SUPPORTING INFORMATION

Mechanochemical synthesis of fluorinated perovskites $KCuF_3$ and $KNiF_3$

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X-Ray powder diffraction pattern

$KCuF_3$

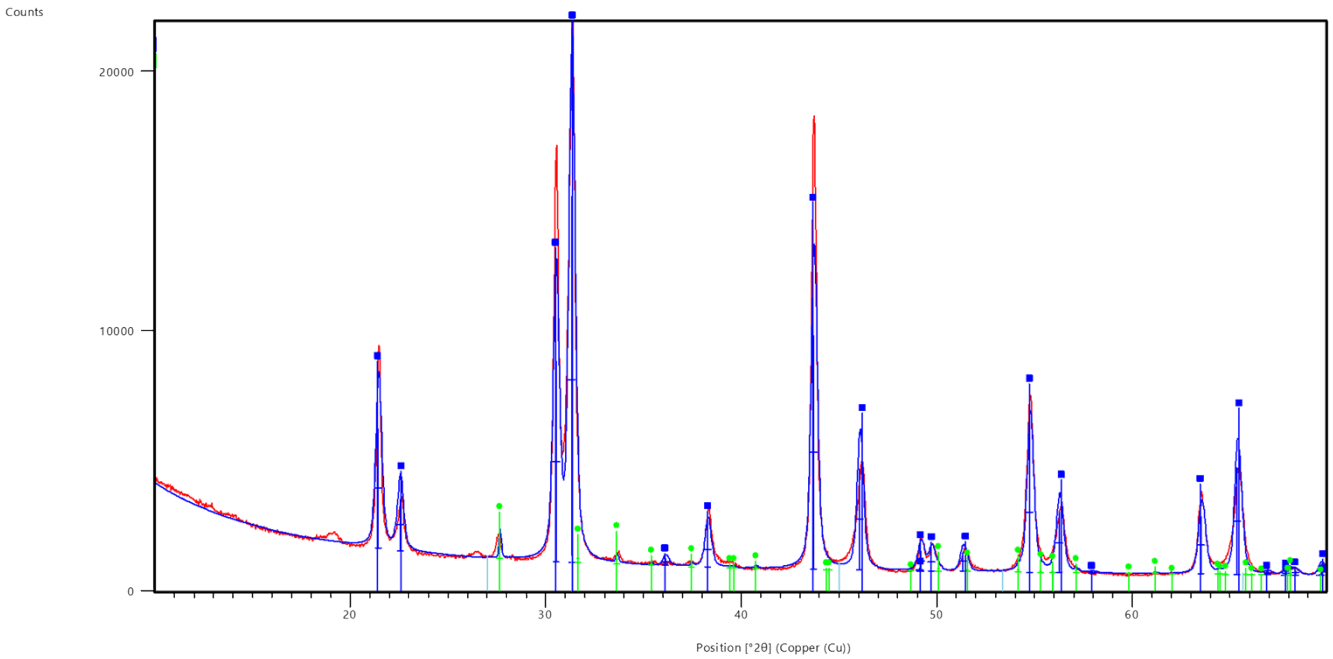

Figure 1. XRD pattern of $KCuF_3$ at 3h of milling and the corresponding Rietveld refinement. R_{wp}= 11.78

Tab 1. *Peak List $KCuF_3$ at 3h of milling with relative peak intensity used for the phase quantification.*

Pos. [°2θ]	Height [cts]	FWHM Left [°2θ]	d-spacing [Å]	Rel. Int. [%]	Matched by
21.4460	4578.34	0.3562	4.14003	32.50	98-001-7011
22.5538	1951.30	0.3562	3.93913	13.85	98-001-7011
27.6538	961.39	0.1000	3.22315	6.83	98-000-6024
30.5149	7707.52	0.3562	2.92715	54.72	98-001-7011
31.3226	14085.51	0.3562	2.85349	100.00	98-001-7011
31.6413	289.42	0.1000	2.82547	2.05	98-000-6024
33.6242	339.77	0.1000	2.66324	2.41	98-000-6024

35.3983	102.09	0.1000	2.53372	0.72	98-000-6024
36.1249	294.67	0.3562	2.48441	2.09	98-001-7011
37.4453	126.69	0.1000	2.39978	0.90	98-000-6024
38.2809	1349.52	0.3562	2.34930	9.58	98-001-7011
39.4103	37.29	0.1000	2.28453	0.26	98-000-6024
39.6121	38.92	0.1000	2.27336	0.28	98-000-6024
40.7356	69.99	0.1000	2.21321	0.50	98-000-6024
43.7012	8961.96	0.3562	2.06965	63.63	98-001-7011
44.3403	19.57	0.1000	2.04129	0.14	98-000-6024
44.4779	22.21	0.1000	2.03530	0.16	98-000-6024
46.0542	3876.45	0.3562	1.96924	27.52	98-001-7011
48.6669	1.05	0.1000	1.86945	0.01	98-000-6024
49.1033	98.52	0.3562	1.85385	0.70	98-001-7011
49.1806	753.20	0.3562	1.85112	5.35	98-001-7011
49.7268	699.19	0.3562	1.83206	4.96	98-001-7011
50.0990	194.45	0.1000	1.81931	1.38	98-000-6024
51.3397	741.01	0.3562	1.77822	5.26	98-001-7011
51.5611	134.00	0.1000	1.77110	0.95	98-001-7011, 98-000-6024
54.1637	166.64	0.1000	1.69199	1.18	98-000-6024
54.7492	4635.35	0.3562	1.67527	32.91	98-001-7011
55.3161	125.90	0.1000	1.65943	0.89	98-000-6024
55.9253	107.41	0.1000	1.64279	0.76	98-000-6024
56.2601	2283.37	0.3562	1.63381	16.21	98-001-7011
57.1159	172.80	0.1000	1.61135	1.23	98-000-6024
57.9519	43.30	0.3562	1.59007	0.31	98-001-7011
59.8111	4.73	0.1000	1.54501	0.03	98-000-6024
61.1709	65.51	0.1000	1.51389	0.47	98-000-6024
62.0176	0.57	0.1000	1.49523	0.00	98-000-6024
63.5228	2210.02	0.3562	1.46338	15.69	98-001-7011
64.3621	48.69	0.1000	1.44631	0.35	98-000-6024
64.4754	45.17	0.1000	1.44404	0.32	98-000-6024
64.7596	44.65	0.1000	1.43839	0.32	
65.3632	4102.93	0.3562	1.42656	29.13	98-001-7011
65.8089	66.01	0.1000	1.41797	0.47	98-000-6024
66.0936	6.07	0.1000	1.41255	0.04	98-000-6024
66.6228	2.35	0.1000	1.40261	0.02	98-000-6024
66.9166	102.98	0.3562	1.39717	0.73	98-001-7011
67.8160	22.46	0.3562	1.38081	0.16	98-001-7011
67.8791	158.29	0.3562	1.37968	1.12	98-001-7011, 98-000-6024

67.9596	7.98	0.1000	1.37824	0.06	98-001-7011, 98-000-6024
68.0790	91.68	0.1000	1.37611	0.65	98-001-7011, 98-000-6024
68.3265	180.89	0.3562	1.37173	1.28	98-001-7011, 98-000-6024
69.5980	23.62	0.3562	1.34975	0.17	98-001-7011
69.6459	0.03	0.1000	1.34893	0.00	98-001-7011
69.6604	398.37	0.3562	1.34869	2.83	98-001-7011

