Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supporting information on

Conversion reactions for sodium-ion batteries

Franziska Klein, Birte Jache, Amrtha Bhide, Philipp Adelhelm*

Institute of Physical Chemistry, Justus-Liebig-University Giessen, Heinrich-Buff-Ring 58, 35392 Giessen

Corresponding author: Dr. Philipp Adelhelm (philipp.adelhelm@uni-giessen.de)

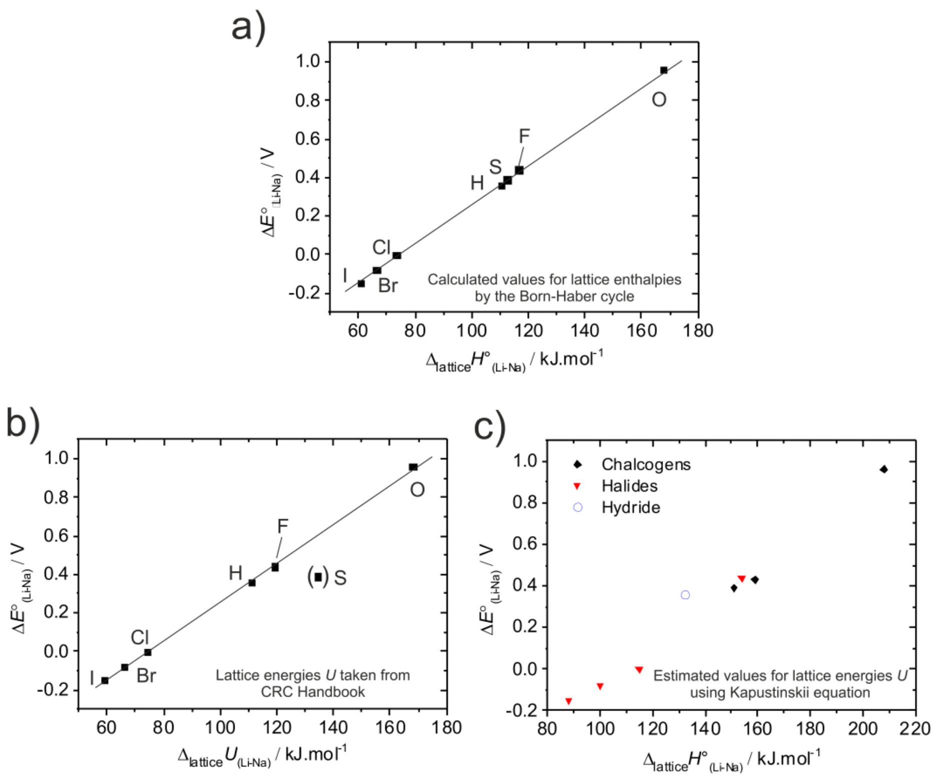

Figure S1

a) Differences in lattice enthalpies $\Delta_{lattice}H°_{(Li\text{-}Na)}$ and differences in cell potentials $\Delta E°_{(Li\text{-}Na)}$ for lithium and sodium based compounds (LiI/NaI, LiBr/NaBr, LiCl/NaCl, LiH/NaH, LiF/NaF, Li_2S/Na_2S, and Li_2O/Na_2O). Values for the lattice enthalpies were calculated by the Born-Haber cycle. Cell potentials have been calculated by using the thermodynamic database from HSC Chemistry 7.0.

As can be seen, a linear relationship between values for $\Delta_{lattice}H°_{(Li\text{-}Na)}$ and $\Delta E°_{(Li\text{-}Na)}$ exists (y=0.0103x-0.7655).

b) X-axis replaced by the differences in lattice energies $\Delta_{lattice}U_{(Li\text{-}Na)}$. Source for lattice energies *U*: CRC Handbook of Chemistry and Physics 84th edition, Chapter 12, page 22. Values for lattice enthalpies can be directly calculated from the lattice energies, however, the differences are negligible (< 0.5 % for the compounds discussed here). The linear behavior is in line with what is shown in a). Interestingly, Li_2S/Na_2S deviates from the linear correlation. This behavior cannot be explained so far but might be due to incorrect thermodynamic data for the reported lattice energies. Estimating the lattice energy by the Kapustinskii equation (c) shows no significant deviation from the linear relationship for sulfides.

