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Supporting Information

Strong negative thermal expansion in hexagonal polymorph of ScF_3

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Abstract: A new hexagonal polymorph of scandium fluoride ScF_3 have been synthesized and thoroughly characterized. The new phase displays two types of negative thermal expansion in a wide temperature range at normal pressure: A relatively weak isotropic at low temperatures and a strong anisotropic above 500 K. The thermal behavior is explained in part by a model of static structure distortions.

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Experimental Procedures

Chemicals and materials

The Sc_2O_3 (extra pure) and concentrated solution of 40 % HF (extra pure) provided by Vekton (Russia) were taken as initial reagents. All aqueous solutions were prepared using Milli-Q high purity water with the resistivity higher than 18 MΩ/cm. The $ScCl_3$ solution was obtained by dissolving stoichiometric oxide in dilute HCl solution. Concentrations of the scandium salt solutions varied in the range of 0.02-0.05 M and their pH values were about 2.0.

The synthesized materials were transferred from the surface of solution to single crystal silicon wafers for further analysis and characterization. Prior to use the wafers were treated in "piranha" solution, i.e. a mixture of 30 % H_2O_2 and concentrated H_2SO_4 (3:7 by volume) for 10 min and then rinsed thoroughly in water.

Synthetic procedures

The ScF_3 crystals were synthesized by GSIT at room temperature in a teflon hermetically sealed reactor similar to that described in [7]: The surface of the scandium salt solution was brought into contact with a HF-containing atmosphere (free evaporation from the surface of HF solution at ambient pressure within the reactor). The processing time varied from 40 to 120 min.

After the washing procedure has been repeated twice, the film was transferred to the silicon substrate surface, dried at room temperature for several hours and analyzed with XRD, SEM, TEM+EDX, TG-MS, and FT-IR spectroscopies. For TEM investigations the as-synthesized structures were transferred on Au grid coated with amorphous carbon supporting film (Plano, Germany).

Characterization

X-Ray powder diffraction data for structure determination was collected with a Bruker D8 Discover diffractometer operating in a parallel-beam linear focus mode in Debye-Scherrer geometry. The primary beam was conditioned with a double-bounce channel-cut Ge220 monochromator to provide CuK_{a1} radiation with the wave length of λ = 1.54056 Å. A thin-walled glass capillary with 0.3 mm internal diameter (Hilgenberg, Germany) was filled with the powderized sample and spinned during data collection within the 2Θ range of 10 – 110 deg. The powder pattern was indexed, structure solved by direct space global optimization procedure and further refined down to R_{wp} = 0.094 with Bruker Topas 5.0 software.

Non-ambient XRD data was collected with a Rigaku Ultima IV diffractometer operating in Bragg-Brentano geometry using filtered CuK_a radiation and equipped with Rigaku R-300 low-temperature and Rigaku SHT-1500 high-temperature attachments (under 10^{-3} atm. vacuum and in nitrogen 99.999 % under pressure of 1.2 atm., respectively) with the temperature stabilization within 0.1 degree. XRD scans were taken with the step of 20° over the temperature range of 93 – 773 K. Each pattern was analyzed by full profile Rietveld refinement with Bruker Topas 5.0 software. No sample displacement parameters have been refined since the sample has not been changed. The only small discrepancy could occur between the data sets obtained in the cooling and in the heating cameras. A small geometric correction was introduced to our low-temperature data.

The samples were analyzed with a scanning electron microscope Zeiss Merlin at the acceleration voltage of 2 kV and a transmission electron microscope Zeiss Libra 200 FE at 200 kV. Elemental composition was determined by energy dispersive X-Ray spectroscopy in TEM with an INCAx-act Energy EDX analyzer (Oxford Instruments). Infrared spectra were recorded with a Bruker Vertex 70 infrared spectrometer. DTA-TG curves were obtained with Netzsch STA 449 F3 calorimeter.

Results and Discussion

A transparent colorless film was formed on the surface of solution during its treatment with gaseous HF. To remove the excess solution the film was transferred to the surface of pure distilled water for 10 min. Depending on the concentration of initial solution we could obtain individual urchin-like clusters or chains at 0.02 M, islands or incomplete films at 0.05 M, or complete films at 0.1 M. Smaller crystals of the cubic phase either occured in the central parts of the urchins (Figure S1 **a**) or they formed continuous films facing the atmosphere, while the elongated prismatic crystals grew on both sides (Figure S1 **b**). In latter case most of the prisms were oriented with their long axes in the normal direction to the film.