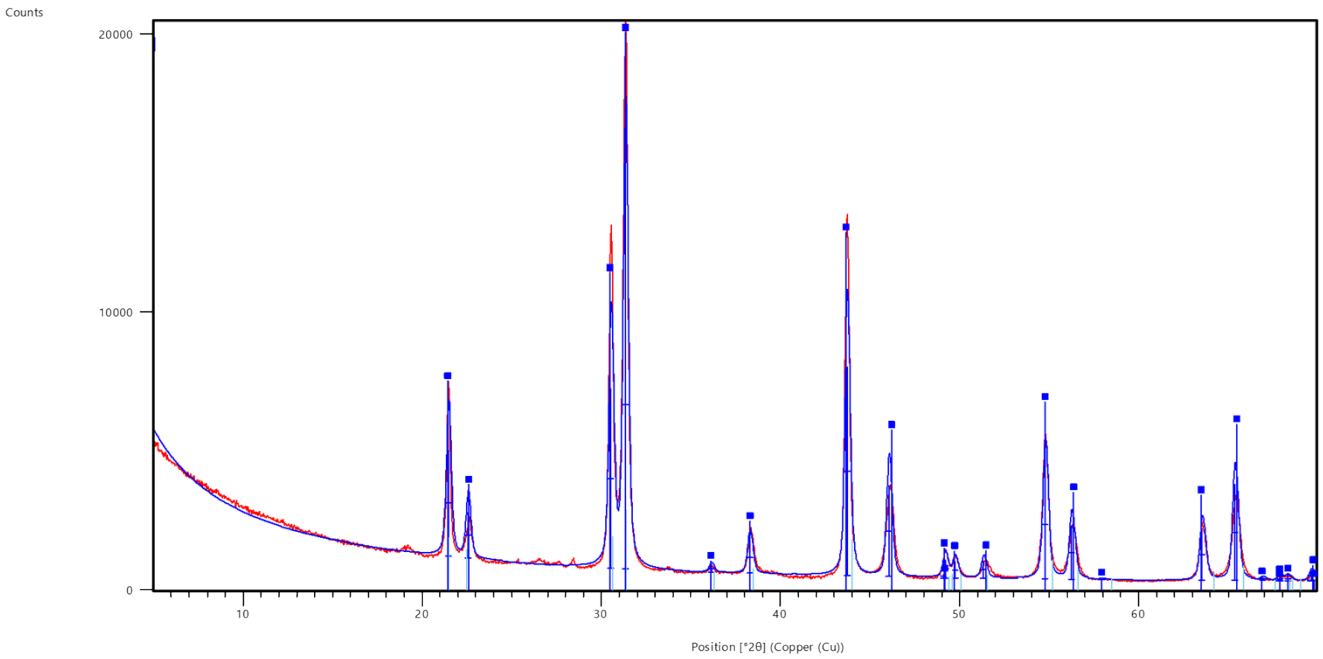

Figure 2. XRD pattern of $KCuF_3$ at 6h of milling and the corresponding Rietveld refinement. R_{wp}= 11.82

Tab 2. *Peak List $KCuF_3$ at 6h of milling with relative peak intensity used for the phase quantification.*

Pos. [°2θ]	Height [cts]	FWHM Left [°2θ]	d-spacing [Å]	Rel. Int. [%]	Matched by
21.4767	3825.11	0.3177	4.13418	32.44	98-001-7011
22.5726	1632.59	0.3177	3.93589	13.85	98-001-7011
30.5422	6446.80	0.3177	2.92460	54.67	98-001-7011
31.3411	11791.23	0.3177	2.85185	100.00	98-001-7011
36.1480	246.65	0.3177	2.48287	2.09	98-001-7011
38.2978	1130.52	0.3177	2.34830	9.59	98-001-7011
43.7228	7503.33	0.3177	2.06868	63.63	98-001-7011

46.0503	3251.96	0.3177	1.96939	27.58	98-001-7011
49.1093	82.60	0.3177	1.85364	0.70	98-001-7011
49.1996	630.77	0.3177	1.85044	5.35	98-001-7011
49.7398	585.79	0.3177	1.83161	4.97	98-001-7011
51.3352	621.62	0.3177	1.77837	5.27	98-001-7011
54.7601	3883.98	0.3177	1.67496	32.94	98-001-7011
56.2544	1915.24	0.3177	1.63396	16.24	98-001-7011
57.9652	36.29	0.3177	1.58974	0.31	98-001-7011
63.5343	1851.97	0.3177	1.46314	15.71	98-001-7011
65.3542	3442.32	0.3177	1.42673	29.19	98-001-7011
66.9249	86.32	0.3177	1.39701	0.73	98-001-7011
67.8143	18.84	0.3177	1.38084	0.16	98-001-7011
67.8881	132.68	0.3177	1.37952	1.13	98-001-7011
68.3304	151.67	0.3177	1.37166	1.29	98-001-7011
69.5765	19.83	0.3177	1.35011	0.17	98-001-7011
69.6494	334.31	0.3177	1.34887	2.84	98-001-7011

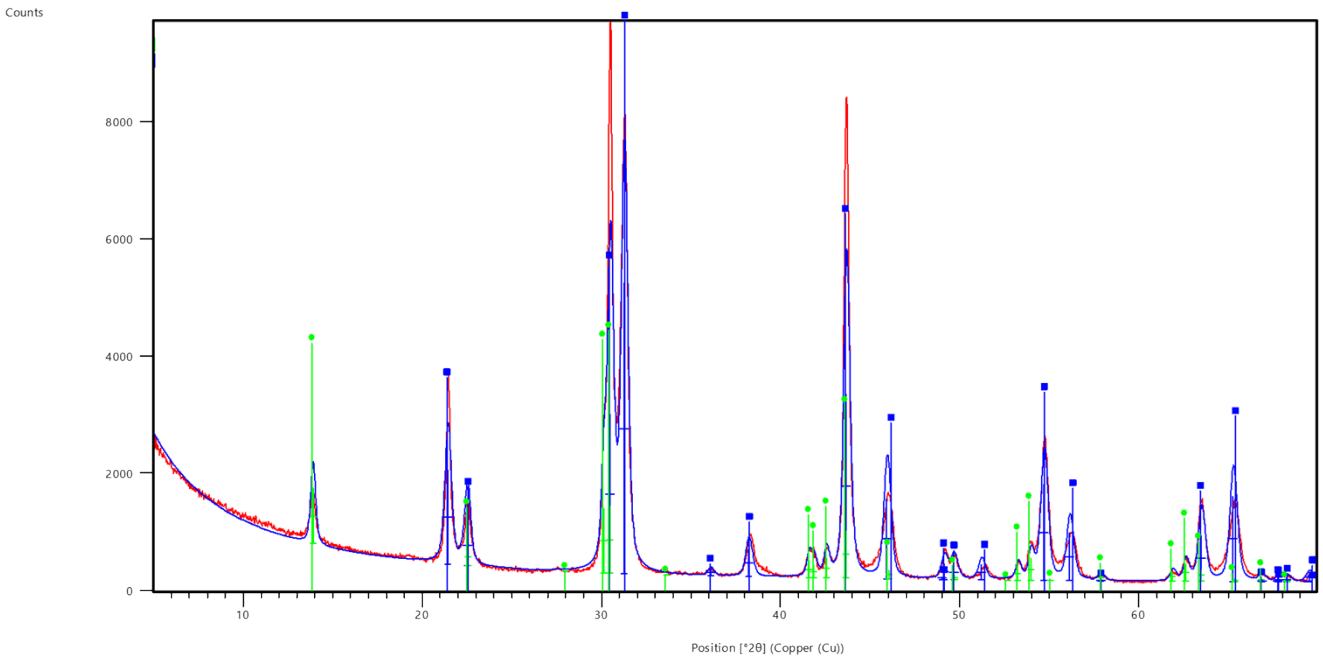

Figure 3. XRD pattern of $KCuF_3$ at 12h of milling and the corresponding Rietveld refinement. R_{wp}=15.18

Tab 3. *Peak List $KCuF_3$ at 12h of milling with relative peak intensity used for the phase quantification.*