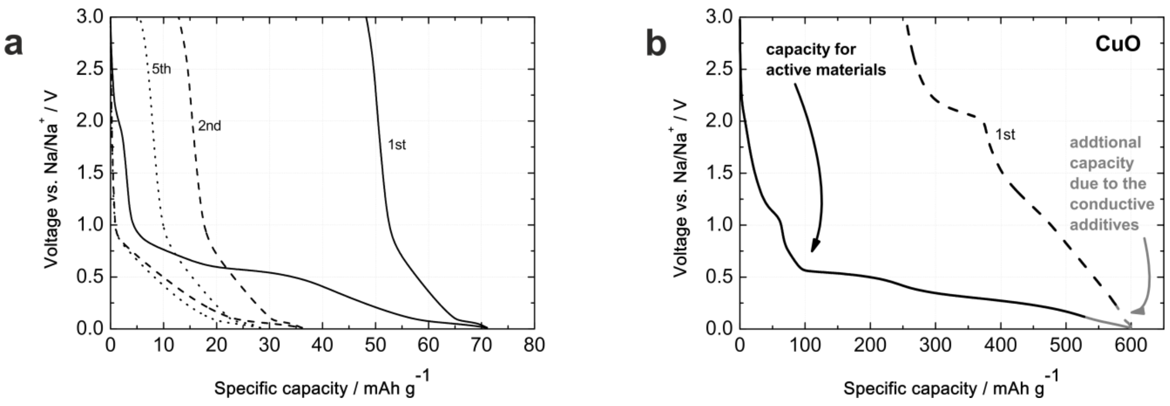

Figure S2 Contribution of the conductive additive (15wt% Super PLi and 10% SFG-44 graphite) to the overall capacity obtained for the CuO electrode.

a: Capacity of an electrode without CuO but the same weight ratio of Super PLi and SFG-44 as the one that is used for the conversion electrodes. The specific capacity has been normalized to the content that is present in the conversion electrode, i.e. 25wt%.

b: Graphical illustration of the amount of capacity that is due to the carbon additive. Upon discharge, the contribution is around 10 %. Upon charge and subsequent cycling, the contribution is below 10 %.

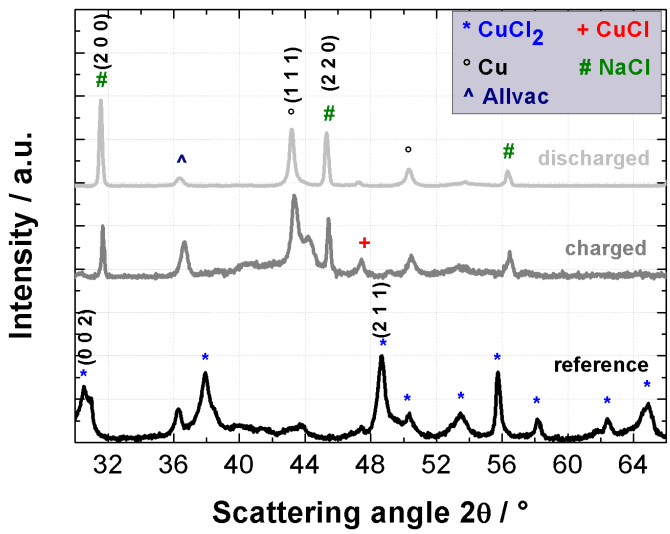

Figure S3 X-ray diffraction pattern of $CuCl_2$ electrodes before (reference) and after the first discharge and charge.

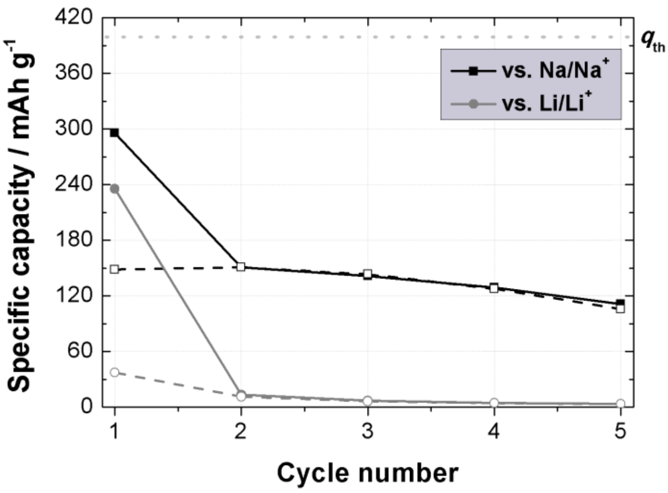

Figure S4 Cycling stability of conversion reactions of $CuCl_2$ with lithium and sodium.

