

A Room-Temperature Polar Ferromagnet ScFeO_3 Transformed from a High-Pressure Orthorhombic Perovskite Phase

Takahiro Kawamoto,¹ Koji Fujita,^{1,*} Ikuya Yamada,^{2,3} Tomohiko Matoba,¹ Sung Joo Kim,⁴ Peng Gao,⁴ Xiaoqing Pan,⁴ Scott D. Findlay,⁵ Cédric Tassel,^{6,7} Hiroshi Kageyama,⁶ Andrew J. Studer,⁸ James Hester,⁸ Tetsuo Irifune,⁹ Hirofumi Akamatsu,¹⁰ and Katsuhisa Tanaka¹

¹*Department of Material Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510, Japan*

²*Nanoscience and Nanotechnology Research Center, Osaka Prefecture University, 1-2 Gakuen-cho, Sakai, Osaka 599-8531, Japan*

³*PRESTO, Japan Science and Technology Agency (JST), Chiyoda-ku, Tokyo 102-0075, Japan*

⁴*Department of Materials Science and Engineering, University of Michigan, Ann Arbor, MI 48109, USA*

⁵*School of Physics, Monash University, VIC 3800, Australia*

⁶*Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510, Japan*

⁷*The Hakubi Center for Advanced Research, Kyoto University, Yoshida-Ushinomiya-cho, Sakyo-ku, Kyoto 606-8302, Japan*

⁸*Bragg Institute, Australian Nuclear Science and Technology Organisation, PMB 1, Menai, NSW 2234, Australia*

⁹*Geodynamics Research Center, Ehime University, 2-5, Bunkyo-Cho, Matsuyama 790-8577, Japan*

¹⁰*Materials Research Institute and Department of Materials Science and Engineering, Pennsylvania State University, University Park, PA 16802, USA*

*To whom correspondence should be addressed. E-mail: fujita@dipole7.kuic.kyoto-u.ac.jp

1. SXRD pattern in the low-angle region

The low-angle region of the SXRD pattern as shown in Figure 1 is enlarged and displayed in Figure S1. There were several unknown peaks with intensities less than 4 % of the main peak of the rhombohedral phase.

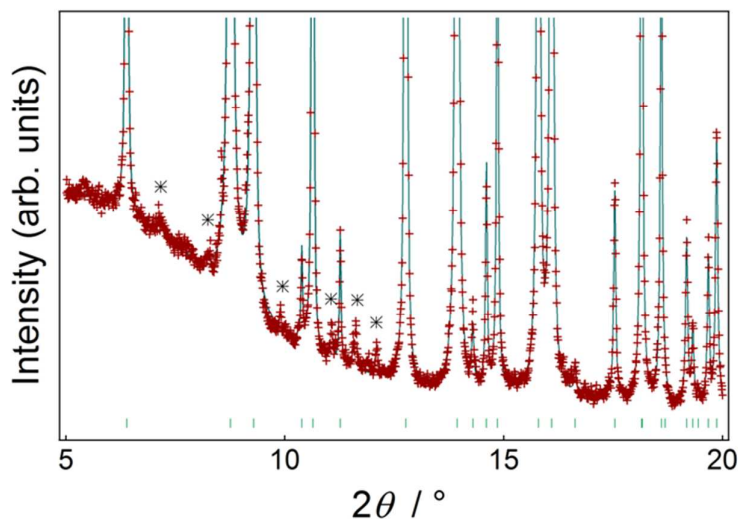


Figure S1. Enlarged view of the low 2θ region for the SXRD pattern shown in Figure 1. The ticks correspond to the positions of the calculated Bragg reflections for LiNbO_3 -type ScFeO_3 . The unknown peaks are marked by an asterisk.

2. Scanning electron microscope (SEM) observation and diffuse reflectance spectroscopy for the powdered LiNbO_3 -type ScFeO_3

An SEM image of powdered sample, taken with JEOL JSM-6705F, is displayed in Figure S2. The sample is observed to have a particle size distribution ranging from 14 to 30 μm ; the average particle size was estimated to be about 19 μm .

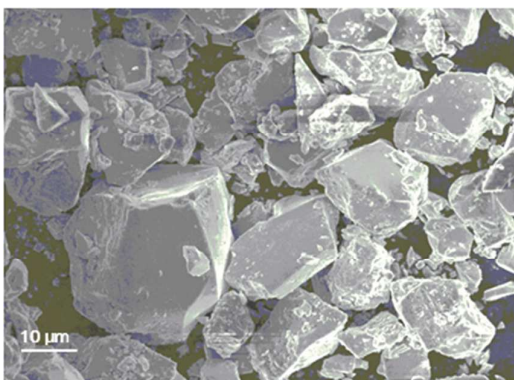


Figure S2. SEM image of powdered LiNbO_3 -type ScFeO_3 .