Pos.	Height	FWHM Left	d-spacing	Rel. Int.	Matched by

[°2θ]	[cts]	[°2θ]	[Å]	[%]	
13.8920	942.06	0.3254	6.36960	19.03	98-001-5372
21.4340	1603.33	0.4317	4.14232	32.39	98-001-7011
22.4962	686.69	0.4317	3.94908	13.87	98-001-7011, 98-001-5372
22.5547	272.21	0.3254	3.93896	5.50	98-001-7011, 98-001-5372
27.9952	0.83	0.3254	3.18461	0.02	98-001-5372
30.1169	1094.36	0.3254	2.96492	22.11	98-001-7011, 98-001-5372
30.4952	2700.41	0.4317	2.92900	54.56	98-001-7011, 98-001-5372
30.4979	1133.32	0.3254	2.92874	22.90	98-001-7011, 98-001-5372
31.2693	4949.61	0.4317	2.85823	100.00	98-001-7011
33.6547	2.61	0.3254	2.66089	0.05	98-001-5372
36.0930	103.36	0.4317	2.48653	2.09	98-001-7011
38.2267	474.58	0.4317	2.35250	9.59	98-001-7011
41.5842	295.34	0.3254	2.16999	5.97	98-001-5372
41.8731	217.24	0.3254	2.15569	4.39	98-001-5372
42.5482	336.63	0.3254	2.12303	6.80	98-001-5372
43.6696	3142.13	0.4317	2.07108	63.48	98-001-7011, 98-001-5372
43.6735	810.00	0.3254	2.07090	16.36	98-001-7011, 98-001-5372
45.9253	1369.07	0.4317	1.97446	27.66	98-001-7011, 98-001-5372
46.0500	144.81	0.3254	1.96941	2.93	98-001-7011, 98-001-5372
49.0155	34.70	0.4317	1.85696	0.70	98-001-7011
49.1437	264.11	0.4317	1.85242	5.34	98-001-7011
49.6669	245.56	0.4317	1.83412	4.96	98-001-7011, 98-001-5372
49.6999	65.19	0.3254	1.83298	1.32	98-001-7011, 98-001-5372
51.2130	261.47	0.4317	1.78232	5.28	98-001-7011
52.6803	0.41	0.3254	1.73608	0.01	
53.2485	222.89	0.3254	1.71889	4.50	98-001-5372
53.9651	368.26	0.3254	1.69775	7.44	98-001-5372
54.6858	1627.61	0.4317	1.67706	32.88	98-001-7011, 98-001-5372

55.0791	5.43	0.3254	1.66601	0.11	98-001-7011, 98-001-5372
56.1337	804.85	0.4317	1.63719	16.26	98-001-7011
57.8650	79.26	0.3254	1.59225	1.60	98-001-7011, 98-001-5372
57.9010	15.20	0.4317	1.59135	0.31	98-001-7011, 98-001-5372
61.8843	149.33	0.3254	1.49813	3.02	98-001-5372
62.6141	292.03	0.3254	1.48241	5.90	98-001-5372
63.4708	775.34	0.4317	1.46445	15.66	98-001-7011, 98-001-5372
63.4769	182.91	0.3254	1.46433	3.70	98-001-7011, 98-001-5372
65.2339	1445.79	0.4317	1.42907	29.21	98-001-7011, 98-001-5372
65.3356	37.85	0.3254	1.42709	0.76	98-001-7011, 98-001-5372
66.8244	62.40	0.3254	1.39887	1.26	98-001-7011, 98-001-5372
66.8561	36.15	0.4317	1.39828	0.73	98-001-7011, 98-001-5372
67.7175	7.90	0.4317	1.38258	0.16	98-001-7011, 98-001-5372
67.8221	55.55	0.4317	1.38070	1.12	98-001-7011, 98-001-5372
68.2506	63.55	0.4317	1.37307	1.28	98-001-7011, 98-001-5372
68.2806	7.37	0.3254	1.37254	0.15	98-001-7011, 98-001-5372
69.4249	8.35	0.4317	1.35269	0.17	98-001-7011
69.5283	140.41	0.4317	1.35093	2.84	98-001-7011

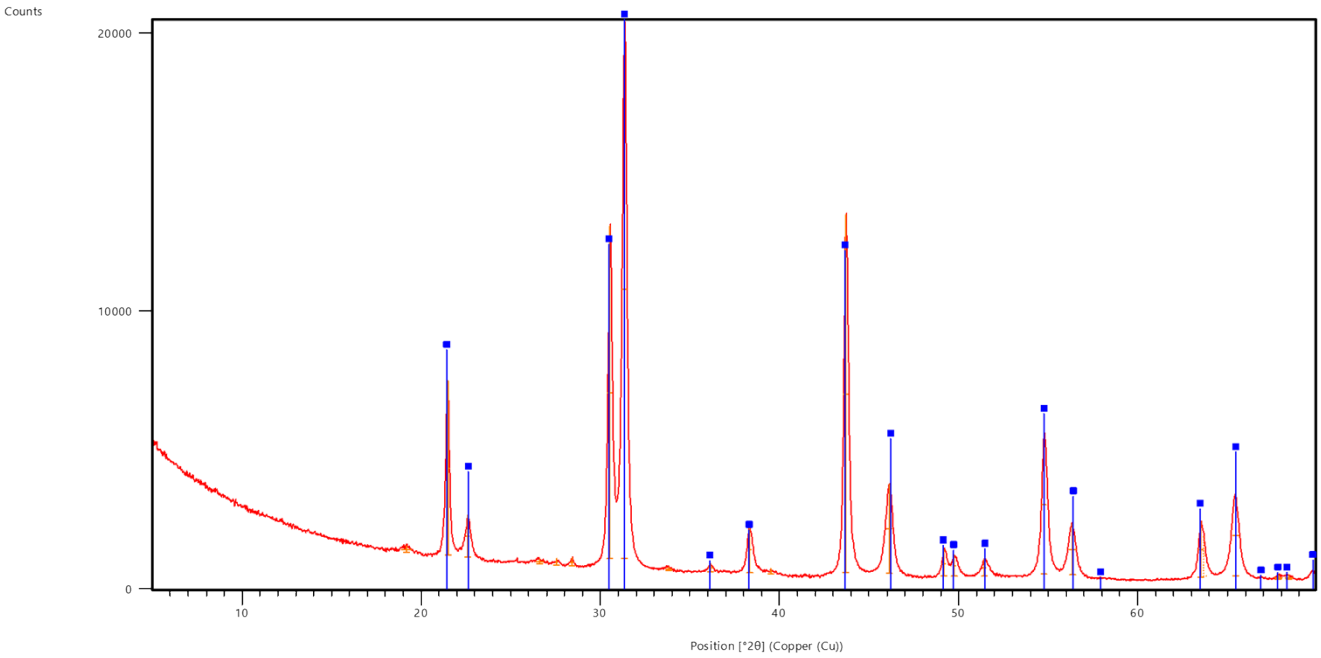

Figure 4. XRD pattern of $KCuF_3$ solvothermal and the corresponding Rietveld refinement. R_{wp}= 21.60

Tab 4. *Peak List $KCuF_3$ at solvothermal with relative peak intensity used for the phase quantification.*

Pos. [°2θ]	Height [cts]	FWHM Left [°2θ]	d-spacing [Å]	Rel. Int. [%]	Matched by
21.4415	4491.59	0.2060	4.14089	8.40	98-001-7011
22.6136	1901.02	0.2060	3.92884	3.55	98-001-7011
24.4766	321.83	0.0902	3.63386	0.60	98-024-0524
28.3378	53499.88	0.0902	3.14689	100.00	98-024-0524
30.5083	7562.12	0.2060	2.92776	14.13	98-001-7011
31.3636	13761.46	0.2060	2.84985	25.72	98-001-7011
36.1276	288.87	0.2060	2.48423	0.54	98-001-7011
38.3126	1319.11	0.2060	2.34743	2.47	98-001-7011
40.5101	35670.40	0.0902	2.22501	66.67	98-024-0524
43.6915	8794.30	0.2060	2.07009	16.44	98-001-7011
46.1817	3764.58	0.2060	1.96409	7.04	98-001-7011
47.9035	206.16	0.0902	1.89744	0.39	98-024-0524
49.1661	96.13	0.2060	1.85163	0.18	98-001-7011
49.1695	739.13	0.2060	1.85151	1.38	98-001-7011
49.7481	684.57	0.2060	1.83132	1.28	98-001-7011
50.1776	11486.10	0.0902	1.81665	21.47	98-024-0524
51.4552	720.77	0.2060	1.77450	1.35	98-001-7011

