Supporting Information

A combined approach for the structural characterization of alkali fluoroscandates: solid state NMR, powder diffraction and DFT calculations

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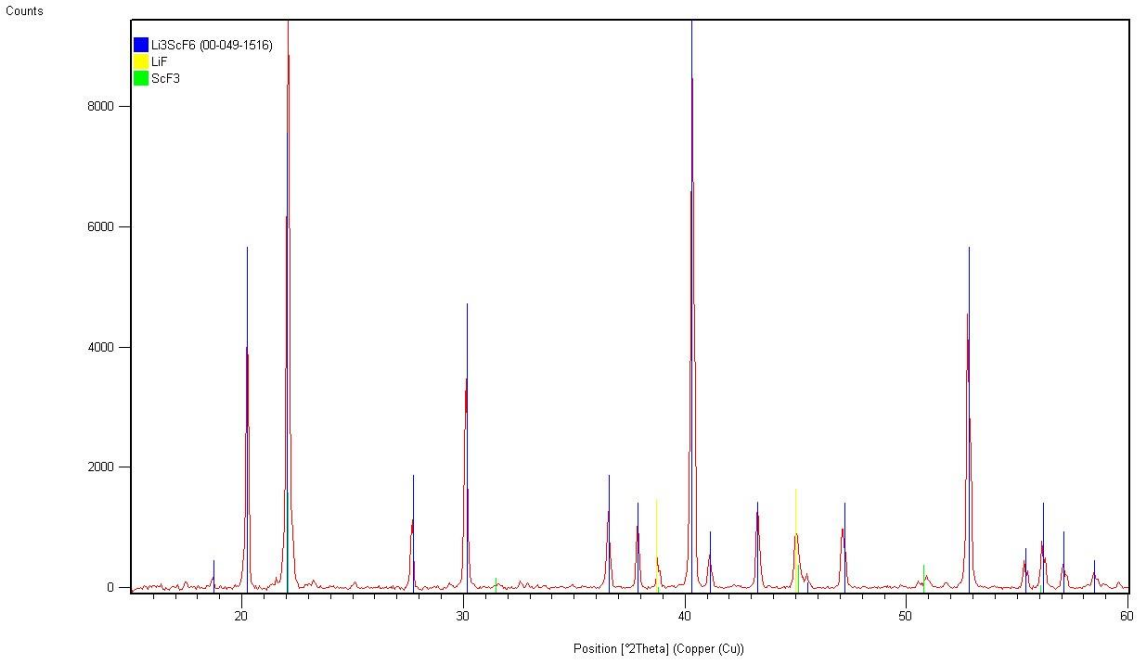
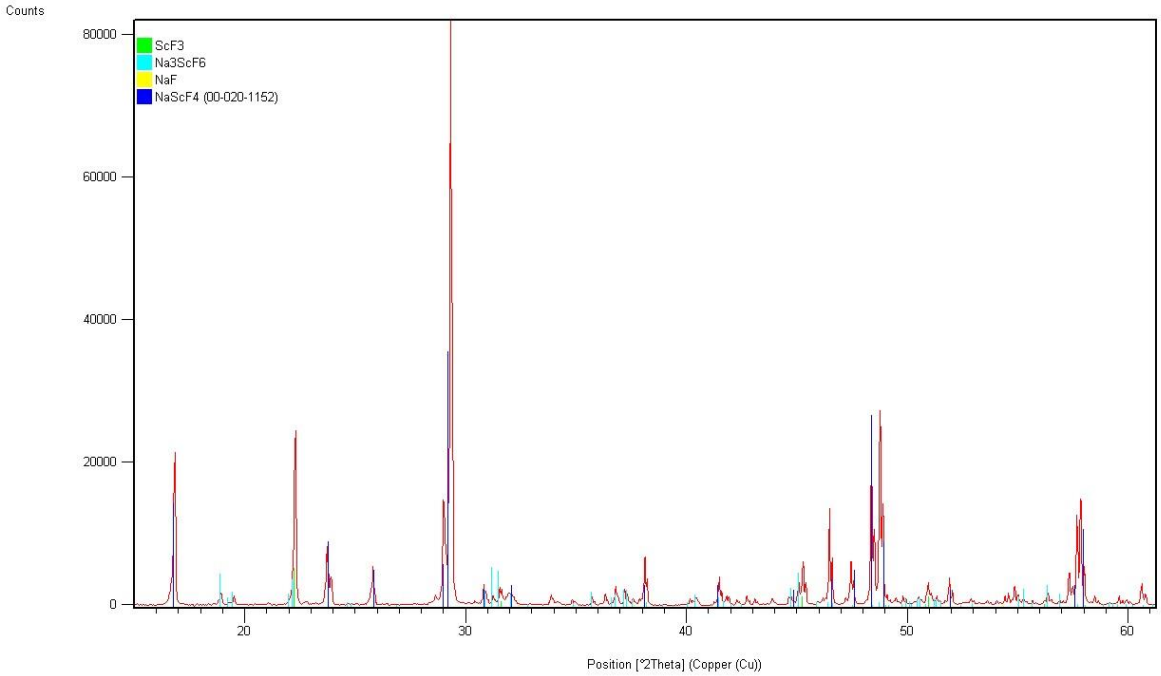
MQMAS experimental details.

