**Electronic Supporting Information**

Revision 1

# Cryogenic Heat Capacity Measurements and Thermodynamic Analysis of Lithium Aluminum Layered Double Hydroxides (LDHs) with Intercalated Chloride

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**Table S1.** Measured molar heat capacity values at constant pressure for LDH 1, using the formula $LiAl_2(OH)_6Cl{\cdot}3.20H_2O$, after subtracting off the 0.36 mol LiCl secondary phase. Note that this subtraction introduces greater error into this measurement since we do not know the hydration level of the LiCl phase. Measurements were performed using a Quantum Design Physical Property Measurement System (PPMS) with a standard uncertainty of 2% $C_{p,m}$ below about $T$ = 10 K and 1% $C_{p,m}$ from $T$ = (10 to 300) K. The standard uncertainty in temperature is about 4 mK.

| $T$ (K) | $C_{p,m}$ ($J{\cdot}K^{-1}{\cdot}mol^{-1}$) | $T$ (K) | $C_{p,m}$ ($J{\cdot}K^{-1}{\cdot}mol^{-1}$) | $T$ (K) | $C_{p,m}$ ($J{\cdot}K^{-1}{\cdot}mol^{-1}$) |
|---|---|---|---|---|---|
| 1.8411 | $6.9688{\cdot}10^{-3}$ | 7.8005 | 0.31792 | 77.232 | 63.581 |
| 1.9156 | $7.4861{\cdot}10^{-3}$ | 8.1397 | 0.36264 | 84.377 | 73.386 |
| 1.9865 | $8.0129{\cdot}10^{-3}$ | 8.4989 | 0.41585 | 92.246 | 83.768 |
| 2.0621 | $8.8753{\cdot}10^{-3}$ | 8.8758 | 0.47944 | 100.81 | 93.636 |
| 2.1429 | 0.010642 | 9.2698 | 0.55035 | 110.91 | 106.07 |
| 2.2306 | 0.011246 | 9.6829 | 0.63265 | 120.96 | 119.56 |
| 2.3221 | 0.011950 | 10.136 | 0.72863 | 131.08 | 132.11 |
| 2.4153 | 0.013265 | 10.626 | 0.84097 | 141.16 | 144.90 |
| 2.5147 | 0.013989 | 11.115 | 0.96201 | 151.21 | 158.44 |
| 2.6206 | 0.015595 | 11.614 | 1.0982 | 161.32 | 171.29 |
| 2.7306 | 0.016573 | 12.129 | 1.2521 | 171.42 | 183.69 |
| 2.8576 | 0.018849 | 12.663 | 1.4230 | 181.50 | 196.20 |
| 2.9907 | 0.020766 | 13.224 | 1.6234 | 191.60 | 209.12 |
| 3.1257 | 0.023742 | 13.812 | 1.8399 | 201.71 | 222.50 |
| 3.2640 | 0.025679 | 14.429 | 2.0849 | 211.80 | 234.91 |
| 3.4091 | 0.028713 | 15.071 | 2.3555 | 221.90 | 247.41 |
| 3.5582 | 0.032413 | 15.578 | 2.5844 | 232.00 | 259.65 |
| 3.7170 | 0.036475 | 17.020 | 3.2793 | 242.12 | 272.39 |
| 3.8799 | 0.041325 | 18.604 | 4.1255 | 252.19 | 284.84 |
| 4.0601 | 0.046374 | 20.291 | 5.1285 | 262.30 | 296.20 |
| 4.2437 | 0.051315 | 22.224 | 6.3494 | 272.39 | 307.10 |
| 4.4317 | 0.058815 | 24.294 | 7.7610 | 282.46 | 317.23 |
| 4.6255 | 0.066504 | 26.559 | 9.4601 | 292.51 | 325.40 |
| 4.8330 | 0.076823 | 29.028 | 11.410 | 302.59 | 332.14 |
| 5.0458 | 0.084120 | 31.729 | 13.677 | | |
| 5.2730 | 0.096585 | 34.677 | 16.367 | | |
| 5.5080 | 0.10856 | 37.914 | 19.426 | | |
| 5.7494 | 0.12509 | 41.435 | 22.863 | | |
| 6.0031 | 0.14396 | 45.302 | 26.951 | | |
| 6.2676 | 0.16085 | 49.521 | 31.297 | | |
| 6.5458 | 0.18279 | 54.120 | 36.472 | | |
| 6.8378 | 0.21324 | 59.151 | 42.169 | | |
| 7.1400 | 0.24035 | 64.647 | 48.495 | | |
| 7.4565 | 0.27430 | 70.656 | 55.473 | | |

