Supporting information:

Topotactic synthesis and crystal structure of a highly fluorinated Ruddlesden-Popper type iron oxide, $Sr_3Fe_2O_{5+x}F_{2-x}$ (x ~ 0.44)

Yoshihiro Tsujimoto,[1] Kazunari Yamaura,[2, 3] Naoaki Hayashi,[4] Katsuaki Kodama,[5]*

Naoki Igawa,[5] Yoshitaka Matsushita,[6] Yoshio Katsuya,[7] Yuichi Shirako,[8] Masaki

Akaogi[8] and Eiji Takayama-Muromachi[2, 3, 9]

[1]International Center for Young Scientists (ICYS) and International Center for Materials Nanoarchitechtonics (MANA), National Institute for Materials Science (NIMS), Namiki 1-1, Tsukuba, Ibaraki 305-0044, Japan, [2]Superconducting Materials Center, NIMS, Namiki 1-1, Tsukuba, Ibaraki 305-0044, Japan, [3]JST, Transformative Research-Project on Iron Pnictides (TRIP), Namiki 1-1, Tsukuba, Ibaraki 305-0044, Japan, [4]Graduate School of Human and Environmental Studies, Kyoto University, Kyoto 606-8501, Japan, [5]Quantum Beam Science Directorate, Japan Atomic Energy Agency, Tokai, Ibaraki 319-1195, Japan, [6]NIMS Beamline Station at SPring-8, NIMS, Kouto 1-1-1, Sayo-cho, Hyogo 679-5148, Japan, [7]SPring-8 Service Co., Ltd., Kouto 1-1-1, Sayo-cho, Hyogo 679-5148, Japan, 8Department of Chemistry, Faculty of Science, Gakushuin University, Mejiro, Toshima-ku, Tokyo 171-8588, Japan, [9]MANA, NIMS, Namiki 1-1, Tsukuba, Ibaraki 305-0044, Japan.

Email: TSUJIMOTO.Yoshihiro@nims.go.jp (Y. T.), n-hayashi@saci.kyoto-u.ac.jp (N. H.).

Supporting information:

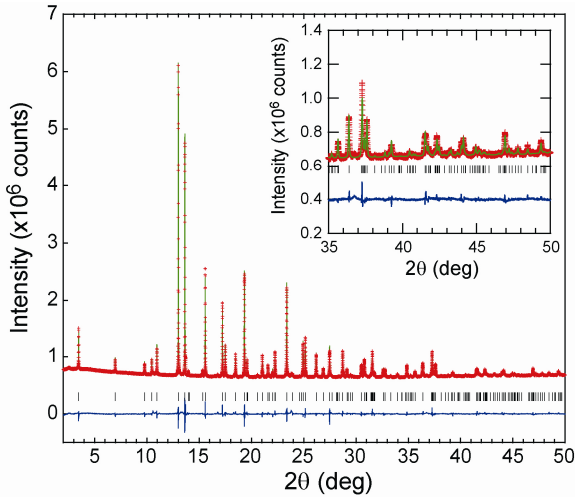

Figure S1. Observed (red crosses), calculated (green solid line), difference (blue solid line) plots from the Rietveld structural refinement against the synchrotron powder X-ray diffraction data collected from $Sr_3Fe_2O_{5+x}F_{2-x}$. The black tick marks represent the allowed Bragg peak positions. During the refinement, all the anions were assumed as oxygen (see Table S1).

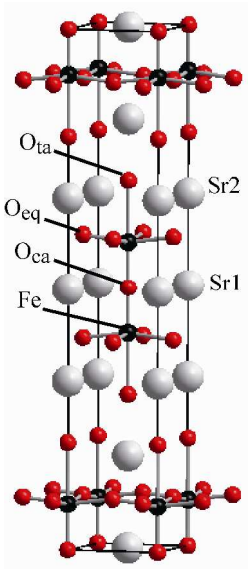

Figure S2. Schematic crystal structure of $Sr_3Fe_2O_{5+x}F_{2-y}$ on the basis of the results of the initial structure refinement using the synchrotron powder X-ray diffraction data. The fluorine site is not taken into consideration.

Table S1 Structural parameters of $Sr_3Fe_2O_{5+x}F_{2-x}$ at room temperature determined by the Rietveld refinement using the synchrotron powder X-ray diffraction data.

Atom	Site	*x*	*y*	*z*	U_{iso} (Å^2)	Occp.
Sr1	2b	0	0	0.5	0.0158(3)	1
Sr2	4e	0	0	0.32355(3)	0.0117(2)	1
Fe	4e	0	0	0.08794(5)	0.0102(2)	1
O_{ca}	2a	0	0	0	0.0263(19)	1
O_{eq}	8g	0	0.5	0.09973(12)	0.0256(9)	1
O_{ta}	4e	0	0	0.2058(2)	0.0184(10)	1

Space group, *I*4/*mmm*; a = 3.87140(1) Å, c = 21.36708(10) Å, V = 320.2438(23) Å^3;

R_{wp} = 1.59%, R_B =5.65%

Bond distances (Å) and angles (°) :