Triple-quantum ^{23}Na and ^{45}Sc MQMAS 2D spectra were acquired using a three-pulse sequence with a zero-quantum filter (Amoureux, J.-P.; Fernandez, C.; Steuernagel, S. Z Filtering in MQMAS NMR. *J. Magn. Reson.* **1996**, *123*, 116-118), a repetition delay of between 0.3 and 0.5 s, and rotor–synchronized sampling of the indirect dimension 30-34 kHz with 32 t_1 and 74-140 t_1 increments for ^{23}Na and ^{45}Sc, respectively. Phase cycling involved the states method (States, D. J.; Haberkorn, R. A.; Ruben, D. J. A two-dimensional nuclear overhauser experiment with pure absorption phase in four quadrants. *J. Magn. Reson.* **1982**, *48*, 286-292) for acquisition of pure absorption line shapes. The optimized excitation and conversion pulses width were 1.7 μs (ν_{rf} = 147 kHz) and 0.8 μs (ν_{rf} = 313 kHz) for ^{23}Na, and 2 μs (ν_{rf} = 125 kHz) and 0.75 μs (ν_{rf} = 333 kHz) for ^{45}Sc, respectively.

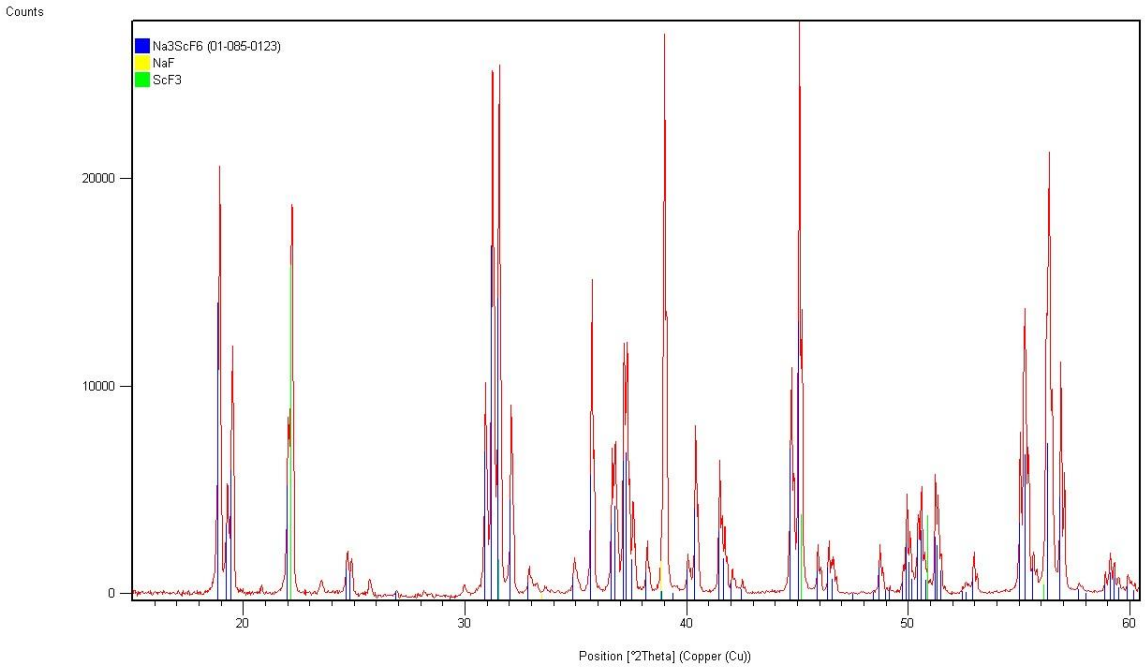
Li_3ScF_6



$NaScF_4$



Na_3ScF_6



KSc_2F_7

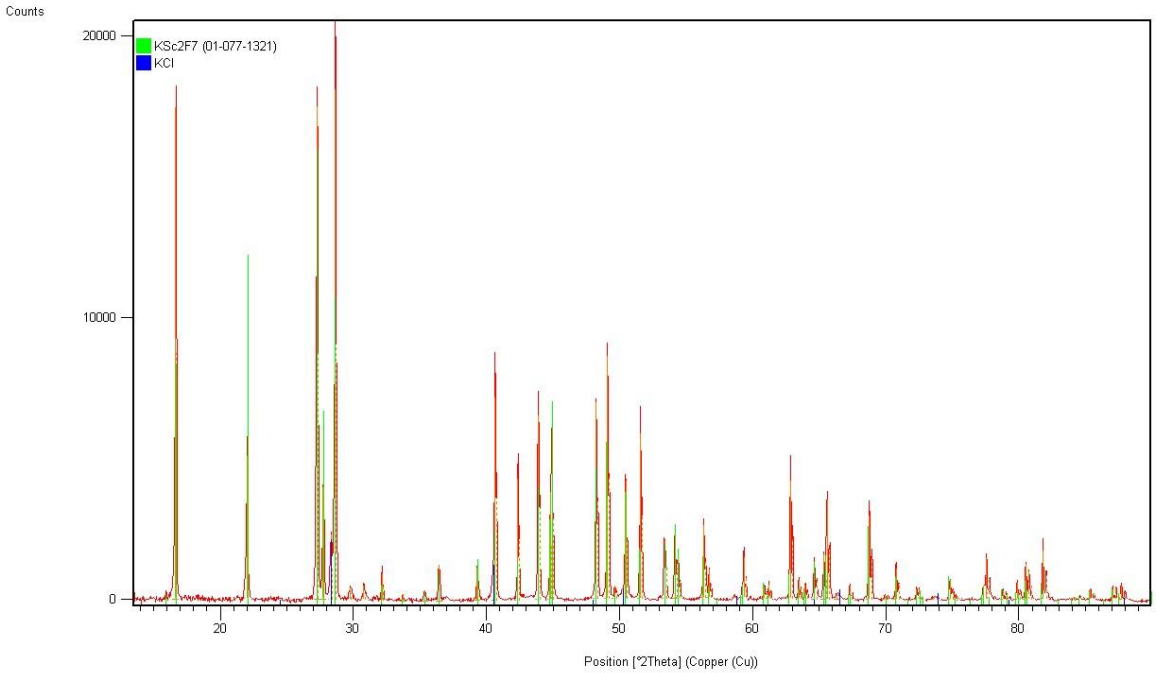


Figure S1. The X-ray patterns of Li_3ScF_6, $NaScF_4$, Na_3ScF_6, and KSc_2F_7.

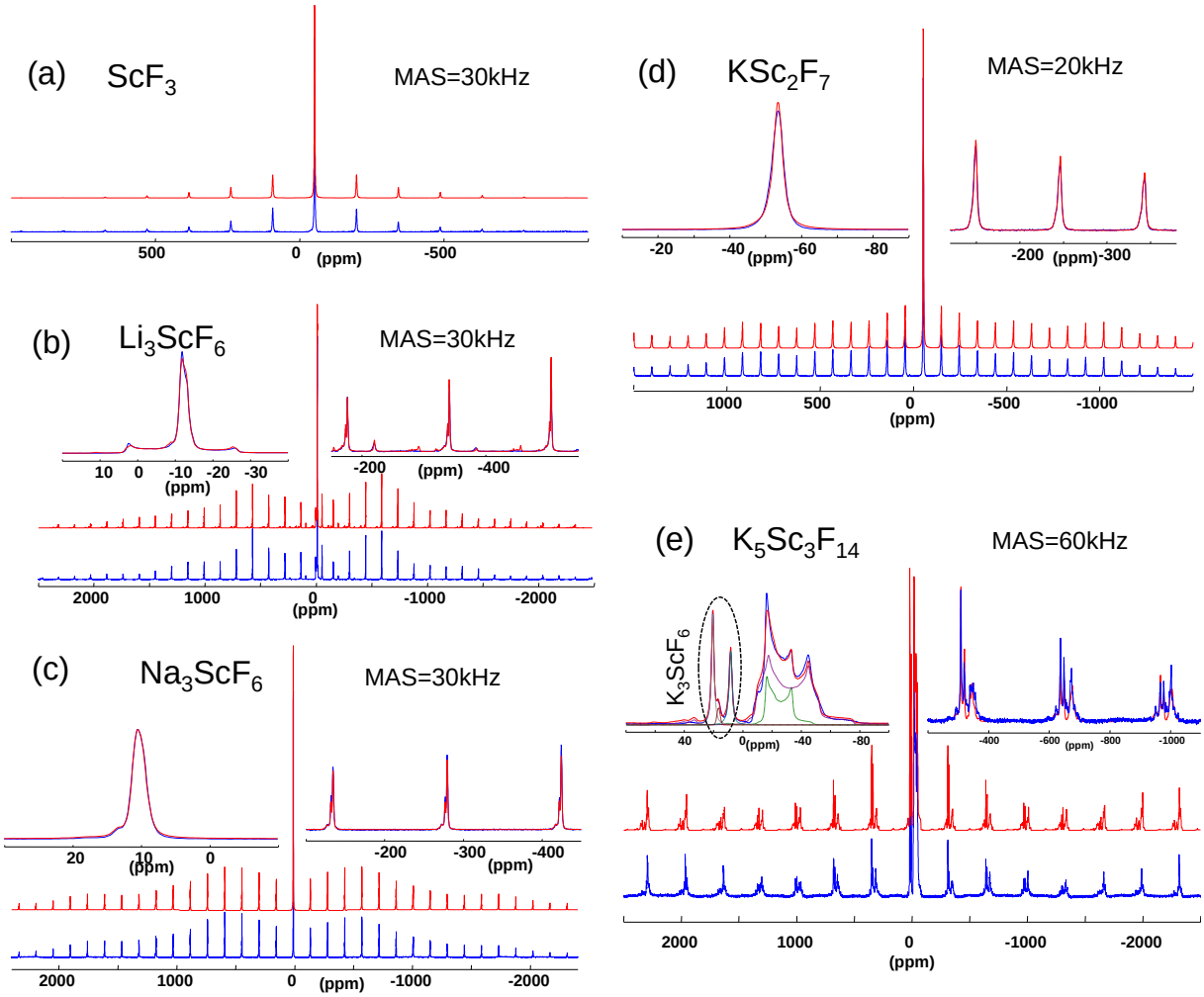


Figure S2. Experimental (blue) and simulated (red) ^{45}Sc MAS NMR spectra at room temperature and at 20 T of ScF_3 (a), Li_3ScF_6 (b), Na_3ScF_6 (c), KSc_2F_7 (d) and at 17.6 T of $K_5Sc_3F_{14}$ (e).