**Table S2.** Measured molar heat capacity values at constant pressure for LDH 2. Measurements were performed using a Quantum Design Physical Property Measurement System (PPMS) with a standard uncertainty of 2% $C_{p,m}$ below about $T$ = 10 K and 1% $C_{p,m}$ from $T$ = (10 to 300) K. The standard uncertainty in temperature is about 4 mK.

| $T$ (K) | $C_{p,m}$ (J·K$^{-1}$·mol$^{-1}$) | $T$ (K) | $C_{p,m}$ (J·K$^{-1}$·mol$^{-1}$) | $T$ (K) | $C_{p,m}$ (J·K$^{-1}$·mol$^{-1}$) |
|---|---|---|---|---|---|
| 1.8326 | $5.6069\cdot10^{-3}$ | 7.7850 | 0.20400 | 77.223 | 57.512 |
| 1.9003 | $5.9423\cdot10^{-3}$ | 8.1328 | 0.24128 | 84.368 | 66.686 |
| 1.9739 | $6.5680\cdot10^{-3}$ | 8.4917 | 0.26626 | 92.229 | 76.745 |
| 2.0527 | $6.9012\cdot10^{-3}$ | 8.8742 | 0.30550 | 100.80 | 86.254 |
| 2.1378 | $7.9444\cdot10^{-3}$ | 9.2682 | 0.34622 | 110.89 | 98.338 |
| 2.2371 | $9.0172\cdot10^{-3}$ | 9.6793 | 0.41322 | 120.94 | 111.23 |
| 2.3335 | $9.7876\cdot10^{-3}$ | 10.121 | 0.46677 | 131.05 | 123.34 |
| 2.4359 | 0.010573 | 10.601 | 0.54434 | 141.15 | 135.52 |
| 2.5408 | 0.011447 | 11.097 | 0.62866 | 151.20 | 148.29 |
| 2.6433 | 0.012277 | 11.606 | 0.72542 | 161.31 | 160.34 |
| 2.7650 | 0.013279 | 12.123 | 0.83618 | 171.40 | 171.84 |
| 2.8858 | 0.014756 | 12.659 | 0.96089 | 181.48 | 183.22 |
| 3.0116 | 0.015789 | 13.216 | 1.1041 | 191.58 | 194.66 |
| 3.1421 | 0.017330 | 13.805 | 1.2661 | 201.69 | 206.39 |
| 3.2795 | 0.018884 | 14.419 | 1.4490 | 211.79 | 217.09 |
| 3.4253 | 0.022433 | 15.066 | 1.6572 | 221.88 | 227.32 |
| 3.5728 | 0.024789 | 15.573 | 1.8335 | 231.98 | 237.01 |
| 3.7284 | 0.028072 | 17.013 | 2.3838 | 242.08 | 246.66 |
| 3.8914 | 0.031650 | 18.597 | 3.0651 | 252.17 | 256.40 |
| 4.0663 | 0.033716 | 20.283 | 3.8896 | 262.27 | 265.86 |
| 4.2450 | 0.037408 | 22.213 | 4.9065 | 272.39 | 274.30 |
| 4.4351 | 0.041681 | 24.284 | 6.1060 | 282.48 | 284.69 |
| 4.6275 | 0.045849 | 26.551 | 7.5551 | 292.58 | 293.40 |
| 4.8313 | 0.052781 | 29.018 | 9.2286 | 302.67 | 302.22 |
| 5.0523 | 0.060470 | 31.722 | 11.213 | | |
| 5.2734 | 0.067341 | 34.673 | 13.572 | | |
| 5.5065 | 0.074154 | 37.904 | 16.283 | | |
| 5.7491 | 0.085116 | 41.432 | 19.383 | | |
| 6.0018 | 0.093764 | 45.294 | 23.070 | | |
| 6.2708 | 0.10729 | 49.511 | 27.036 | | |
| 6.5448 | 0.12802 | 54.111 | 31.789 | | |
| 6.8374 | 0.13718 | 59.139 | 37.134 | | |
| 7.1391 | 0.15725 | 64.637 | 43.117 | | |
| 7.4559 | 0.17870 | 70.645 | 49.751 | | |