54.7671	4540.11	0.2060	1.67476	8.49	98-001-7011
56.3665	2224.28	0.2060	1.63098	4.16	98-001-7011
57.9458	42.48	0.2060	1.59023	0.08	98-001-7011
58.6325	4984.34	0.0902	1.57323	9.32	98-024-0524
63.5077	2168.99	0.2060	1.46369	4.05	98-001-7011
64.4938	55.81	0.0902	1.44367	0.10	98-024-0524
65.4569	4001.32	0.2060	1.42474	7.48	98-001-7011
66.3820	12970.68	0.0902	1.40711	24.24	98-024-0524
66.9073	101.04	0.2060	1.39734	0.19	98-001-7011
67.8600	21.97	0.2060	1.38002	0.04	98-001-7011
67.8628	155.37	0.2060	1.37997	0.29	98-001-7011
68.3367	177.27	0.2060	1.37155	0.33	98-001-7011
69.7467	22.95	0.2060	1.34723	0.04	98-001-7011
69.7494	388.59	0.2060	1.34719	0.73	98-001-7011

$KNiF_3$

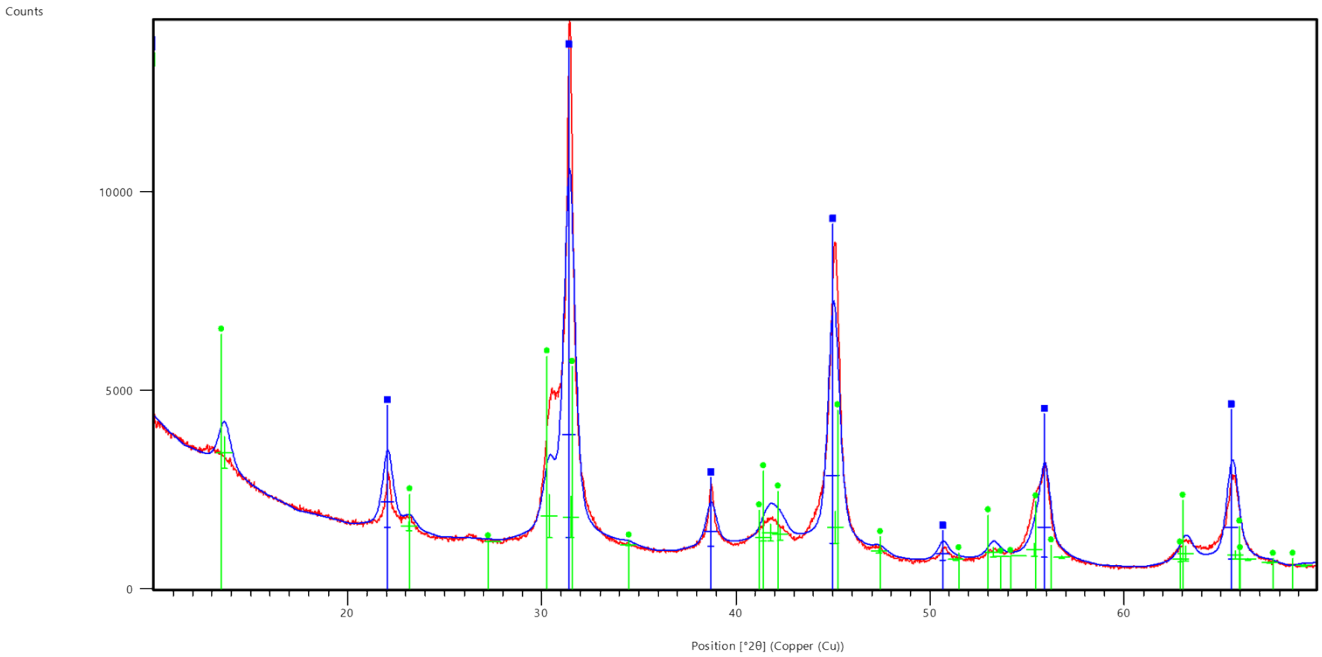

Figure 5. XRD pattern of $KNiF_3$ at 3h of milling and the corresponding Rietveld refinement. R_{wp}= 11.81

Tab 5. *Peak List $KNiF_3$ at 3h of milling with relative peak intensity used for the phase quantification.*

Pos. [°2θ]	Height [cts]	FWHM Left [°2θ]	d-spacing [Å]	Rel. Int. [%]	Matched by

13.6484	780.68	0.7588	6.48272	14.00	98-063-1720
22.0550	1294.75	0.6409	4.02707	25.87	98-018-9369
23.1747	219.74	0.7588	3.83497	4.22	98-063-1720
27.5044	1.63	0.7588	3.24032	0.03	98-063-1720
30.3700	1091.48	0.7588	2.94079	18.97	98-063-1720
31.3932	5205.41	0.6409	2.84723	100.00	98-018-9369, 98-063-1720
31.4918	1044.18	0.7588	2.83854	20.06	98-018-9369, 98-063-1720
34.4675	34.06	0.7588	2.59999	0.65	98-063-1720
38.7033	742.59	0.6409	2.32462	14.27	98-018-9369
41.4351	183.95	0.7588	2.17746	3.53	98-063-1720
41.7862	412.60	0.7588	2.15996	7.93	98-063-1720
42.2991	296.95	0.7588	2.13495	5.70	98-063-1720
44.9947	3409.90	0.6409	2.01312	67.51	98-018-9369, 98-063-1720
45.1400	819.51	0.7588	2.00697	15.74	98-018-9369, 98-063-1720
47.3820	104.06	0.7588	1.91710	2.00	98-063-1720
50.6580	307.64	0.6409	1.80054	5.91	98-018-9369
51.3445	39.44	0.7588	1.77807	0.76	98-018-9369, 98-063-1720
53.2525	253.42	0.7588	1.71877	4.87	98-063-1720
53.6799	0.75	0.7588	1.70609	0.01	98-063-1720
54.5435	2.88	0.7588	1.68110	0.06	98-063-1720
55.3826	335.08	0.7588	1.65760	6.44	98-018-9369, 98-063-1720
55.8942	1527.01	0.6409	1.64363	29.34	98-018-9369, 98-063-1720
56.7877	72.78	0.7588	1.61987	1.40	98-063-1720
62.9346	85.19	0.7588	1.47563	1.64	98-063-1720
63.1962	363.57	0.7588	1.47015	6.98	98-063-1720
65.5270	1598.05	0.6409	1.42339	30.70	98-018-9369, 98-063-1720
65.7528	202.69	0.7588	1.41905	3.89	98-018-9369, 98-063-1720
66.3976	36.04	0.7588	1.40682	0.69	98-018-9369, 98-063-1720
67.5175	26.71	0.7588	1.38618	0.51	98-063-1720
69.2735	43.03	0.7588	1.35527	0.83	98-018-9369, 98-063-1720