For Li_3ScF_6 (b), Na_3ScF_6 (c), KSc_2F_7 (d) and K_3ScF_6 (e), in the left: expansions of the ^{45}Sc MAS spectra in the region of the CT; in the right: expanded ST sideband revealing their complex line shape.

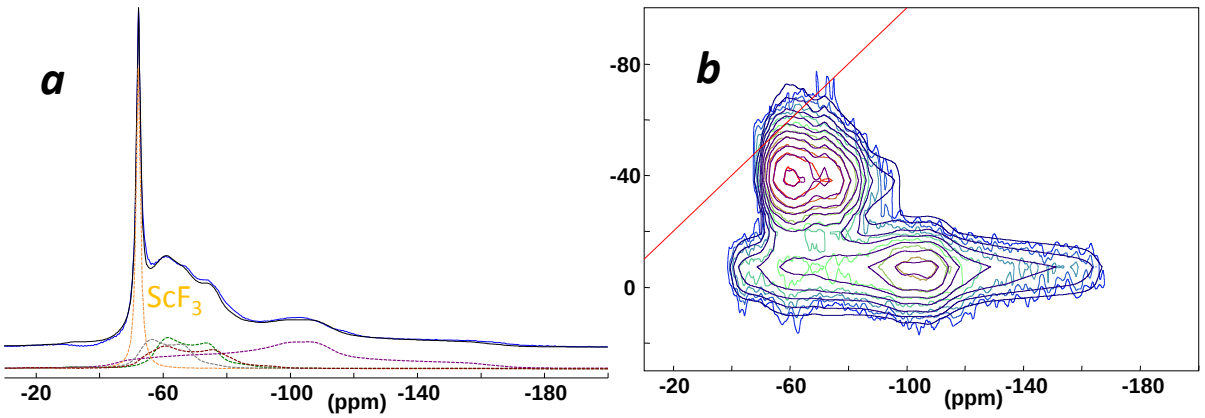


Figure S3. ^{45}Sc MAS (a) and MQMAS (b) NMR experimental (color lines) spectra at 9.4 T and at spinning rate 30 kHz and its simulation (black line) with the parameters reported in the Table 7 of $NaScF_4$.

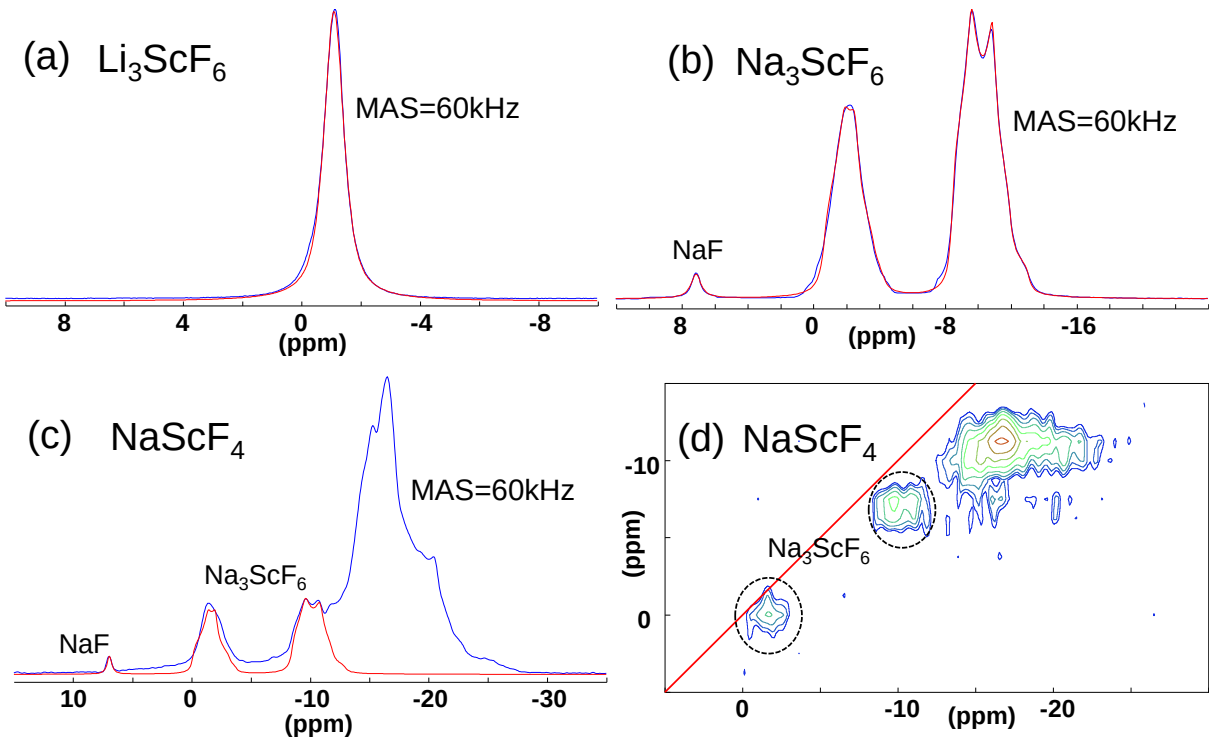


Figure S4. Experimental (blue) and simulated (red) (a) ^{7}Li MAS NMR spectra of Li_3ScF_6, (b) and (c) ^{23}Na MAS NMR spectra of Na_3ScF_6, and $NaScF_4$ at 17.6 T and at spinning rate 60 kHz. (d) ^{23}Na MQMAS NMR spectrum of $NaScF_4$.