Table S1: Additional thermodynamic data for lithium and sodium based conversion reactions. The theoretical capacity q [Ah.kg^{-1}] is calculated by $q_{th}=(z \cdot F)/(3.6 \cdot M)$ with z being the number of transferred electrons, F as Faraday constant and M as molar mass of the compound before conversion. The theoretical energy density w_{th} is calculated by $w_{th}=E° \cdot q$.
The general conversion reaction is

$$M_aX_b + (b \cdot c) \cdot A \rightleftharpoons a \cdot M + b \cdot A_cX$$

A= Li or Na

Values for $\Delta E°$(Li–Na) within a class of compounds (hydrides, oxides, sulfides, fluorides, chlorides, bromides, iodides) are always the same due to the following reactions.

Hydrides

$$Li + NaH \rightleftharpoons LiH + Na \quad \Delta_r G = -34.82\ kJ.mol^{-1};\ E° = +0.36\ V$$

Compound	z	q_{th} / Ah.kg^{-1}	$\Delta_r G$ / kJ.mol^{-1}		ΔE °/ V		ΔE°(Li–Na)	w_{th} / Wh.kg^{-1}	
			vs. Na/Na$^+$	vs. Li/Li$^+$	vs. Na/Na$^+$	vs. Li/Li$^+$		Na	Li
TiH_2	2	1074	38.03	− 31.62	− 0.20	0.16	0.36	− 110	138
CuH	1	415	− 88.68	− 123.9	0.92	1.28	0.36	281	480
MgH_2	2	2036	− 30.72	− 100.37	0.16	0.52	0.36	118	695
CaH_2	2	1273	+ 75.43	+ 5.78	− 0.39	− 0.03	0.36	− 238	− 29

Nitrides

Compound	z	q_{th} / Ah.kg^{-1}	$\Delta_r G$ / kJ.mol^{-1}		ΔE° / V		ΔE°(Li–Na)	w_{th} / Wh.kg^{-1}	
			vs. Na/Na$^+$	vs. Li/Li$^+$	vs. Na/Na$^+$	vs. Li/Li$^+$		Na	Li
TiN	3	1299	n/a	180.56	n/a	− 0.62	n/a	n/a	− 606
VN	3	1238	n/a	62.47	n/a	− 0.22	n/a	n/a	− 202
CrN	3	1218	n/a	− 35.8	n/a	0.12	n/a	n/a	115
Mn_4N	3	344	n/a	− 24.34	n/a	0.08	n/a	n/a	27
Mn_3N_2	6	834	n/a	− 110.75	n/a	0.19	n/a	n/a	131
Fe_4N	3	339	n/a	− 132.33	n/a	0.46	n/a	n/a	142
Co_3N	3	421	n/a	− 163.00	n/a	0.56	n/a	n/a	214
Ni_3N	3	423	n/a	− 155.47	n/a	0.54	n/a	n/a	205
Cu_3N	3	393	n/a	n/a	n/a	n/a	n/a	n/a	n/a

Phosphides

Compound	*z*	q_{th} / Ah.kg^{-1}	$\Delta_r G$ / kJ.mol^{-1}		ΔE °/ V		ΔE°(Li–Na)	w_{th} / Wh.kg^{-1}	
			vs. Na/Na$^+$	vs. Li/Li$^+$	vs. Na/Na$^+$	vs. Li/Li$^+$		Na	Li
CrP	3	969	− 67.41	n/a	0.23	n/a	n/a	123	n/a
MnP	3	936	− 62.87	n/a	0.22	n/a	n/a	113	n/a
FeP	3	926	− 91.87	n/a	0.32	n/a	n/a	164	n/a
FeP_2	6	1365	− 228.93	n/a	0.40	n/a	n/a	249	n/a
Fe_3P	3	405	− 28.87	n/a	0.10	n/a	n/a	0	n/a
Fe_2P	3	564	− 49.56	n/a	0.17	n/a	n/a	65	n/a
CoP	3	894	−40.59	n/a	0.14	n/a	n/a	71	n/a
CoP_3	3	1589	− 296.36	n/a	0.34	n/a	n/a	229	n/a
NiP_2	6	1333	− 252.88	n/a	0.44	n/a	n/a	272	n/a
NiP_3	9	1591	− 418.95	n/a	0.48	n/a	n/a	325	n/a
Ni_2P	3	542	− 14.49	n/a	0.05	n/a	n/a	19	n/a
CuP_2	6	1281	− 258.76	n/a	0.45	n/a	n/a	273	n/a
Cu_3P	3	363	− 14.99	n/a	0.05	n/a	n/a	14	n/a