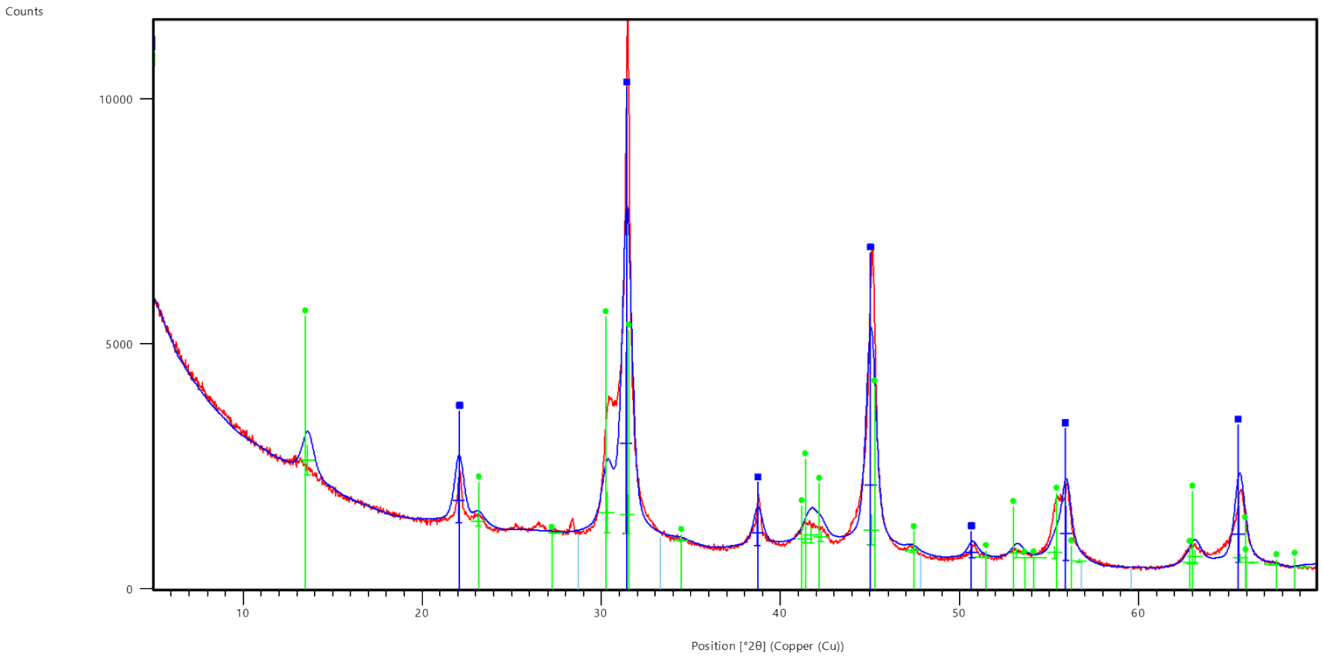

Figure 6. XRD pattern of $KNiF_3$ at 6h of milling and the corresponding Rietveld refinement. R_{wp}= 11.51

Tab 6. *Peak List $KNiF_3$ at 6h of milling with relative peak intensity used for the phase quantification.*

Pos. [°2θ]	Height [cts]	FWHM Left [°2θ]	d-spacing [Å]	Rel. Int. [%]	Matched by
13.6097	589.98	0.7516	6.50107	15.95	98-063-1720
22.0515	920.66	0.6197	4.02770	24.89	98-018-9369
23.1346	165.73	0.7516	3.84153	4.48	98-063-1720
27.4494	1.23	0.7516	3.24669	0.03	98-063-1720
30.3191	823.39	0.7516	2.94560	22.26	98-063-1720
31.3985	3698.30	0.6197	2.84676	100.00	98-018-9369, 98-063-1720
31.4467	787.25	0.7516	2.84251	21.29	98-018-9369, 98-063-1720
34.4176	25.70	0.7516	2.60364	0.69	98-063-1720
38.7158	527.26	0.6197	2.32390	14.26	98-018-9369
41.3687	138.82	0.7516	2.18080	3.75	98-063-1720
41.7136	311.59	0.7516	2.16356	8.43	98-063-1720
42.2373	224.10	0.7516	2.13794	6.06	98-063-1720
45.0137	2419.96	0.6197	2.01231	65.43	98-018-9369, 98-063-1720
45.0848	617.90	0.7516	2.00930	16.71	98-018-9369, 98-063-

					1720
47.3230	78.47	0.7516	1.91935	2.12	98-063-1720
50.6832	218.09	0.6197	1.79971	5.90	98-018-9369, 98-063-1720
51.2840	29.74	0.7516	1.78002	0.80	98-018-9369, 98-063-1720
53.1743	191.27	0.7516	1.72111	5.17	98-063-1720
53.6107	0.57	0.7516	1.70813	0.02	98-063-1720
54.4587	2.18	0.7516	1.68352	0.06	98-063-1720
55.3152	252.66	0.7516	1.65946	6.83	98-018-9369, 98-063-1720
55.9254	1083.17	0.6197	1.64279	29.29	98-018-9369, 98-063-1720
56.6949	54.98	0.7516	1.62231	1.49	98-018-9369, 98-063-1720
62.8545	64.27	0.7516	1.47732	1.74	98-063-1720
63.1113	274.39	0.7516	1.47193	7.42	98-063-1720
65.5701	1132.92	0.6197	1.42256	30.63	98-018-9369, 98-063-1720
65.6806	152.83	0.7516	1.42043	4.13	98-018-9369, 98-063-1720
66.2989	27.20	0.7516	1.40868	0.74	98-018-9369, 98-063-1720
67.4420	20.15	0.7516	1.38755	0.54	98-063-1720
69.1659	32.48	0.7516	1.35712	0.88	98-063-1720

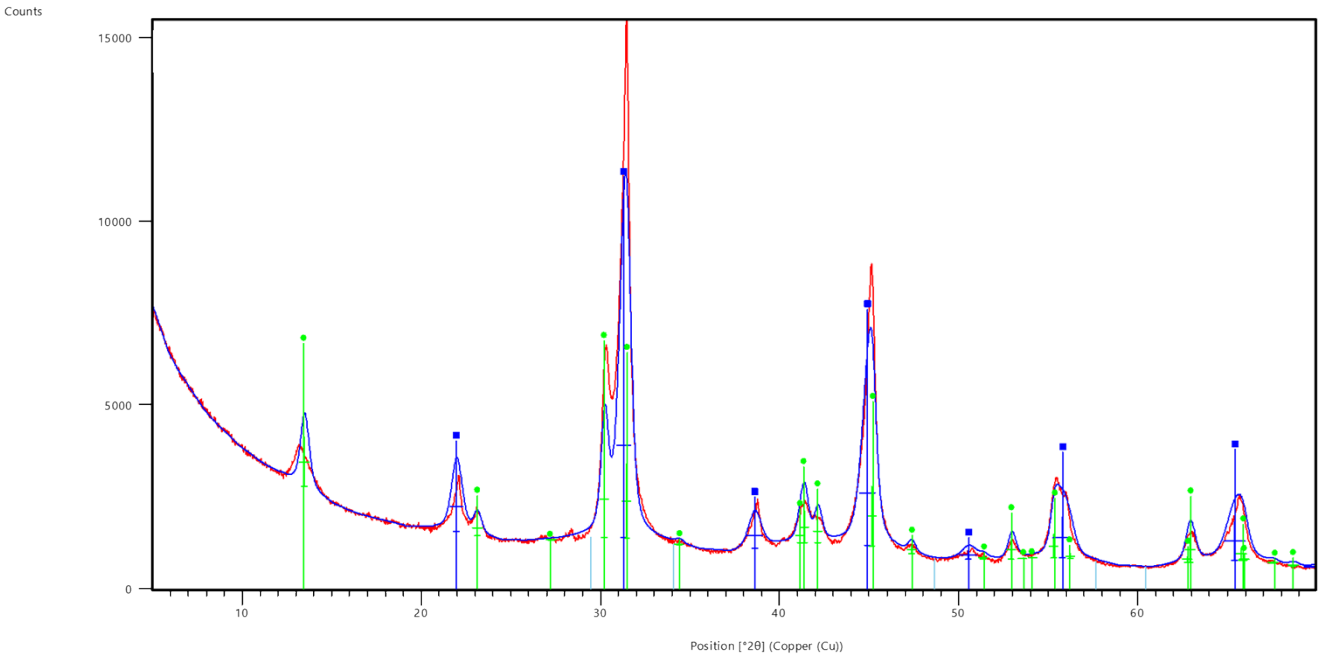

Figure 7. XRD pattern of $KNiF_3$ at 12h of milling and the corresponding Rietveld refinement. R_{wp}= 10.34

Tab 7. *Peak List $KNiF_3$ at 12h of milling with relative peak intensity used for the phase quantification.*

Pos. [°2θ]	Height [cts]	FWHM Left [°2θ]	d-spacing [Å]	Rel. Int. [%]	Matched by
13.4864	1341.33	0.5714	6.56021	26.63	98-063-1720
21.9774	1339.98	0.7198	4.04113	26.60	98-018-9369
23.1317	402.10	0.5248	3.84200	7.98	98-063-1720
27.2287	3.16	0.5090	3.27250	0.06	98-063-1720
30.2232	2117.80	0.4992	2.95473	42.05	98-063-1720
31.3046	5036.93	0.7691	2.85509	100.00	98-018-9369, 98-063-1720
31.4783	2015.58	0.4957	2.83972	40.02	98-018-9369, 98-063-1720
34.4057	66.99	0.4885	2.60451	1.33	98-063-1720
38.6057	669.87	0.8249	2.33027	13.30	98-018-9369
41.1550	374.69	0.4794	2.19162	7.44	98-063-1720
41.3858	849.51	0.4793	2.17994	16.87	98-063-1720
42.1242	601.03	0.4790	2.14341	11.93	98-063-1720
44.8890	2868.53	0.8846	2.01761	56.95	98-018-9369, 98-063-1720
45.1451	1632.62	0.4794	2.00676	32.41	98-018-9369, 98-063-