**Table S3.** Measured molar heat capacity values at constant pressure for LDH 3. Measurements were performed using a Quantum Design Physical Property Measurement System (PPMS) with a standard uncertainty of 2% $C_{p,m}$ below about $T$ = 10 K and 1% $C_{p,m}$ from $T$ = (10 to 300) K. The standard uncertainty in temperature is about 4 mK.

| $T$ (K) | $C_{p,m}$ (J·K$^{-1}$·mol$^{-1}$) | $T$ (K) | $C_{p,m}$ (J·K$^{-1}$·mol$^{-1}$) | $T$ (K) | $C_{p,m}$ (J·K$^{-1}$·mol$^{-1}$) |
|---|---|---|---|---|---|
| 1.8518 | $5.9742\cdot10^{-3}$ | 7.7932 | 0.30151 | 77.206 | 59.013 |
| 1.9236 | $6.5697\cdot10^{-3}$ | 8.1301 | 0.34876 | 84.334 | 68.035 |
| 1.9952 | $7.4268\cdot10^{-3}$ | 8.4869 | 0.40002 | 92.213 | 77.510 |
| 2.0703 | $8.2167\cdot10^{-3}$ | 8.8636 | 0.46539 | 100.77 | 86.219 |
| 2.1497 | $8.5120\cdot10^{-3}$ | 9.2578 | 0.53421 | 110.86 | 97.413 |
| 2.2344 | $9.7576\cdot10^{-3}$ | 9.6697 | 0.61547 | 121.01 | 109.39 |
| 2.3279 | 0.010526 | 10.131 | 0.71575 | 131.06 | 120.87 |
| 2.4183 | 0.011423 | 10.623 | 0.83355 | 141.13 | 132.56 |
| 2.5170 | 0.012600 | 11.111 | 0.95445 | 151.19 | 145.18 |
| 2.6243 | 0.013226 | 11.606 | 1.0852 | 161.29 | 157.30 |
| 2.7287 | 0.015869 | 12.119 | 1.2413 | 171.38 | 169.40 |
| 2.8603 | 0.016658 | 12.651 | 1.4168 | 181.46 | 181.75 |
| 2.9855 | 0.018953 | 13.215 | 1.6131 | 191.55 | 194.74 |
| 3.1247 | 0.020112 | 13.802 | 1.8291 | 201.65 | 208.34 |
| 3.2628 | 0.022276 | 14.421 | 2.0685 | 211.73 | 222.18 |
| 3.4059 | 0.025925 | 15.061 | 2.3379 | 221.82 | 236.06 |
| 3.5545 | 0.027599 | 15.564 | 2.5650 | 231.93 | 248.63 |
| 3.7105 | 0.032147 | 17.004 | 3.2518 | 242.01 | 259.22 |
| 3.8746 | 0.035645 | 18.589 | 4.0764 | 252.09 | 268.53 |
| 4.0467 | 0.041605 | 20.283 | 5.0425 | 262.17 | 276.75 |
| 4.2298 | 0.044979 | 22.210 | 6.2502 | 272.26 | 284.18 |
| 4.4287 | 0.051368 | 24.277 | 7.6186 | 282.31 | 292.06 |
| 4.6204 | 0.057895 | 26.540 | 9.2446 | 292.36 | 298.02 |
| 4.8257 | 0.064680 | 29.009 | 11.131 | 302.39 | 299.95 |
| 5.0377 | 0.076033 | 31.700 | 13.305 | | |
| 5.2630 | 0.085962 | 34.664 | 15.879 | | |
| 5.5021 | 0.097982 | 37.890 | 18.788 | | |
| 5.7420 | 0.11226 | 41.417 | 21.990 | | |
| 5.9943 | 0.12939 | 45.279 | 25.846 | | |
| 6.2588 | 0.14675 | 49.497 | 29.741 | | |
| 6.5364 | 0.16990 | 54.097 | 34.516 | | |
| 6.8279 | 0.19638 | 59.123 | 39.679 | | |
| 7.1306 | 0.22661 | 64.622 | 45.410 | | |
| 7.4471 | 0.25704 | 70.629 | 51.653 | | |

