Supplementary Information

Structural Stability and Polymorphic Transitions in *Ln*SI (*Ln* = lanthanides)

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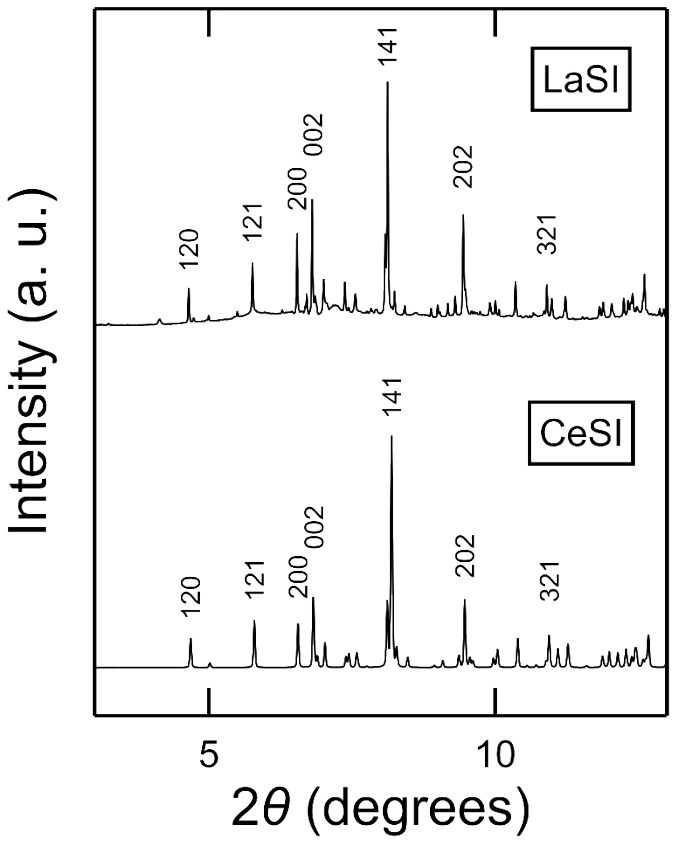

Section 1. Laboratory XRD pattern of LaSI

Figure S1: XRD patterns of LaSI synthesized using a mixture of La_2S_3 and LaI_3 in a molecular ratio of 1:1, compared with a simulated pattern from SrI_2-type CeSI. The diffraction peaks of LaSI are indexed in an orthorhombic symmetry, and corresponding Miller indices are given to the reflections.

Section 2. Another schematic showing the phase transition from FeOCl-type structure to SmSI-type structure

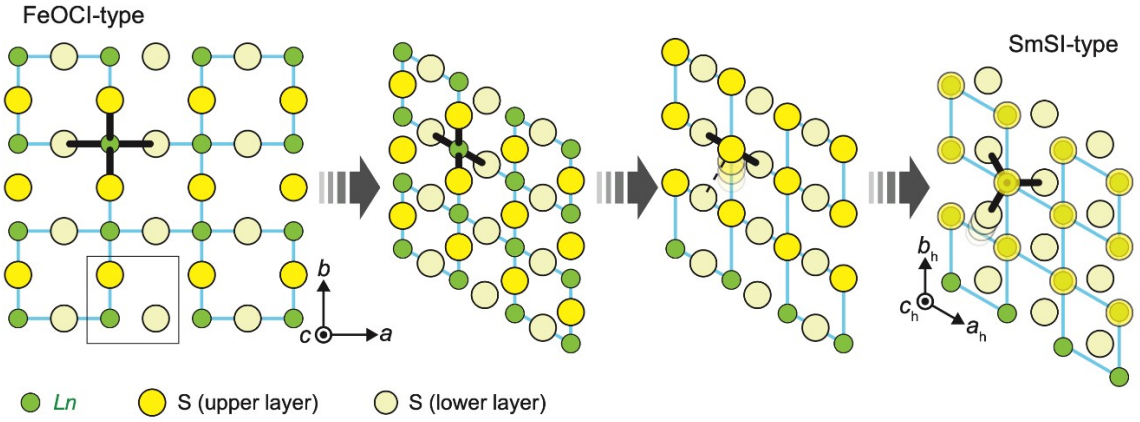

Figure S2: Schematic representation of the phase transformation from the (left) FeOCl-type to (right) SmSI-type structures, and (middle) hypothetical sheared states. The stacking of upper S, lower S, and *Ln* layers along the *c* axis are illustrated from front to back. The black lines and blue diamonds represent the unit cell of the FeOCl- and SmSI-type structure, respectively.