					1720
47.3501	207.08	0.4812	1.91832	4.11	98-063-1720
50.5448	241.87	0.9474	1.80431	4.80	98-018-9369
51.3492	77.14	0.4883	1.77792	1.53	98-063-1720
52.9366	502.23	0.4924	1.72828	9.97	98-063-1720
53.5507	1.47	0.4942	1.70990	0.03	98-063-1720
54.1166	5.75	0.4960	1.69335	0.11	98-063-1720
55.3219	642.75	0.5001	1.65927	12.76	98-018-9369, 98-063-1720
55.7737	1121.38	1.0131	1.64690	22.26	98-018-9369, 98-063-1720
56.2428	143.22	0.5036	1.63427	2.84	98-018-9369, 98-063-1720
62.7592	153.48	0.5359	1.47934	3.05	98-063-1720
62.9304	657.47	0.5370	1.47572	13.05	98-063-1720
65.3919	1030.22	1.1542	1.42600	20.45	98-018-9369, 98-063-1720
65.7899	347.71	0.5558	1.41834	6.90	98-018-9369, 98-063-1720
65.9183	63.43	0.5567	1.41588	1.26	98-018-9369, 98-063-1720
67.5256	44.86	0.5685	1.38604	0.89	98-063-1720
68.6749	73.36	0.5776	1.36562	1.46	98-063-1720
69.9177	7.99	1.2302	1.34436	0.16	98-018-9369
69.9177	31.95	1.2302	1.34436	0.63	98-018-9369

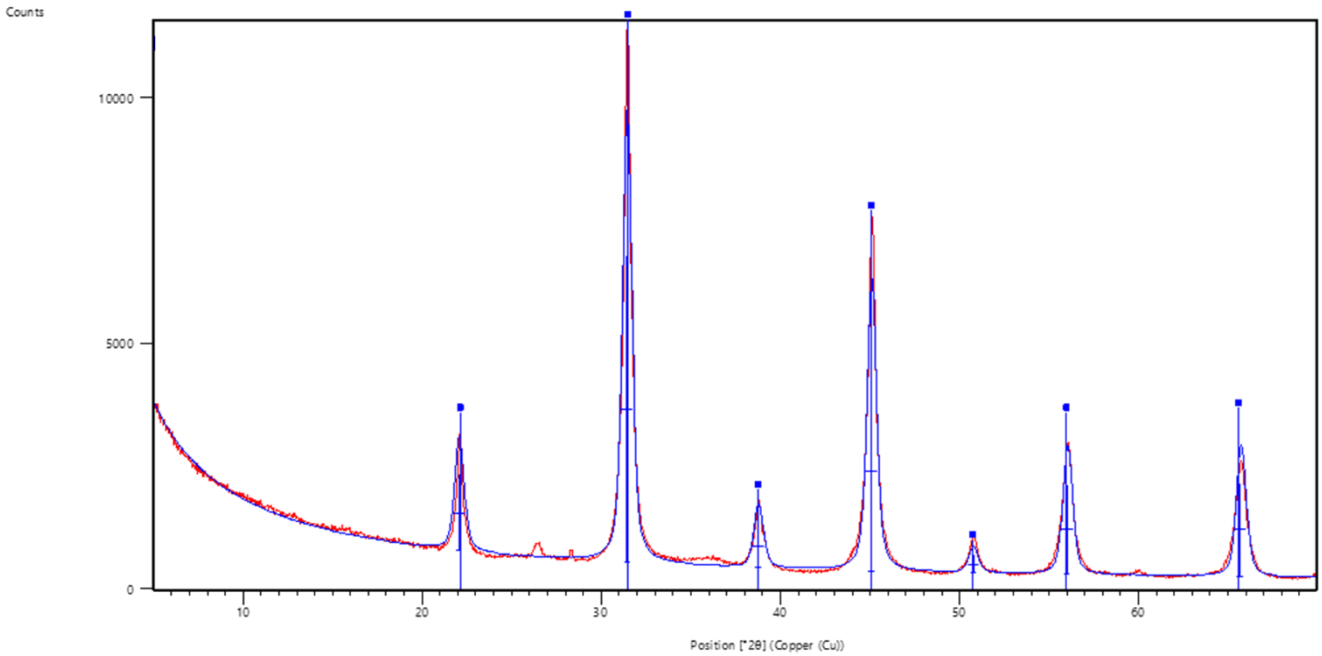

Figure 8. XRD pattern of $KNiF_3$ solvothermal and the corresponding Rietveld refinement. R_{wp}= 11.42

Tab 8. *Peak List $KNiF_3$ solvothermal with relative peak intensity used for the phase quantification.*

Pos. [°2θ]	Height [cts]	FWHM Left [°2θ]	d-spacing [Å]	Rel. Int. [%]	Matched by
22.0615	1556.73	0.6155	4.02590	24.93	98-018-9369
31.4280	6244.44	0.6155	2.84415	100.00	98-018-9369
38.7614	889.18	0.6155	2.32127	14.24	98-018-9369
45.0738	4077.22	0.6155	2.00976	65.29	98-018-9369
50.7570	366.60	0.6155	1.79726	5.87	98-018-9369
56.0126	1823.30	0.6155	1.64044	29.20	98-018-9369
65.6835	1904.86	0.6155	1.42038	30.50	98-018-9369

XPS survey

$KCuF_3$

6h:

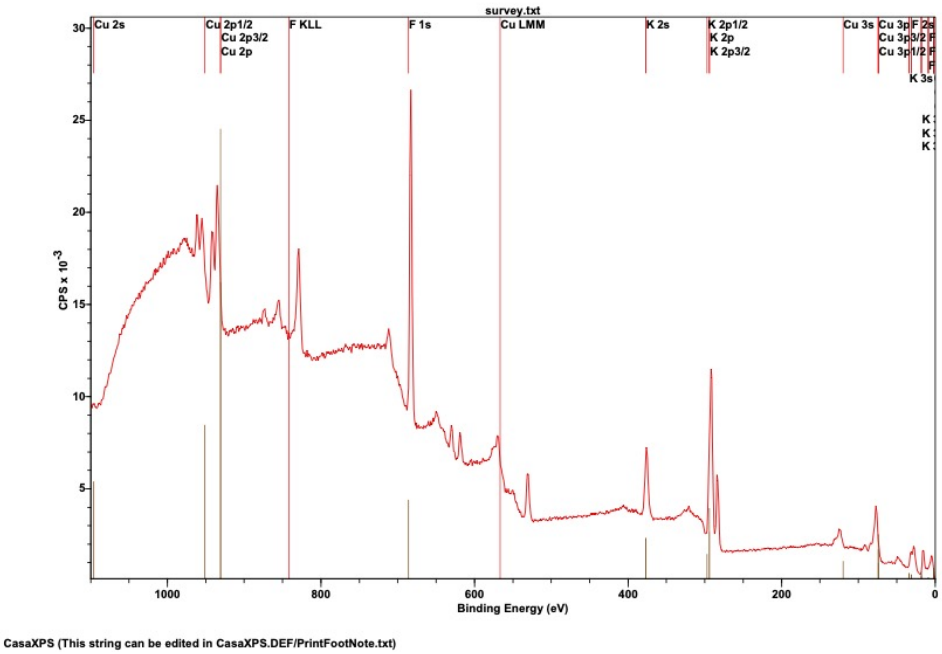

Figure 9. XPS survey $KCuF_3$ 6h of milling.