**Table S4.** Measured molar heat capacity values at constant pressure for LDH 4. Measurements were performed using a Quantum Design Physical Property Measurement System (PPMS) with a standard uncertainty of 2% $C_{p,m}$ below about $T$ = 10 K and 1% $C_{p,m}$ from $T$ = (10 to 300) K. The standard uncertainty in temperature is about 4 mK.

| $T$ (K) | $C_{p,m}$ (J·K$^{-1}$·mol$^{-1}$) | $T$ (K) | $C_{p,m}$ (J·K$^{-1}$·mol$^{-1}$) | $T$ (K) | $C_{p,m}$ (J·K$^{-1}$·mol$^{-1}$) |
|---|---|---|---|---|---|
| 1.8478 | 0.026739 | 7.8865 | 0.19490 | 77.340 | 45.599 |
| 1.9172 | 0.026208 | 8.2353 | 0.22590 | 84.487 | 52.569 |
| 1.9969 | 0.026052 | 8.6008 | 0.25192 | 92.357 | 60.266 |
| 2.0796 | 0.026008 | 8.9818 | 0.28774 | 100.92 | 67.738 |
| 2.1666 | 0.025410 | 9.3789 | 0.32875 | 111.01 | 77.131 |
| 2.2596 | 0.025003 | 9.7939 | 0.37646 | 121.06 | 87.279 |
| 2.3571 | 0.024909 | 10.236 | 0.43887 | 131.18 | 96.615 |
| 2.4578 | 0.024283 | 10.698 | 0.49674 | 141.26 | 106.28 |
| 2.5629 | 0.024957 | 11.175 | 0.56892 | 151.33 | 116.22 |
| 2.6759 | 0.023646 | 11.672 | 0.65032 | 161.45 | 125.78 |
| 2.7941 | 0.024527 | 12.189 | 0.75030 | 171.55 | 134.65 |
| 2.9153 | 0.025193 | 12.727 | 0.86940 | 181.63 | 144.09 |
| 3.0451 | 0.024902 | 13.292 | 0.99695 | 191.72 | 152.99 |
| 3.1796 | 0.027077 | 13.881 | 1.1482 | 201.83 | 161.26 |
| 3.3203 | 0.027144 | 14.497 | 1.3157 | 211.93 | 169.61 |
| 3.4672 | 0.030216 | 15.138 | 1.5078 | 222.04 | 177.27 |
| 3.6181 | 0.031603 | 15.645 | 1.6688 | 232.14 | 184.85 |
| 3.7767 | 0.034181 | 17.091 | 2.1783 | 242.22 | 192.07 |
| 3.9465 | 0.035547 | 18.679 | 2.8016 | 252.30 | 199.47 |
| 4.1230 | 0.038216 | 20.400 | 3.5581 | 262.40 | 206.34 |
| 4.3076 | 0.043573 | 22.309 | 4.4899 | 272.52 | 211.99 |
| 4.4974 | 0.046543 | 24.387 | 5.5474 | 282.60 | 218.71 |
| 4.6949 | 0.050762 | 26.652 | 6.8339 | 292.70 | 225.71 |
| 4.9000 | 0.055596 | 29.125 | 8.2953 | 302.81 | 231.59 |
| 5.1157 | 0.062617 | 31.828 | 9.9751 | | |
| 5.3418 | 0.068478 | 34.784 | 11.902 | | |
| 5.5782 | 0.075793 | 38.017 | 14.074 | | |
| 5.8246 | 0.085537 | 41.546 | 16.609 | | |
| 6.0849 | 0.095119 | 45.405 | 19.480 | | |
| 6.3525 | 0.10606 | 49.618 | 22.480 | | |
| 6.6321 | 0.11888 | 54.220 | 25.958 | | |
| 6.9350 | 0.13973 | 59.256 | 30.047 | | |
| 7.2340 | 0.15185 | 64.754 | 34.621 | | |
| 7.5533 | 0.17260 | 70.763 | 39.615 | | |