A typical TEM-EDX spectrum and a STEM image of the analyzed crystal are shown in Figure S2.

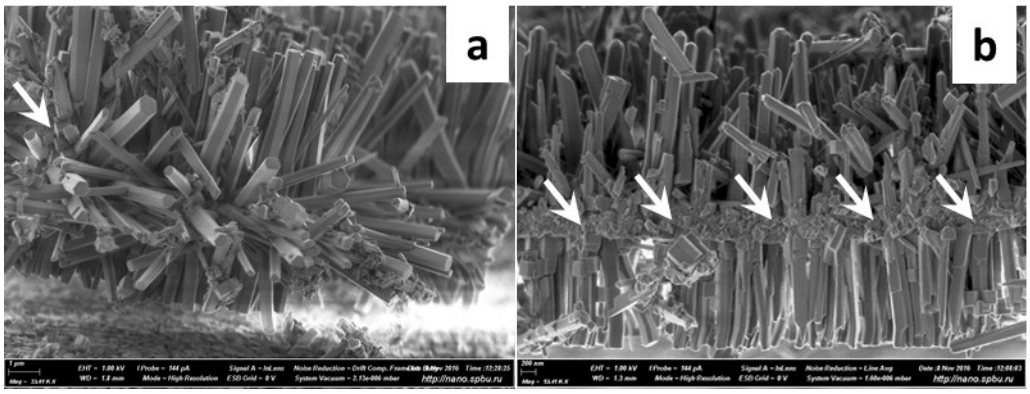

Figure S1. SEM images of urchin-like clusters (**a**) and a cross-sectional view of a film (**b**). Some crystals of *c*-ScF_3 are arrowed..

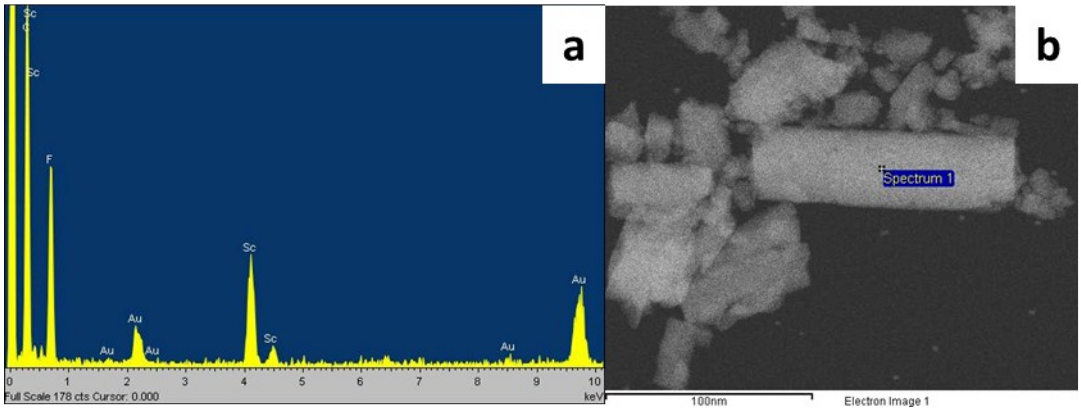

Figure S2. a- TEM-EDX spectrum of the crystal shown in STEM image of **b**.

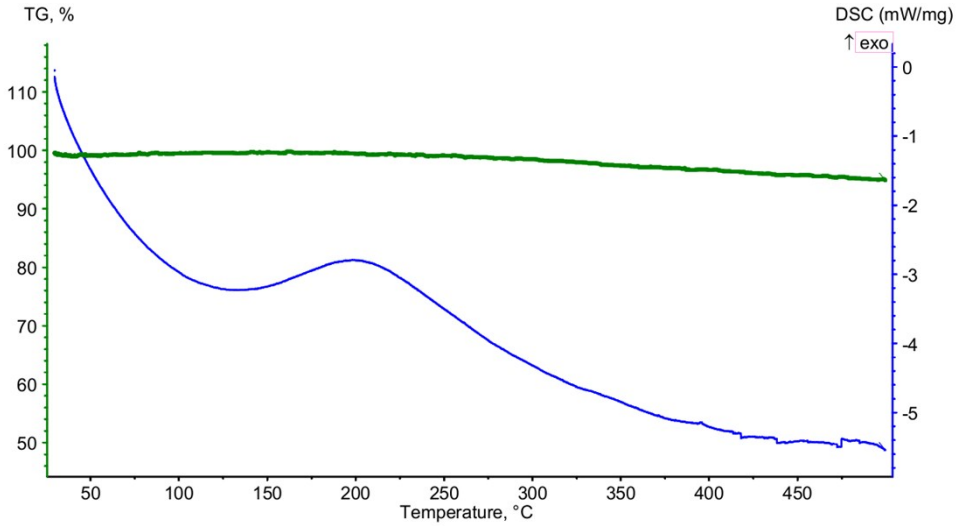

Figure S3. TG and DSC curves of a powder sample of ScF_3.