12h:

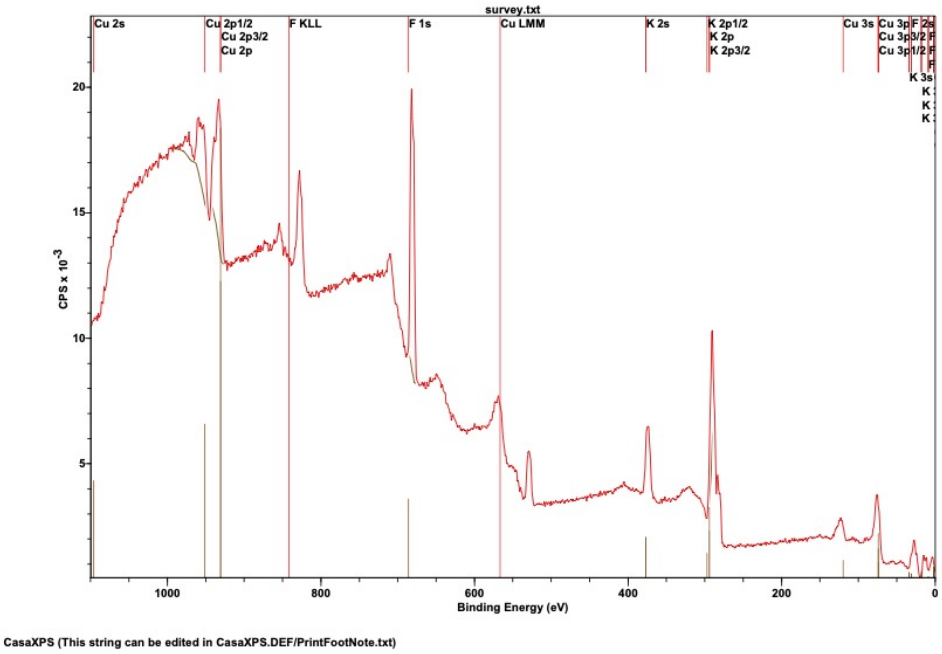

Figure 10. XPS survey $KCuF_3$ 6h of milling.

Solvothermal:

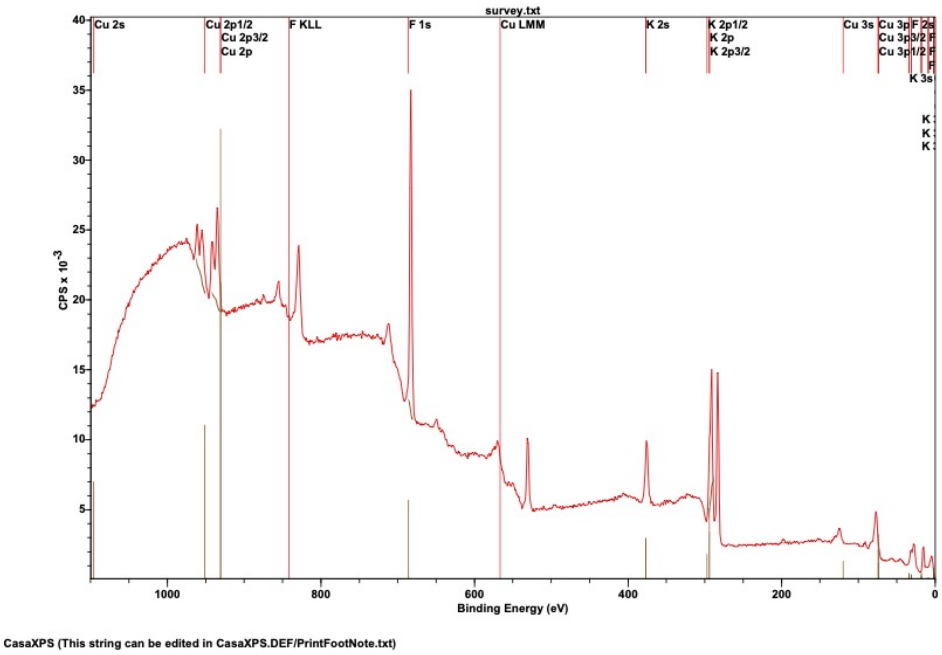

Figure 11. XPS survey $KCuF_3$ solvothermal.

$KNiF_3$

6h:

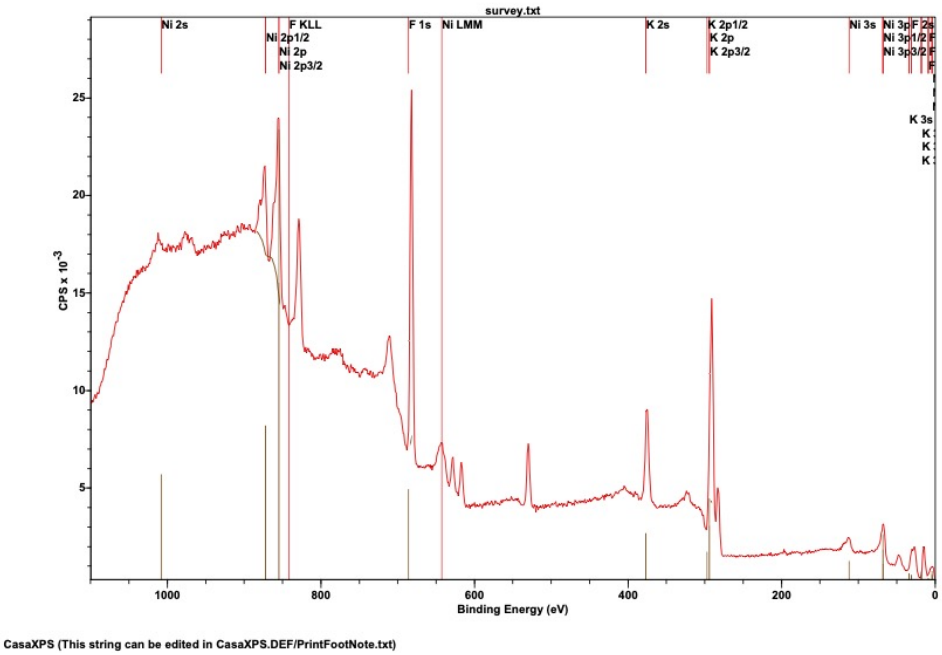

Figure 12. XPS survey $KNiF_3$ 6h of milling.

12h:

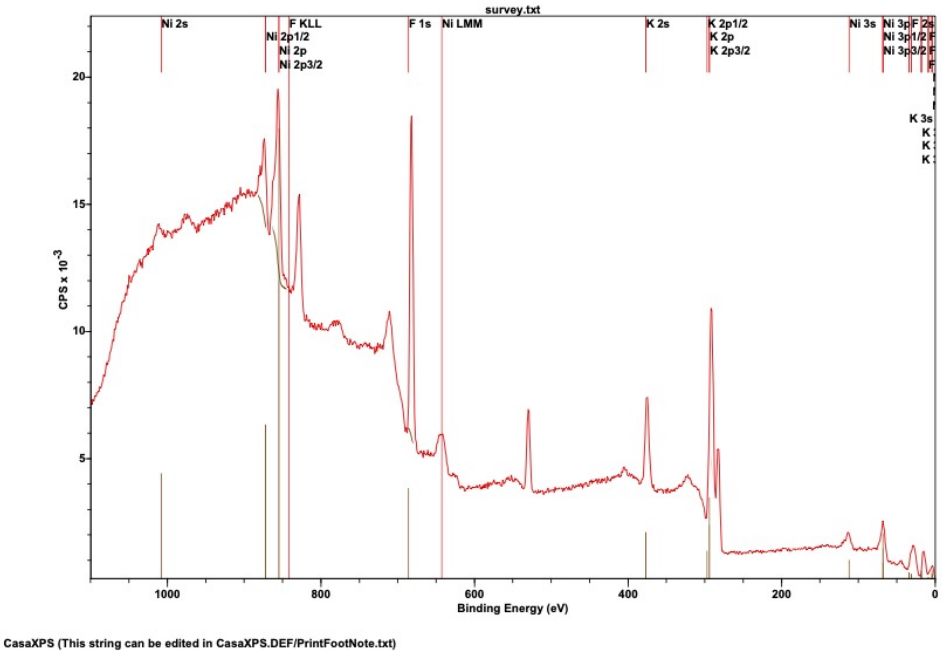

Figure 13. XPS survey $KNiF_3$ 12h of milling.