Fe-O_{ca} = 1.8790(11), Fe-O_{eq} = 1.9520(4), Fe-O_{ta} = 2.520(4),

Sr1-O_{ca} = 2.73749(1), Sr1-O_{eq} = 2.879(2),

Sr2-O_{eq} = 2.537(2), Sr2-O_{ta}(1) = 2.8087(9), Sr2-O_{ta}(2) = 2.514(4)

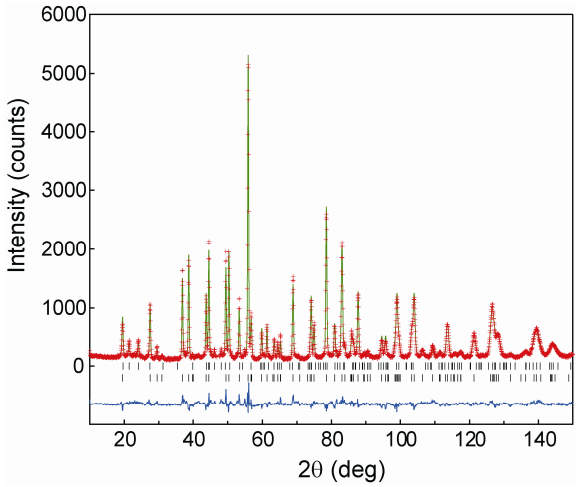

Figure S3. Observed (red crosses), calculated (green solid line), difference (blue solid line) plots from the Rietveld structural refinement against the neutron powder diffraction data collected from $Sr_3Fe_2O_{5.44}F_{1.56}$. The nuclear and magnetic Bragg reflections are indicated by the bottom and upper tick marks, respectively. A model where 78% of the terminal apical anion sites is occupied by F but the rest by O, was used during the refinement (see Table S3).

Table S2. Finally refined structural parameters of $Sr_3Fe_2O_{5.44}F_{1.56}$ at room temperature on the basis of the neutron powder diffraction data.

Atom	Site	*x*	*y*	*z*	U_{iso} (Å^2)	Occp.
Sr1	2b	0	0	0.5	0.0146(11)	1
Sr2	4e	0	0	0.32330(13)	0.0045(6)	1
Fe	4e	0	0	0.08782(11)	0.0026(4)	1
O_{ca}	2a	0	0	0	0.0188(12)	1
O_{eq}	8g	0	0.5	0.09902(12)	0.0098(4)	1
O_{ta}/F	16m	0.054(2)	0.054	0.2065(3)	0.036(3)	0.25

Space group, *I*4/*mmm*; a = 3.87267(6) Å, c = 21.3465(5) Å, V = 320.146(11) Å^3;
R_{wp} = 9.10%, R_B = 3.74%, S = 1.58

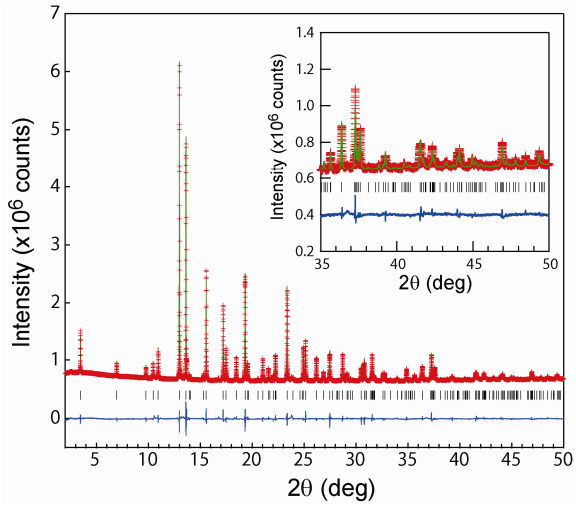

Figure S4. Observed (red crosses), calculated (green solid line), difference (blue solid line) plots from the Rietveld structural refinement against the neutron powder diffraction data collected from $Sr_3Fe_2O_{5.44}F_{1.56}$. The black tick marks represent the allowed Bragg peak positions. A model where 78% of the terminal apical anion sites is occupied by F but the rest by O, was used during the refinement (see Table S4).

Table S3. Finally refined structural parameters of $Sr_3Fe_2O_{5.44}F_{1.56}$ at room temperature on the basis of the synchrotron powder X-ray diffraction data.

Atom	Site	*x*	*y*	*z*	U_{iso} (Å^2)	Occp.
Sr1	2b	0	0	0.5	0.0168(3)	1
Sr2	4e	0	0	0.32348(3)	0.0118(2)	1
Fe	4e	0	0	0.08783(5)	0.0102(2)	1
O_{ca}	2a	0	0	0	0.027(2)	1
O_{eq}	8g	0	0.5	0.09884(11)	0.0238(8)	1
O_{ta}/F	16m	0.043(2)	0.043	0.20567(17)	0.025(2)	0.25

Space group, *I*4/*mmm*; a = 3.87140(1) Å, c = 21.36730(8) Å, V = 320.2474(17) Å^3;
R_{wp} = 1.53%, R_B = 5.43%