Note: The standard free enthalpy of formation of Na_3P is an estimate taken from ref JM Sangster, Journal of Phase Equilibria and Diffusion, Vol. 31, No 1, 2010, pages 62-67

Oxides

$$2\cdot \mathrm{Li} + \mathrm{Na_2O} \rightleftarrows \mathrm{Li_2O} + 2\cdot \mathrm{Na} \qquad \Delta_r G = -184.85\ \mathrm{kJ.mol^{-1}};\ E° = +0.96\ \mathrm{V}$$

Compound	z	q_{th} / Ah.kg^{-1}	$\Delta_r G$ / kJ.mol^{-1}		$\Delta E°$ / V		$\Delta E°$(Li–Na)	w_{th} / Wh kg^{-1}	
			vs. Na/Na$^+$	vs. Li/Li$^+$	vs. Na/Na$^+$	vs. Li/Li$^+$		Na	Li
TiO_2	4	1342	137.00	− 232.88	− 0.35	0.60	0.96	− 221	601
VO_2	4	1293	− 93.37	− 463.07	0.24	1.20	0.96	148	1162
CrO_2	4	1276	− 223.24	− 592.93	0.58	1.54	0.96	352	1474
MnO	2	756	− 13.47	− 198.31	0.07	1.03	0.96	32	649
MnO_2	4	1233	− 287.48	− 657.18	0.74	1.70	0.96	446	1592
Mn_2O_3	6	1019	− 247.93	−802.47	0.43	1.39	0.96	233	1117
FeO	2	746	− 125.72	− 310.56	0.65	1.61	0.96	296	1006
Fe_2O_3	6	1007	− 384.66	− 939.20	0.66	1.62	0.96	359	1296
CoO	2	715	− 162.10	− 346.95	0.84	1.80	0.96	372	1085
Co_3O_4	8	891	− 710.30	− 1449.68	0.92	1.88	0.96	465	1359
NiO	2	718	− 164.72	− 349.56	0.85	1.81	0.96	379	1096
CuO	2	674	− 246.71	− 431.55	1.28	2.24	0.96	546	1283
Cu_2O	2	375	− 230.44	− 415.29	1.19	2.15	0.96	338	735
ZnO	2	659	− 58.15	− 243.00	0.30	1.26	0.96	129	724
RuO_2	4	806	− 499.94	− 869.64	1.30	2.25	0.96	617	1502
Al_2O_3	6	1577	453.51	− 101.17	− 0.78	0.17	0.96	− 525	196
Ga_2O_3	6	858	− 130.51	− 685.05	0.23	1.18	0.96	111	831
In_2O_3	6	579	− 298.17	− 852.71	0.52	1.47	0.96	199	742

Sulfides

$$2\cdot Li + Na_2S \rightleftarrows Li_2S + 2\cdot Na \qquad \Delta_r G = -74.80\ kJ.mol^{-1};\ E° = +0.39\ V$$

Compound	z	q_{th} / Ah.kg^{-1}	$\Delta_r G$ / kJ.mol^{-1}		$\Delta E°$ / V		$\Delta E°$(Li–Na)	w_{th} / Wh.kg^{-1}	
			vs. Na/Na$^+$	vs. Li/Li$^+$	vs. Na/Na$^+$	vs. Li/Li$^+$		Na	Li
TiS_2	4	957	− 320.46	− 470.06	0.83	1.22	0.39	436	934
MnS	2	616	− 138.57	− 213.37	0.72	1.11	0.39	289	588
MnS_2	4	900	− 488.78	− 638.38	1.27	1.65	0.39	643	1208
FeS	2	610	− 257.48	− 332.28	1.33	1.72	0.39	534	907
FeS_2	4	894	− 548.77	− 698.38	1.42	1.81	0.39	719	1313
Co_3S_4	8	703	− 1095.73	− 1394.94	1.42	1.81	0.39	622	1075
CoS	2	589	− 261.00	− 335.80	1.35	1.74	0.39	529	889
NiS	2	591	− 266.41	− 341.21	1.38	1.77	0.39	541	906
Ni_3S_2	4	446	− 505.20	− 654.80	1.31	1.70	0.39	422	679
CuS	2	561	− 304.02	− 378.82	1.58	1.96	0.39	596	961
Cu_2S	2	337	− 269.15	− 343.95	1.39	1.78	0.39	364	552
ZnS	2	550	− 159.25	− 234.06	0.83	1.21	0.39	308	584
Al_2S_3	6	1071	− 435.51	− 659.92	0.75	1.14	0.39	420	956
Ga_2S_3	6	682	− 567.56	− 791.97	0.98	1.37	0.39	422	793
In_2S_3	6	494	− 731.95	− 956.36	1.26	1.65	0.39	438	723