Solvothermal:

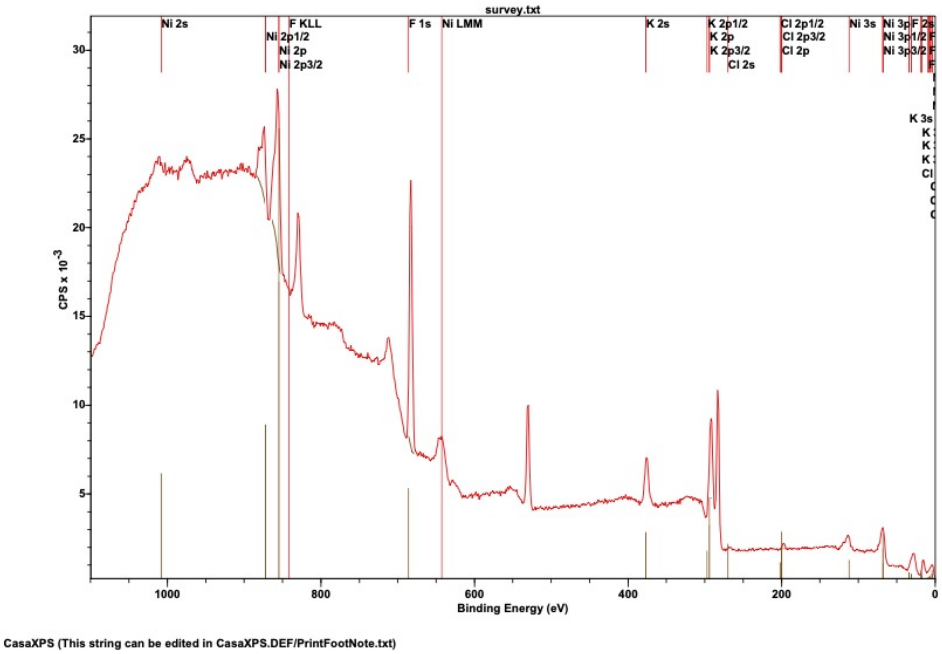

Figure 14. XPS survey $KNiF_3$ solvothermal.

Green metrics

Solvothermal process

Atom Economy evaluation:
Considering the molecular weight of the reagents of the two solvothermal reaction and the two desired products it's possible to estimate the theoretical atom economy.

$$Reagents\ MW = CuCl_2 + 3KF = 134.45\frac{g}{mol} + 3 \times 58.09\frac{g}{mol} = 308.72\frac{g}{mol}$$

$$KCuF_3\ molecular\ weight = 159.63\frac{g}{mol}$$

$$AE\ KCuF_3 = \frac{159.63\frac{g}{mol}}{308.72\frac{g}{mol}} \times 100 = 51.7\%$$

$$Reagents\ MW = NiCl_2 * 6H_2O + 3KF = 237.69\frac{g}{mol} + 3 \times 58.09\frac{g}{mol} = 411.96\ \frac{g}{mol}$$

$$KNiF_3\ molecular\ weight = 154.78\frac{g}{mol}$$

$$AE\ KNiF_3 = \frac{154.78\frac{g}{mol}}{411.96\frac{g}{mol}} \times 100 = 37.6\%$$

Process mass intensity (PMI) evaluation:
The total mass used in the process is the sum of the reagents and the solvent employed in the solvothermal synthesis.

$$PMI\ KCuF_3 = \frac{0.261g\ (KF) + 0.201g\ (CuCl_2) + 40g\ (EtOH) + 5g\ (H_2O)}{0.238g\ (KCuF_3)} = 191.0$$

$$PMI\ KNiF_3 = \frac{0.174g\ (KF) + 0.236g\ (NiCl_2 * 6H_2O) + 40g\ (EtOH) + 5g\ (H_2O)}{0.154g\ (KNiF_3)} = 294.9$$

Energy consumption evaluation:
The oven used in the solvothermal synthesis and for the drying process is a Vacuum drying oven VC-20 Renggli AG/ SalvisLab with the following specifications:

Tab 9. *Oven parameters.*

Volume	liters	20
Max load capacity	Kg	37
Heating up velocity to 150°C from 20°C	min	58
Nominal wattage while heating	W	900
Energy consumption		
At 100°C	W	185
At 150°C	W	243
Maximum temperature	°C	200
Working temperature range	°C	15-25

To evaluate how much perovskites could be produced with this equipment it was evaluated how many autoclaves could be heated in this model VC-20.

Knowing the weight of the autoclave implemented, 2.15Kg, and the maximum load of the oven, 37 Kg, it was determined that a maximum of 17 autoclaves can be heated at the same time. A total of 2.61g of $KNiF_3$ and 4.05g of $KCuF_3$ are then produced considering a complete yield of reaction.

To evaluate the energy consumption of the oven it was considered a value of 900W for 60 minutes of heating from 25 to 185°C and an average consumption of 250 W for maintaining the temperature reached for the 15 hours left.

For the drying process an average consumption of 185W for 12 hours was considered.

Energy usage:

Synthesis: $(1h \times 900W) + (15h \times 250W) = 4650\,Wh$ or 16.7 MJ

Drying process: $12h \times 185W = 2220\,Wh$ or 8.0 MJ

Total energy consumption: 16.7 MJ + 8.0 MJ = 24.7 MJ

Considering the amount of final product obtainable for the two perovskites:

$KCuF_3$: $\frac{24.7\ MJ}{4.05g} = 6.1\frac{MJ}{g}$

$KNiF_3$: $\frac{24.7\ MJ}{2.61g} = 9.5\frac{MJ}{g}$

Mechanochemical process

Atom Economy evaluation:
Considering the molecular weight of the reagents of the two solvothermal reaction and the two desired products it's possible to estimate the theoretical atom economy.

$Reagents\ MW = CuF_2 + KF = 101.54\frac{g}{mol} + 58.09\frac{g}{mol} = 159.63\frac{g}{mol}$

$KCuF_3\ molecular\ weight = 159.63\frac{g}{mol}$

$$AE\ KCuF_3 = \frac{159.63\frac{g}{mol}}{159.63\frac{g}{mol}} \times 100 = 100\%$$

$Reagents\ MW = NiF_2 + KF = 96.69\frac{g}{mol} + 58.09\frac{g}{mol} = 154.78\,\frac{g}{mol}$

$KNiF_3\ molecular\ weight = 154.78\frac{g}{mol}$

$$AE\ KNiF_3 = \frac{154.78\frac{g}{mol}}{154.78\frac{g}{mol}} \times 100 = 100\%$$

Process mass intensity (PMI) evaluation:
The total mass used in the process is the sum of the reagents and the solvent employed in the solvothermal synthesis.

$$PMI\ KCuF_3 = \frac{0.730g\ (KF) + 1.27g\ (CuF_2)}{2.0g\ (KCuF_3)} = 1.0$$

$$PMI\ KNiF_3 = \frac{0.750g\ (KF) + 1.25g\ (NiF_2)}{2.0g\ (KNiF_3)} = 1.0$$

Energy consumption evaluation:
For the mechanochemical process a TOB-ZQM Series from TOB NEW ENERGY has been employed. The specifications of the instrument are listed in the table below.

Tab 10. *Ball-miller parameters.*

Dimension	mm	600*400*500
weight	Kg	60
Ball milling tank volume	mL	50
Medium diameters	mm	5
Maximum revolution speed	rpm	450
Total power	W	550
Number of rotating jars		4

To evaluate the energy consumption of the ball miller it was considered a value of 420 W comparing the consumption of the ball miller at 350rpm knowing the consumption of 550 W at 450 rpm.

Energy usage:

Synthesis 3h: $3h \times 420W = 1280\ Wh$ or 4.6 MJ

Synthesis 6h: $6h \times 420W = 2560\ Wh$ or 9.2 MJ

Synthesis 12h: $12h \times 420W = 5130\ Wh$ or 18.5 MJ

Considering the implementation of 4 jars inside the ball miller it is possible to produce 7.96g of $KCuF_3$ and 7.96g of $KNiF_3$.

$KCuF_3$ and $KNiF_3$ 3h: $\frac{4.6\ MJ}{7.96g} = 0.58\frac{MJ}{g}$

$KCuF_3$ and $KNiF_3$ 6h: $\frac{9.2\ MJ}{7.96g} = 1.16\frac{MJ}{g}$

$KCuF_3$ and $KNiF_3$ 12h: $\frac{18.5\ MJ}{7.96g} = 2.32\frac{MJ}{g}$