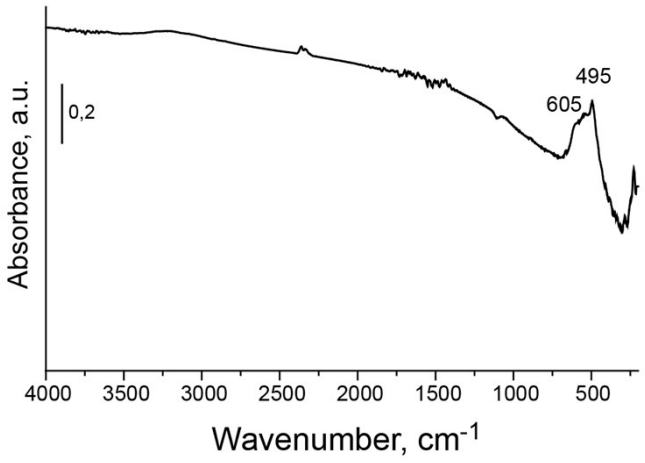

Figure S4. FT-IR spectrum of a fresh sample of ScF_3. The absorption bands in the 600-480 cm^{-1} region are related to the Sc-F vibration, particularly the band at 605 cm^{-1} corresponds to $\upsilon_1(a'_1)$ fundamental frequency in ScF_3, and the two components at 495 cm^{-1} (*s*) and 550 cm^{-1} (*v*) are associated with the rotation of the octahedral [ScF_6] groups.

Table S1. Experimentally measured and calculated structural amplitudes F^2_{hkl} (model of undistorted structure with Sp. Gr. *P6/mmm*)

H	K	L	F^2_{calc}	F^2_{meas}	σ
0	1	0	25.25	24.79	0.44
0	0	1	39.26	39.34	1.40
1	1	0	18.96	18.96	0.37
0	1	1	9.26	9.89	0.44
0	2	0	59.31	63.36	0.95
1	1	1	6.86	6.25	0.39
0	2	1	3.90	3.45	0.25
2	1	0	0.19	0.22	0.00
0	3	0	29.26	28.93	0.42
2	1	1	12.44	12.90	0.83
0	0	2	54.11	54.48	1.78
0	3	1	22.21	21.86	1.54
2	2	0	82.05	89.89	1.32
0	1	2	20.86	20.74	0.96
3	1	0	31.14	30.30	0.41
1	1	2	16.91	16.21	1.30
2	2	1	36.44	35.69	2.03
0	2	2	63.77	66.63	3.40
3	1	1	21.17	22.56	1.43
0	4	0	66.20	66.51	1.01
2	1	2	0.26	0.28	0.01
0	4	1	32.75	33.11	2.15
3	2	0	23.82	22.33	0.51
0	3	2	27.40	26.09	2.25
4	1	0	8.36	7.61	0.09
3	2	1	18.27	16.89	1.32
2	2	2	88.75	89.04	5.98
4	1	1	3.54	3.71	0.16
3	1	2	32.28	32.33	2.89
0	5	0	0.33	0.35	0.01
0	0	3	10.51	9.99	0.39
0	1	3	3.44	3.31	0.10
3	3	0	0.31	0.34	0.01