Section 3. The DFT total energy of CeSI as a function of pressure

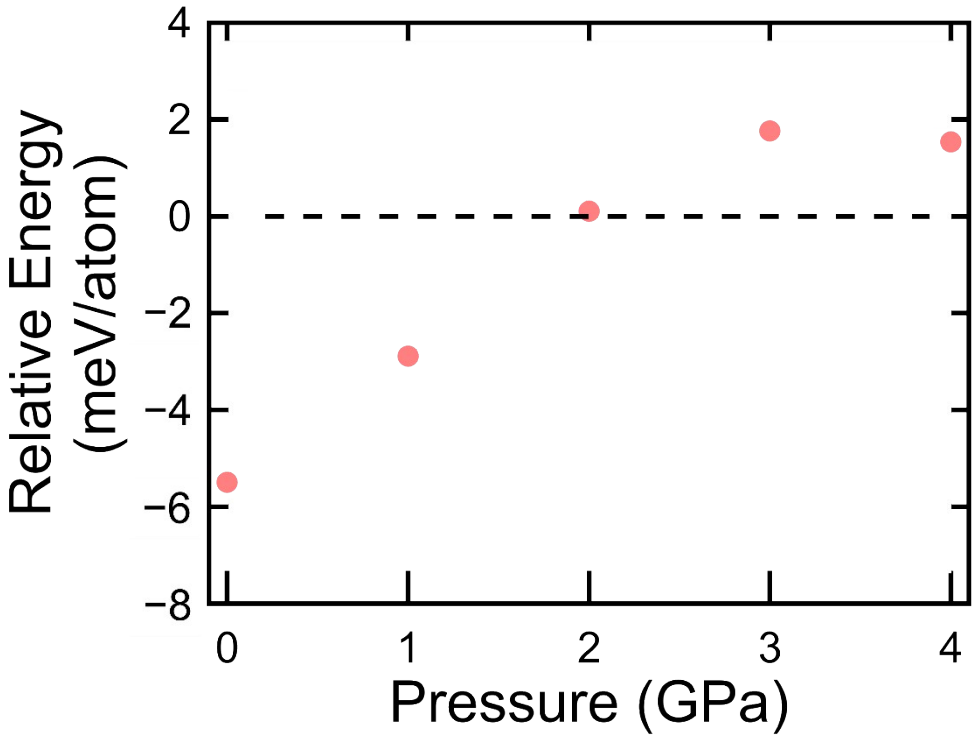

Figure S3: Relative energy of the SmSI-type structure compared to the SrI_2-type structure in CeSI as a function of pressure. The most stable polymorph switches from SmSI-type to SrI_2-type at 2 GPa.

Section 4. The detailed explanation about the calculation of the α value (compressibility of the anions)

The following is the detail of the fitting to obtain the α value. Fitting the DFT-calculated results with the equation was performed primarily using the polymorphic phase boundary between the FeOCl- and SmSI-type structures. The critical cation-to-anion ratio of the transformation between the FeOCl- and SmSI-type, $\left.\frac{r_{\text{cation}}}{r_{\text{anion}}}\right|_{\text{c}}$, can be expressed with the critical pressure, P_{c}, and the anion-to-cation ratio at ambient pressure, $\left.\frac{r_{\text{cation}}}{r_{\text{anion}}}\right|_{P\,=\,0\ \text{GPa}}$, as follows:

$$\left.\frac{r_{\text{cation}}}{r_{\text{anion}}}\right|_{\text{c}} = \left.\frac{r_{\text{cation}}}{r_{\text{anion}}}\right|_{P\,=\,0\ \text{GPa}} \times \frac{1}{1\ -\ \alpha P_{\text{c}}} = \left.\frac{r_{\text{cation}}}{2.02}\right|_{P\,=\,0\ \text{GPa}} \times \frac{1}{1\ -\ \alpha P_{\text{c}}}.$$

We additionally assume that $\left.\frac{r_{\text{cation}}}{r_{\text{anion}}}\right|_{\text{c}}$ under high pressure is identical to that at ambient pressure, which can be estimated as $\left.\frac{r_{Tb}}{2.02}\right|_{P\,=\,0\ \text{GPa}}$ = 0.45468. Then, the equation can be written as

$$0.45468 = \left.\frac{r_{\text{cation}}}{2.02}\right|_{P\,=\,0\ \text{GPa}} \times \frac{1}{1\ -\ \alpha P_{\text{c}}},$$

or

$$\left.\frac{r_{\text{cation}}}{2.02}\right|_{P\,=\,0\ \text{GPa}} = 0.45468\ (1\ -\ \alpha P_{\text{c}}).$$

The DFT-calculated results (Fig. 6 of the main manuscript) provide a set of P_{c} and $\left.\frac{r_{cation}}{2.02}\right|_{P\,=\,0\ \text{GPa}}$ as summarized in Table R1. The last equation with the α being a variable was fitted to the data set (Table S1) with the least-square method (Fig. S4), and the obtained α value was $\alpha = 7.3(3) \times 10^{-3}$ GPa^{-1}. As plotted in Fig. 6 of the main manuscript,

this α value optimized for the FeOCl–SmSI boundary reproduces well the other boundary between SmSI and SrI_2 types.

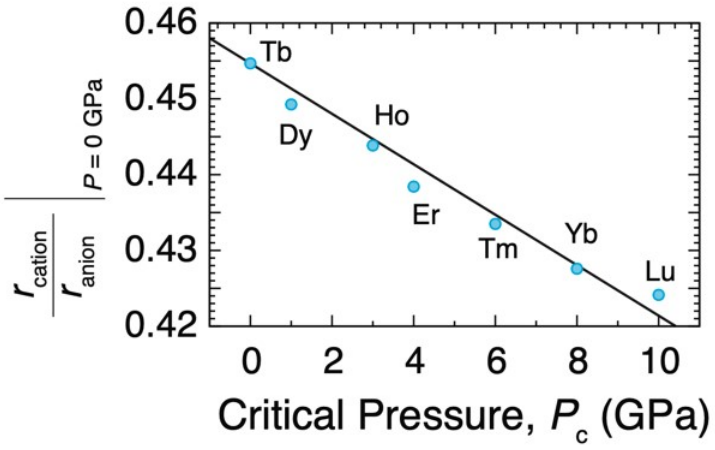

Figure S4: The cation-to-anion ratio (blue circles) calculated for Tb–Lu at ambient pressure as a function of critical pressure for transformation from FeOCl- to SmSI-type. The result of linear fitting is depicted by a black line.

Table S1: Dataset of the cation-to-anion ratio and critical pressure for Tb–Lu plotted in Fig. S4.

Ln	Critical Pressure, P_c (GPa)	r_{cation} / r_{anion} (P = 0 GPa)
Tb	0	0.45468
Dy	1	0.44926
Ho	3	0.44384
Er	4	0.43842
Tm	6	0.43350
Yb	8	0.42759
Lu	10	0.42414