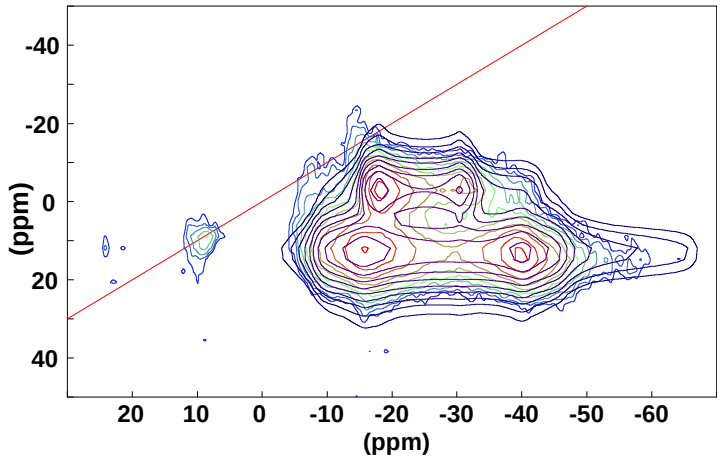


Figure S5. ^{45}Sc MQMAS NMR experimental (color lines) spectrum at 20 T and at spinning rate 30 kHz and its simulation (black line) with the parameters reported in the Table 2 of $K_5Sc_3F_{14}$.

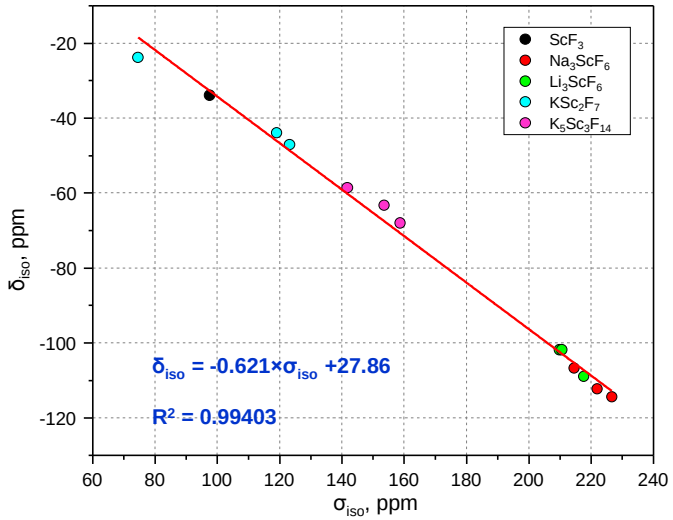


Figure S6. Correlation between calculated isotropic ^{19}F magnetic shielding constants (σ_{iso}) and experimentally determined isotropic (δ_{iso}) chemical shift values listed in Table 1. The red line represents the linear regression calculated on all these values: $\delta_{iso} = -0.621 \times \sigma_{iso} + 27.86$), with $R^2 = 0.99403$.