0	4	2	75.66	74.55	5.60
0	5	1	3.53	3.14	0.17
4	2	0	49.33	43.84	0.54
1	1	3	2.84	2.53	0.10
0	2	3	6.52	6.38	0.35
3	3	1	3.24	3.50	0.13
3	2	2	26.73	25.03	2.36
4	2	1	21.91	21.33	1.87
5	1	0	11.49	10.54	0.30
4	1	2	10.49	10.45	0.90
2	1	3	0.88	0.90	0.01
5	1	1	9.28	9.35	0.86
0	3	3	7.13	6.99	0.50
0	6	0	14.54	12.35	0.13
0	5	2	0.17	0.17	0.01
4	3	0	2.87	2.85	0.09
2	2	3	18.15	16.86	1.61
3	3	2	0.17	0.16	0.00
3	1	3	8.26	8.27	0.49
0	6	1	6.14	5.68	0.51
5	2	0	7.79	6.51	0.25
4	2	2	66.87	64.48	5.53
4	3	1	1.14	1.31	0.06
0	4	3	16.98	17.31	1.36
5	2	1	6.50	6.45	0.62
5	1	2	14.77	14.69	1.19
6	1	0	2.15	1.84	0.03
3	2	3	7.76	7.67	0.56
0	0	4	10.54	10.64	0.34
6	1	1	0.87	0.89	0.04
0	1	4	4.70	5.02	0.12
4	1	3	2.30	2.53	0.04
0	6	2	21.41	21.47	2.16
4	4	0	11.55	12.95	0.15
4	3	2	4.29	4.86	0.17
1	1	4	4.15	4.30	0.25
5	3	0	7.57	8.91	0.11
0	7	0	3.16	3.72	0.04
0	2	4	20.51	24.39	1.24
5	2	2	10.68	10.76	0.90
0	5	3	0.60	0.64	0.01
4	4	1	6.65	8.52	0.10
5	3	1	7.56	8.99	0.07
0	7	1	2.97	3.53	0.03
6	2	0	44.97	48.77	0.39
2	1	4	0.72	0.76	0.01
3	3	3	0.58	0.60	0.01
4	2	3	15.88	17.27	1.25
6	1	2	3.36	3.32	0.13
0	3	4	6.69	6.67	0.29
6	2	1	40.67	48.80	0.42

Table S2. Atomic coordinates in the unit cell of undistorted structure (Sp. Gr. *P6/mmm*) at room temperature. ICSD deposition code # 434103.

Site	Np	x	y	z	Atom	Occ	Beq

Sc	3	0.50000	0.00000	0.00000	Sc	1	0.88(3)
F1	6	0.21274(13)	0.4255(3)	0.00000	F-1	1	1.78(5)
F2	3	0.50000	0.00000	0.50000	F-1	1	1.67(5)

Table S3. Atomic coordinates in the unit cell of distorted structure (Sp. Gr. *P6₃/mmc*) at room temperature. ICSD deposition code # 434104.

Site	Np	x	y	z	Atom	Occ	Beq
Sc1	6	0.50000	0.00000	0.00000	Sc+3	1	0.63(2)
F2	6	0.5012(10)	0.4988(10)	0.25000	F-1	1	1.16(5)
F3	12	0.4259(3)	0.21297(13)	-0.0012(10)	F-1	1	1.69(5)

Table S4. Experimental powder diffraction pattern of *h*-ScF_3 at room temperature (indexing for Sp. Gr. *P6₃/mmc*).

h	k	l	m	d	2Theta	I
0	1	0	6	6.76911	13.06839	3.49e+004
0	0	2	2	4.01144	22.14199	9.72e+003
1	1	0	6	3.90814	22.73493	5.58e+003
0	1	2	12	3.45098	25.79543	1.57e+003
0	2	0	6	3.38455	26.31072	2.06e+004
1	1	2	12	2.79928	31.94512	596
0	2	2	12	2.58682	34.64842	285
2	1	0	12	2.55848	35.04451	53
0	1	3	12	2.48722	36.08255	1.48
0	3	0	6	2.25637	39.92297	3.9e+003
0	3	1	12	2.17210	41.54189	0.252
2	1	2	24	2.15709	41.84444	821
0	2	3	12	2.09832	43.07402	6.02
0	0	4	2	2.00572	45.16961	2.98e+003
0	3	2	12	1.96661	46.11918	1.26e+003
2	2	0	6	1.95407	46.43235	6.04e+003
0	1	4	12	1.92308	47.22575	988
3	1	0	12	1.87741	48.44708	2.29e+003
2	1	3	24	1.84871	49.24888	6.38
1	1	4	12	1.78444	51.14783	636
2	2	2	12	1.75673	52.01442	1.52e+003
0	2	4	12	1.72549	53.02876	2.38e+003
3	1	2	24	1.70040	53.87392	1.01e+003
0	4	0	6	1.69228	54.15361	4.89e+003
2	1	4	24	1.57849	58.41811	16.8
0	1	5	12	1.56131	59.12413	31.1
0	4	2	12	1.55921	59.21175	1.36e+003
3	2	0	12	1.55294	59.47483	950
0	3	4	12	1.49907	61.84110	693
4	1	0	12	1.47714	62.86308	362
0	2	5	12	1.44989	64.18400	17.3
3	2	2	24	1.44821	64.26755	502
0	4	3	12	1.43002	65.18546	9.36
2	2	4	12	1.39964	66.78259	2.07e+003
4	1	2	24	1.38615	67.51936	129
3	1	4	24	1.37065	68.38783	738
2	1	5	24	1.35936	69.03577	9.54
0	5	0	6	1.35382	69.35835	23.8
3	2	3	24	1.34294	70.00214	5.19
0	0	6	2	1.33715	70.34999	248
0	1	6	12	1.31180	71.91819	69.8