Fluorides

$$Li + NaF \rightleftarrows LiF + Na \quad \Delta_r G = -42.31\ kJ.mol^{-1};\ E° = +0.44\ V$$

Compound	z	q_{th} / Ah.kg^{-1}	$\Delta_r G$ / kJ.mol^{-1}		$\Delta E°$ / V		$\Delta E°$(Li–Na)	w_{th} / Wh.kg^{-1}	
			vs. Na/Na$^+$	vs. Li/Li$^+$	vs. Na/Na$^+$	vs. Li/Li$^+$		Na	Li
ScF_3	3	789	− 99.18	− 226.10	0.34	0.78	0.44	161	512
TiF_3	3	767	− 277.17	− 404.09	0.96	1.40	0.44	443	893
VF_2	2	603	− 146.77	− 231.38	0.76	1.20	0.44	302	625
VF_3	3	745	− 412.54	− 539.46	1.43	1.86	0.44	648	1164
CrF_3	3	738	− 548.75	− 675.67	1.89	2.33	0.44	856	1446
MnF_2	2	577	− 280.24	− 364.86	1.45	1.89	0.44	560	949
FeF_2	2	571	− 424.06	− 508.68	2.20	2.64	0.44	842	1312
FeF_3	3	712	− 714.06	− 840.98	2.47	2.91	0.44	1091	1748
CoF_2	2	553	− 464.67	− 549.28	2.41	2.85	0.44	903	1377
NiF_2	2	554	− 482.81	− 567.42	2.50	2.94	0.44	940	1425
CuF_2	2	528	− 597.13	− 681.74	3.09	3.53	0.44	1124	1641
ZnF_2	2	518	− 379.19	− 463.81	1.96	2.40	0.44	705	1099

Chlorides

$$Li + NaCl \rightleftarrows LiCl + Na \quad \Delta_r G = +0.07\ kJ.mol^{-1};\ E° = -0.0007\ V$$

Compound	z	q_{th} / Ah.kg^{-1}	$\Delta_r G$ / kJ.mol^{-1}		$\Delta E°$ / V		$\Delta E°$(Li–Na)	w_{th} / Wh.kg^{-1}	
			vs. Na/Na$^+$	vs. Li/Li$^+$	vs. Na/Na$^+$	vs. Li/Li$^+$		Na	Li
$ScCl_3$	3	531	− 299.32	− 299.12	1.03	1.03	0.00	377	483
$TiCl_4$	4	565	− 801.12	− 800.86	2.08	2.08	0.00	1018	1023
VCl_2	2	440	− 362.64	− 362.51	1.88	1.88	0.00	600	742
VCl_3	3	511	− 640.93	− 640.73	2.21	2.21	0.00	787	999
$MnCl_2$	2	426	− 327.73	− 327.59	1.70	1.70	0.00	530	651
$FeCl_2$	2	423	− 466.26	− 466.16	2.42	2.42	0.00	750	921
$FeCl_3$	3	496	− 818.22	− 818.02	2.83	2.83	0.00	983	1242
$CoCl_2$	2	413	− 498.56	− 498.43	2.58	2.58	0.00	788	963
$NiCl_2$	2	414	− 509.10	− 508.97	2.64	2.64	0.00	805	985
$CuCl$	1	271	− 264.52	− 264.45	2.74	2.74	0.00	602	693
$CuCl_2$	2	399	− 593.22	− 593.09	3.07	3.07	0.00	913	1111
$ZnCl_2$	2	393	− 397.83	− 397.70	2.06	2.06	0.00	606	736