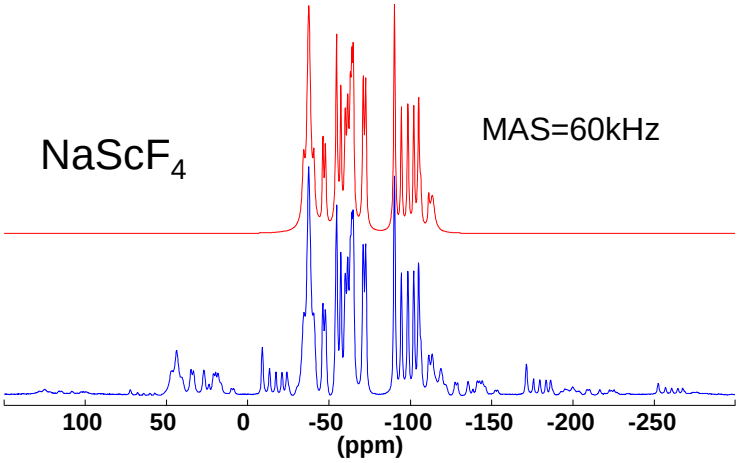
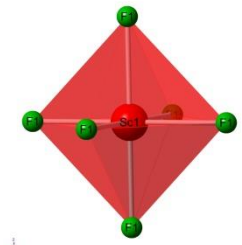
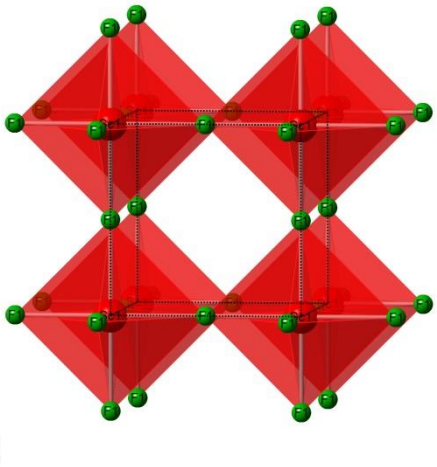
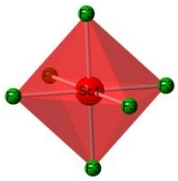
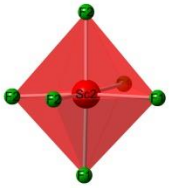
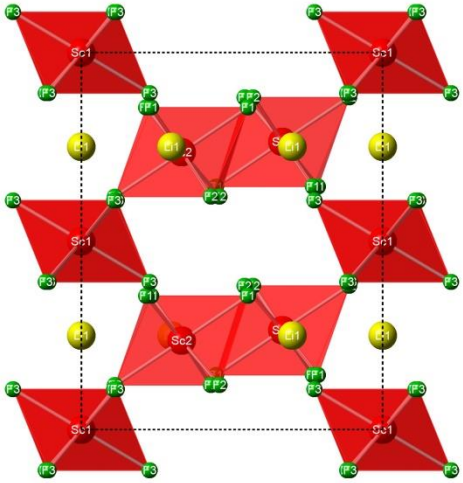
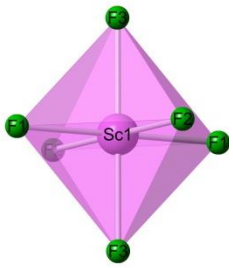
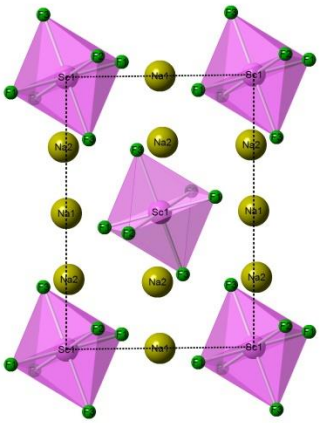
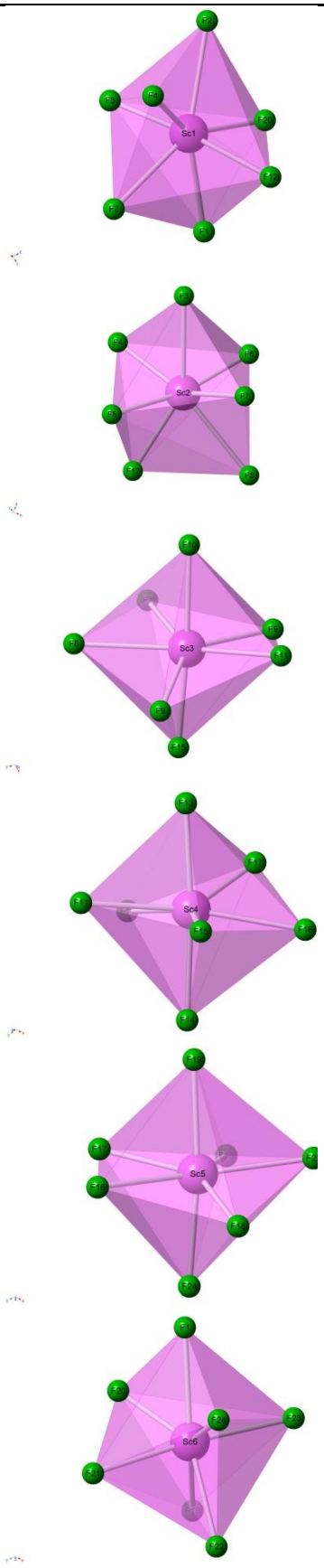
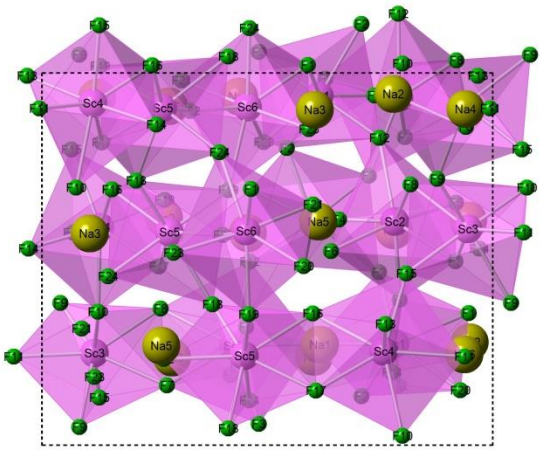


Figure S7. Experimental (blue) and simulated (red, only isotropic resonances) ^{19}F MAS NMR spectra at room temperature, and at 20 T and, at spinning rate 60 kHz with the parameters reported in the Table 6 of $NaScF_4$.

