.765                            | H-Eu-H                           | 58.994         | 2.810                            | 58.427                           |
|                  |                                   |                                 |                |                                  |                                  |

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 A₀* state (structure optimized for A₀ state)

| Bond length (Å) | Bond angle (Å) | Sr₂LiSiO₄H | Bond length (Å) | Bond angle (Å) | Sr₂LiSiO₄F |
|----------------|----------------|------------|----------------|----------------|------------|
| 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        | O1-Eu-H        | 120.654    |            |         |
|                |                |            |                | 2.787          |            |            |         |
| Eu-O2          | 2.849          | O2-Eu-O2   | 55.493         | O2-Eu-O2       | 55.406     |            |         |
|                | 2.848          |            |                | 2.857          |            |            |         |
|                | 2.937          |            |                | 2.905          |            |            |         |
|                | 2.935          |            |                | 2.905          |            |            |         |
| Eu-O3          | 2.362          | O3-Eu-H    | 83.227         | O3-Eu-O3       | 83.222     | O3-Eu-F    | 82.447  |
|                |                |            | 83.222         |                |            |            |         |
| Eu-H           | 2.574          | H-Eu-H     | 63.615         | Eu-F           | 2.634      | F-Eu-F     | 62.592  |
|                |                |            |                |                |            |            |         |

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) Sr$_2$LiSiO$_4$F and (b) Sr$_2$LiSiO$_4$H. (c) Configuration coordinate diagram. Band structures showing the $A^*$ states of (d) Sr$_2$LiSiO$_4$F (left) and Sr$_2$LiSiO$_4$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 Sr$_2$LiSiO$_4$F and Sr$_2$LiSiO$_4$H.
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