Bromides

$$\text{Li} + \text{NaBr} \rightleftarrows \text{LiBr} + \text{Na} \quad \Delta_r G = +7.24\ \text{kJ.mol}^{-1};\ E° = -0.08\ \text{V}$$

Compound	z	q_{th} / Ah.kg^{-1}	$\Delta_r G$ / kJ.mol^{-1}		$\Delta E°$ / V		$\Delta E°$(Li–Na)	w_{th} / Wh.kg^{-1}	
			vs. Na/Na$^+$	vs. Li/Li$^+$	vs. Na/Na$^+$	vs. Li/Li$^+$		Na	Li
$ScBr_3$	3	282	− 329.81	− 308.10	1.14	1.06	− 0.08	259	280
$TiBr_4$	4	292	− 805.66	− 776.71	2.09	2.01	− 0.08	487	546
VBr_2	2	277	− 350.34	− 335.86	1.82	1.74	− 0.08	379	415
VBr_3	3	291	− 633.87	− 612.15	2.19	2.11	− 0.08	447	546
$CrBr_3$	3	276	− 674.75	− 653.04	2.33	2.26	− 0.08	520	580
$MnBr_2$	2	250	− 327.08	− 312.6	1.69	1.62	− 0.08	348	380
$FeBr_2$	2	249	− 460.85	− 446.37	2.39	2.31	− 0.08	489	540
$FeBr_3$	3	272	− 802.39	− 780.67	2.77	2.70	− 0.08	611	685
$CoBr_2$	2	245	− 496.87	− 482.39	2.57	2.50	− 0.08	521	576
$NiBr_2$	2	245	− 504.07	−489.59	2.61	2.54	− 0.08	529	585
CuBr	1	187	− 248.01	−240.76	2.57	2.50	− 0.08	414	445
$CuBr_2$	2	240	− 576.19	− 561.71	2.99	2.91	− 0.08	594	658
$ZnBr_2$	2	238	− 385.69	− 371.21	2.00	1.92	− 0.08	395	431

Iodides

$$\text{Li} + \text{NaI} \rightleftarrows \text{LiI} + \text{Na} \quad \Delta_r G = +14.33\ \text{kJ.mol}^{-1};\ E° = -0.15\ \text{V}$$

Compound	z	q_{th} / Ah.kg^{-1}	$\Delta_r G$ / kJ.mol^{-1}		$\Delta E°$ / V		$\Delta E°$(Li–Na)	w_{th} / Wh.kg^{-1}	
			vs. Na/Na$^+$	vs. Li/Li$^+$	vs. Na/Na$^+$	vs. Li/Li$^+$		Na	Li
ScI_3	3	189	− 291.96	− 248.92	1.01	0.86	− 0.15	164	156
TiI_4	4	193	− 767.74	− 710.44	1.99	1.84	− 0.15	329	338
VI_2	2	176	− 305.18	− 276.53	1.58	1.43	− 0.15	242	241
VI_3	3	186	− 573.51	− 530.54	1.98	1.83	− 0.15	318	326
MnI_2	2	174	− 325.84	− 297.19	1.69	1.54	− 0.15	255	256
FeI_2	2	173	− 457.44	− 428.79	2.37	2.22	− 0.15	357	368
FeI_3	3	184	− 747.02	− 704.04	2.58	2.43	− 0.15	410	428
CoI_2	2	171	− 474.05	− 445.40	2.46	2.31	− 0.15	367	379
NiI_2	2	172	− 474.95	− 446.30	2.46	2-31	− 0.15	368	380
CuI	1	140	− 215.36	− 201.03	2.23	2.08	− 0.15	280	283
ZnI_2	2	168	− 358.91	− 330.26	1.86	1.71	− 0.15	273	275

Table S2: Volume expansion for a series of lithium (A = Li) and sodium (A = Na) based conversion reactions.

$$M_aX_b + (b \cdot c)\,A \rightleftarrows a \cdot M + b \cdot A_cX$$

$$\text{volume expansion (\%)} = 100 \cdot \left(\frac{V(b \cdot A_cX) + V(a \cdot M)}{V(M_aX_b)} \right) - 100$$

Hydrides

Compound	Volume expansion / %	
	Na	Li
TiH_2	239.3	125.5
MgH_2	167.2	83.8
CaH_2	144.3	82.7