Compound	polyhedron	crystal structure
ScF_3		
Li_3ScF_6	 	
Na_3ScF_6		

$NaScF_4$


Sc1
Sc2
Sc3
Sc4
Sc5
Sc6


Sc4
Sc5
Sc6
Na3
Na2
Na4
Na3
Sc5
Sc6
Na5
Sc2
Sc3
Sc3
Na5
Sc5
Sc4

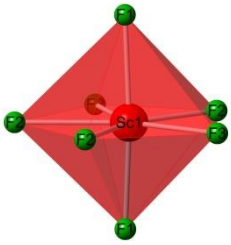
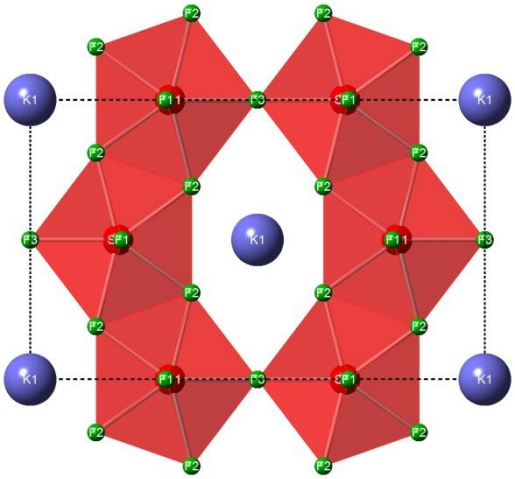
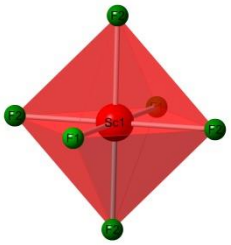
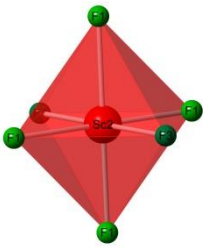
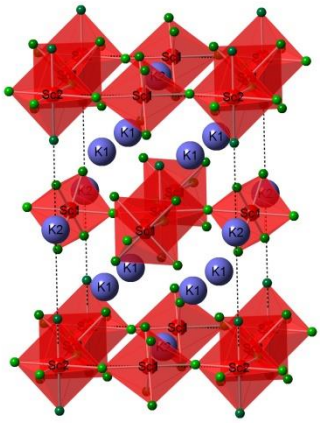
KSc_2F_7		
$K_5Sc_3F_{14}$	 	

Table S1. Polyhedra and crystal structure of the studied compounds.

Li_3ScF_6

atom	Experimental structure			Geometry Optimization			Δ=GO-ES		
	x	y	z	x	y	z	Δx	Δy	Δz
Li1	0.0000	0.7000	0.2500	0.0000	0.7003	0.2500	0.0000	0.0003	0.0000
Li2	0.6372	0.6574	0.4629	0.6388	0.6593	0.4627	0.0016	0.0019	-0.0002
Sc1	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Sc2	0.6667	0.3333	0.2639	0.6667	0.3333	0.2642	0.0000	0.0000	0.0003
F1	0.7846	0.5535	0.1450	0.7845	0.5543	0.1440	-0.0001	0.0008	-0.0010
F2	0.5416	0.4298	0.3817	0.5406	0.4300	0.3825	-0.0010	0.0002	0.0008
F3	0.1179	0.2267	0.1076	0.1183	0.2281	0.1083	0.0004	0.0014	0.0006

$NaScF_4$

atom	Experimental structure			Geometry Optimization			Δ=GO-ES		
	x	y	z	x	y	z	Δx	Δy	Δz
Na3	0.2888	1.3946	0.7647	0.29216	1.39495	0.76562	0.00336	0.00035	0.00092
Na2	0.2710	1.0508	0.3896	0.27128	1.05154	0.38682	0.00028	0.00074	-0.00278
Na1	-0.3829	0.5626	0.7294	-0.38243	0.56326	0.72876	0.00047	0.00066	-0.00064
Na4	0.4567	1.3963	0.4296	0.45717	1.39506	0.43026	0.00047	-0.00124	0.00066
Na5	0.1221	1.3870	0.0658	0.12480	1.38714	0.06568	0.00270	0.00014	-0.00012
Na6	0.2815	1.2188	0.0888	0.28074	1.21751	0.08607	-0.00076	-0.00129	-0.00273
Sc1	-0.2168	0.3842	0.7278	-0.21808	0.38351	0.72609	-0.00128	-0.00069	-0.00171
Sc2	-0.2173	0.5749	0.3988	-0.21702	0.57566	0.39709	0.00028	0.00076	-0.00171
Sc3	-0.0549	0.8841	0.4184	-0.05356	0.88422	0.42107	0.00134	0.00012	0.00267
Sc4	0.1284	1.2417	0.4139	0.13161	1.24277	0.41538	0.00321	0.00107	0.00148
Sc5	0.2826	1.5506	0.4268	0.28588	1.55153	0.43182	0.00328	0.00093	0.00502
Sc6	0.4557	1.5471	0.0907	0.45623	1.54655	0.09369	0.00053	-0.00055	0.00299
F1	-0.0533	0.4105	0.6448	-0.05386	0.40684	0.64743	-0.00056	-0.00366	0.00263