We also measured the diffuse reflectance spectrum at RT with JASCO V-570. The spectrum was transformed to optical absorption spectrum utilizing Kubelka–Munk (K-M) function,

$$F(R_{\infty}) = \frac{\alpha}{S} = \frac{(1 - R_{\infty})^2}{2R_{\infty}}, \quad (1)$$

where α is the absorption coefficient, R_{∞} is the reflectance, and S is the scattering coefficient. As shown in Figure S3, several absorption bands, which are ascribed to the d-d transitions of Fe^{3+} ions, are observed in the wavelength range of 500 to 1200 nm.¹

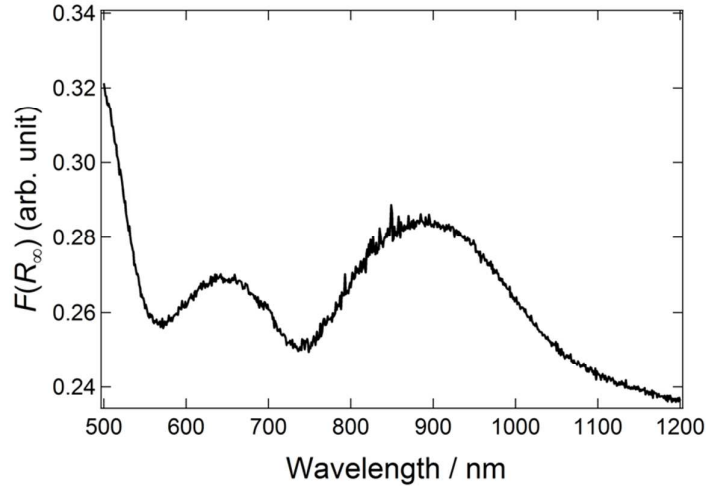


Figure S3. Optical absorption spectrum transformed from the diffuse reflectance spectrum using Eq. (1) for powdered LiNbO_3 -type ScFeO_3 .

3. Calculations of Born effective charge and polarization

The first-principles calculations were performed in order to obtain the Born effective charges for the parent perovskite structure with $R\bar{3}c$ symmetry, where Sc and Fe ions are present at the A and B sites, respectively, using the projector augmented-wave (PAW) method^{2,3} and the PBEsol functional⁴ as implemented in the VASP code.^{5,6} The PAW data sets with radial cutoffs of 1.4, 1.2 and 0.8 Å for Sc, Fe, and O, respectively, were used with a plane-wave cutoff energy of 700 eV. The following states were described as valence electrons: 3s, 3p, 3d, 4s for Sc; 3p, 3d, 4s for Fe; and 2s, 2p for O. k -point mesh sampling of $3 \times 3 \times 2$ was used for a unit cell containing 30 atoms. The lattice constants and internal coordinates were optimized under the constraint of the symmetry until the residual stress and force converged to less than 0.001 GPa and 0.001 eV/Å, respectively. We used an antiferromagnetic configuration where the Fe spins are aligned ferromagnetically within the layers and antiferromagnetically between the layers. The Born effective charge tensors calculated for Sc and Fe are listed in Table S1. It is found that $Z_{\text{Sc},33} = 3.35$ and $Z_{\text{Fe},33} = 3.37$ are close to the

formal charges of Sc^{3+} and Fe^{3+} , respectively.

The polarization of the experimental polar $R3c$ structure was calculated by using the following equation:

$$P = \frac{e}{V} \sum_i \mathbf{Z}_i \mathbf{u}_i, \quad (2)$$

where e is the elementary charge, V is the volume of unit cell, $\mathbf{Z}_i$ is the Born effective charge tensor of i th atom in the parent $R\bar{3}c$ phase, and $\mathbf{u}_i$ is the displacement vector of the i th atom in the transformation from the parent to the polar structure. The polarization was also calculated using formal charges according to Eq. (2) by replacing the diagonal elements of $\mathbf{Z}_i$ with the formal charges and letting the non-diagonal elements be zero.

Table S1. Born effective charge tensors $\mathbf{Z}_i$ (in atomic units) of Sc and Fe in the LiNbO_3 -type structure (space group $R3c$).

Sc	4.27	0.00	0.00
	0.00	4.27	0.00
	0.00	0.00	3.35
Fe	3.95	0.07	0.00
	-0.07	3.95	0.00
	0.00	0.00	3.37

References

- [1] Wood, D. L.; Remeika, J. P.; Kolb, E. D. *J. Appl. Phys.* **1970**, *41*, 5315.
- [2] Blöchl, P. E. *Phys. Rev. B* **1994**, *50*, 17953.
- [3] Kresse, G.; Joubert, D. *Phys. Rev. B* **1999**, *59*, 1758.
- [4] Perdew, J. P.; Ruzsinszky, A.; Csonka, G. I.; Vydrov, O. A.; Scuseria, G. E.; Constantin, L. A.; Zhou, X.; Burke, K. *Phys. Rev. Lett.* **2008**, *100*, 136406.
- [5] Kresse, G.; Hafner, J. *Phys. Rev. B* **1993**, *48*, 13115.
- [6] Kresse, G.; Furthmüller, J. *Phys. Rev. B* **1996**, *54*, 11169.