Nitrides

Compound	Volume expansion / %	
	Na	Li
TiN	n/a	220.9
VN	n/a	239.5
CrN	n/a	209.8
Mn_4N	n/a	n/a
Mn_3N_2	n/a	n/a
Fe_4N	n/a	54.6
Co_3N	n/a	n/a
Ni_3N	n/a	n/a
Cu_3N	n/a	n/a

Phosphides

Compound	Volume expansion / %	
	Na	Li
CrP	327.9	217.7
MnP	314.3	207.8
FeP	n/a	n/a
FeP_2	429.2	284.6
Fe_3P	167.4	110.8
Fe_2P	241.5	162.1
CoP	374.7	251.4
Co_3P	n/a	n/a
NiP_2	392.3	257.3
NiP_3	n/a	n/a
Ni_2P	248.9	166.6
CuP_2	308.2	196.7
Cu_3P	130.9	82.0

Oxides

Compound	Volume expansion / %	
	Na	Li
TiO_2	245.4	113.5
VO_2	230.4	100.0
CrO_2	260.0	114.9
MnO	162.7	68.3
MnO_2	262.3	116.7
Mn_2O_3	176	69
FeO	187.4	83.3
Fe_2O_3	215.4	92.8
CoO	192.3	85.0
Co_3O_4	227.8	101.3
NiO	205.0	92.9
CuO	172.8	74.0
Cu_2O	74.0	21.7
ZnO	151.2	65.3
RuO_2	190.0	100.5
Al_2O_3	296.2	150.9
Ga_2O_3	262.5	134.1
In_2O_3	193.0	96.4

Sulfides

Compound	Volume expansion / %	
	Na	Li
TiS_2	185.0	100.5
MnS	127.3	62.8
MnS_2	166.1	84.5
FeS	165.0	89.4
FeS_2	281.6	164.2
Co_3S_4	199.8	110.3
CoS	191.7	107.6
NiS	193.2	108.6
Ni_3S_2	153.8	85.3
CuS	144.7	74.8
Cu_2S	97.9	48.5
ZnS	109.1	51.8
Al_2S_3	96.6	40.0
Ga_2S_3	132.0	66.7
In_2S_3	115.2	58.7

Fluorides

Compound	Volume expansion / %	
	Na	Li
ScF_3	55.1	14.5
TiF_3	58.9	14.1
VF_2	72.1	25.4
VF_3	67.8	18.6
CrF_3	83.2	28.2
MnF_2	61.0	16.0
FeF_2	62.6	16.8
FeF_3	79.8	25.6
CoF_2	69.6	21.2
NiF_2	78.9	27.8
CuF_2	55.4	11.6
ZnF_2	88.5	38.1

Chlorides

Compound	Volume expansion / %	
	Na	Li
$ScCl_3$	51.7	20.9
$TiCl_4$	n/a	n/a
VCl_2	65.8	31.3
VCl_3	70.8	33.6
$MnCl_2$	45.2	14.5
$FeCl_2$	52.3	19.9
$FeCl_3$	57.4	22.6
$CoCl_2$	56.7	23.2
$NiCl_2$	65.9	30.4
$CuCl_2$	53.8	21.1
CuCl	42.5	15.4
$ZnCl_2$	34.8	7.0

Bromides

Compound	Volume expansion / %	
	Na	Li
$ScBr_3$	53.2	24.1
$TiBr_4$	27.6	1.7
VBr_2	58.2	27.5
VBr_3	44.4	15.3
$CrBr_3$	66.2	32.3
$MnBr_2$	46.3	17.5
$FeBr_2$	53.4	23.1
$FeBr_3$	57.5	25.3
$CoBr_2$	59.1	27.5
$NiBr_2$	65.3	32.4
CuBr	36.1	11.7
$CuBr_2$	52.4	22.2
$ZnBr_2$	46.7	18.5

Iodides

Compound	Volume expansion / %	
	Na	Li
ScI_3	52.3	25.8
TiI_4	54.0	27.4
VI_2	61.5	32.0
VI_3	58.6	29.7
CrI_3	48.7	22.0
MnI_2	45.8	19.7
FeI_2	52.4	20.0
CoI_2	60.8	31.8
NiI_2	65.1	35.3
CuI	43.0	19.3
ZnI_2	35.1	11.4