F2	-0.2910	0.4566	0.8681	-0.29651	0.45468	0.86141	-0.00551	-0.00192	-0.00669
F3	-0.2065	0.5188	0.6093	-0.20717	0.52050	0.60955	-0.00067	0.00170	0.00025
F4	-0.3409	0.3966	0.3930	-0.34654	0.39710	0.39186	-0.00564	0.00050	-0.00114
F5	-0.0817	0.5471	0.3484	-0.08286	0.54215	0.34760	-0.00116	-0.00495	-0.00080
F6	-0.3586	0.5820	0.4784	-0.35781	0.58436	0.47700	0.00079	0.00236	-0.00140
F7	-0.0826	0.7228	0.5055	-0.07930	0.72065	0.50129	0.00330	-0.00215	-0.00421
F8	-0.1827	0.7365	0.2987	-0.18297	0.73938	0.29756	-0.00027	0.00288	-0.00114
F9	-0.1235	0.9595	0.2840	-0.12145	0.96483	0.28601	0.00205	0.00533	0.00201
F10	0.0760	0.8756	0.3075	0.08102	0.87763	0.31155	0.00502	0.00203	0.00405
F11	0.0686	1.0624	0.4282	0.07223	1.06327	0.42651	0.00363	0.00087	-0.00169
F12	0.4610	1.2094	0.5067	0.45926	1.20873	0.50564	-0.00174	-0.00067	-0.00106
F13	0.2716	1.2385	0.3407	0.27495	1.23857	0.33387	0.00335	0.00007	-0.00683
F14	-0.0302	1.2240	0.4710	-0.03051	1.22318	0.46678	-0.00031	-0.00082	-0.00422
F15	0.0651	1.1919	0.2049	0.06345	1.19329	0.20554	-0.00165	0.00139	0.00064
F16	0.1548	1.3992	0.3126	0.15747	1.40246	0.31456	0.00267	0.00326	0.00196
F17	0.2592	1.3921	0.5196	0.26638	1.39019	0.51817	0.00718	-0.00191	-0.00143
F18	0.2090	1.6219	0.2883	0.20961	1.62377	0.29543	0.00061	0.00187	0.00713
F19	0.4130	1.5416	0.3143	0.41933	1.54394	0.31973	0.00633	0.00234	0.00543
F20	0.4920	1.4198	0.1851	0.49166	1.41794	0.18574	-0.00034	-0.00186	0.00064
F21	0.3102	1.3985	0.0193	0.31072	1.39696	0.01768	0.00052	-0.00154	-0.00162
F22	0.3288	1.5986	0.1017	0.32580	1.59471	0.10257	-0.00300	-0.00389	0.00087
F23	0.5920	1.7082	0.1498	0.58972	1.71037	0.14826	-0.00228	0.00217	-0.00154
F24	0.4597	1.6062	-0.1207	0.46184	1.61051	-0.11654	0.00214	0.00431	0.00416

Na_3ScF_6

atom	Experimental structure			Geometry Optimization			Δ=GO-ES		
	x	y	z	x	y	z	Δx	Δy	Δz
Na1	0.5000	0.5000	0.0000	0.5000	0.5000	0.0000	0.0000	0.0000	0.0000

Na2	0.5139	-0.0531	0.2431	0.5143	-0.0546	0.2421	0.0004	-0.0015	-0.0010
Sc1	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
F2	-0.2956	0.1774	0.0533	-0.2977	0.1774	0.0548	-0.0021	0.0000	0.0015
F1	0.1685	0.2870	-0.0754	0.1692	0.2891	-0.0767	0.0007	0.0021	-0.0013
F3	0.1218	0.0652	0.2301	0.1245	0.0665	0.2315	0.0027	0.0013	0.0014

KSc_2F_7

atom	Experimental structure			Geometry Optimization			Δ=GO-ES		
	x	y	z	x	y	z	Δx	Δy	Δz
K1	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0	0	0
Sc1	0.6925	-0.6925	0.5000	0.6926	-0.6926	0.5000	0.0001	0.0001	0
F2	0.7014	-0.7014	0.0000	0.7015	-0.7015	0.0000	0.0001	0.0001	0
F1	1.0447	0.3349	0.5000	1.0446	0.3331	0.5000	0.0001	-0.0018	0
F3	0.5000	-0.5000	0.5000	0.5000	-0.5000	0.5000	0	0	0

$K_5Sc_3F_{14}$

atom	Experimental structure			Geometry Optimization			Δ=GO-ES		
	x	y	z	x	y	z	Δx	Δy	Δz
K1	0.7181	0.2181	0.2500	0.7156	0.2156	0.2500	-0.0025	-0.0025	0
K2	0.5000	0.5000	0.0000	0.5000	0.5000	0.0000	0	0	0
Sc1	0.5000	0.0000	0.0000	0.5000	0.0000	0.0000	0	0	0
Sc2	1.0000	0.0000	0.0000	1.0000	0.0000	0.0000	0	0	0
F1	0.0620	0.2487	0.0000	0.0751	0.2481	0.0000	0.0131	-0.0006	0.0000
F2	0.4561	0.1786	0.1192	0.4566	0.1790	0.1178	0.0005	0.0004	-0.0014
F3	1.0000	0.0000	0.1705	1.0000	0.0000	0.1694	0	0	-0.0011

Table S2. Atom coordinates x,y,z of Li_3ScF_6, $NaScF_4$, Na_3ScF_6, KSc_2F_7, and $K_5Sc_3F_{14}$: before and after Geometry Optimization, and their differences between coordinates: Δx, Δy, Δz.