0	3	5	12	1.30765	72.18245	0.426
3	3	0	6	1.30271	72.49892	21.5
0	4	4	12	1.29341	73.10464	1.53e+003
4	1	3	24	1.29301	73.13085	74.6
0	5	2	12	1.28274	73.81291	81.7
4	2	0	12	1.27924	74.04843	1.37e+003
1	1	6	12	1.26515	75.01440	37.3
4	2	1	24	1.26328	75.14417	2.22
0	2	6	12	1.24361	76.54526	116
3	3	2	12	1.23902	76.88087	92.6
3	2	4	24	1.22791	77.70605	457
3	1	5	24	1.21977	78.32322	12.6
4	2	2	24	1.21877	78.40003	511
5	1	0	12	1.21577	78.63097	360
5	1	1	24	1.20204	79.70650	0.912
4	1	4	24	1.18940	80.72756	195
2	1	6	24	1.18506	81.08437	15.9
5	1	2	24	1.16350	82.91279	244
0	3	6	12	1.15033	84.07758	113
0	6	0	6	1.12818	86.12202	386
0	5	4	12	1.12212	86.70181	2.83
0	6	1	12	1.11719	87.18021	9.75
4	3	0	12	1.11283	87.60820	74.3
2	2	6	12	1.10352	88.53970	233
4	3	1	24	1.10228	88.66513	5.21
3	1	6	24	1.08914	90.02377	123
4	1	5	24	1.08676	90.27516	1.58
0	6	2	12	1.08605	90.35040	123
0	2	7	12	1.08557	90.40117	9.45
5	2	0	12	1.08392	90.57672	135
4	2	4	24	1.07855	91.15543	1.03e+003
5	2	1	24	1.07417	91.63329	1.4
4	3	2	24	1.07234	91.83462	46.7
0	4	6	12	1.04916	94.48006	243
5	2	2	24	1.04640	94.80777	123
2	1	7	24	1.04597	94.85872	7.37
5	1	4	24	1.03968	95.61607	188
0	6	3	12	1.03947	95.64127	48.8
0	5	5	12	1.03473	96.22303	1.45
6	1	0	12	1.03228	96.52646	29.9
6	1	1	24	1.02384	97.59090	8.02
3	2	6	24	1.01328	98.96375	91.6
0	0	8	2	1.00286	100.36730	153
6	1	2	24	0.99971	100.80164	17.9
0	1	8	12	0.99203	101.87967	74.8
4	1	6	24	0.99131	101.98219	48.3
0	6	4	12	0.98330	103.14156	331
4	4	0	6	0.97704	104.07298	255
4	3	4	24	0.97309	104.67032	109
1	1	8	12	0.97139	104.93097	49.2
5	1	5	24	0.96903	105.29528	14.1
0	7	0	6	0.96702	105.60815	151
5	3	0	12	0.96702	105.60815	151
6	1	3	24	0.96303	106.23595	2.27
0	2	8	12	0.96154	106.47245	361
0	7	1	12	0.96007	106.70796	0.838
5	3	1	24	0.96007	106.70796	0.838
5	2	4	24	0.95358	107.76147	148
0	5	6	12	0.95135	108.13181	14.7
4	4	2	12	0.94928	108.47585	135
0	4	7	12	0.94897	108.52939	61.9
0	7	2	12	0.94009	110.04781	134

5	3	2	24	0.94009	110.04781	134
6	2	0	12	0.93871	110.28891	1.03e+003
2	1	8	24	0.93369	111.17709	14.3
3	3	6	12	0.93309	111.28470	9
4	2	6	24	0.92435	112.88617	220
0	6	5	12	0.92290	113.15932	16.3
6	1	4	24	0.91785	114.12016	5.25
0	3	8	12	0.91642	114.39657	62.8

References

No additional references