**Table S5.** Measured molar heat capacity values at constant pressure for LDH 5. Measurements were performed using a Quantum Design Physical Property Measurement System (PPMS) with a standard uncertainty of 2% $C_{p,m}$ below about $T$ = 10 K and 1% $C_{p,m}$ from $T$ = (10 to 300) K. The standard uncertainty in temperature is about 4 mK.

| $T$ (K) | $C_{p,m}$ (J·K$^{-1}$·mol$^{-1}$) | $T$ (K) | $C_{p,m}$ (J·K$^{-1}$·mol$^{-1}$) | $T$ (K) | $C_{p,m}$ (J·K$^{-1}$·mol$^{-1}$) |
|---|---|---|---|---|---|
| 1.8544 | 0.027132 | 7.8887 | 0.22121 | 77.367 | 44.266 |
| 1.9206 | 0.027196 | 8.2379 | 0.24886 | 84.517 | 50.893 |
| 2.0003 | 0.027837 | 8.6030 | 0.28090 | 92.386 | 58.104 |
| 2.0829 | 0.027882 | 8.9840 | 0.31599 | 100.95 | 65.441 |
| 2.1700 | 0.028258 | 9.3803 | 0.35806 | 111.04 | 74.363 |
| 2.2626 | 0.028246 | 9.7954 | 0.40632 | 121.09 | 83.850 |
| 2.3603 | 0.028284 | 10.243 | 0.46491 | 131.21 | 92.805 |
| 2.4610 | 0.028934 | 10.705 | 0.52752 | 141.29 | 101.78 |
| 2.5661 | 0.030114 | 11.182 | 0.59911 | 151.35 | 110.99 |
| 2.6742 | 0.030990 | 11.677 | 0.67977 | 161.48 | 119.71 |
| 2.7903 | 0.030605 | 12.195 | 0.77771 | 171.59 | 128.13 |
| 2.9105 | 0.031634 | 12.733 | 0.89021 | 181.67 | 136.52 |
| 3.0405 | 0.033858 | 13.298 | 1.0208 | 191.75 | 144.67 |
| 3.1760 | 0.035086 | 13.886 | 1.1641 | 201.83 | 152.48 |
| 3.3185 | 0.038113 | 14.503 | 1.3332 | 211.96 | 159.93 |
| 3.4650 | 0.039363 | 15.145 | 1.5184 | 222.06 | 166.89 |
| 3.6199 | 0.042185 | 15.652 | 1.6717 | 232.15 | 173.81 |
| 3.7758 | 0.044612 | 17.099 | 2.1589 | 242.24 | 180.46 |
| 3.9450 | 0.047917 | 18.687 | 2.7679 | 252.33 | 187.30 |
| 4.1205 | 0.051057 | 20.410 | 3.5175 | 262.43 | 193.33 |
| 4.3046 | 0.057219 | 22.318 | 4.3945 | 272.54 | 199.03 |
| 4.4937 | 0.060665 | 24.402 | 5.3874 | 282.64 | 204.81 |
| 4.6904 | 0.066326 | 26.662 | 6.6018 | 292.73 | 210.33 |
| 4.8963 | 0.070938 | 29.136 | 8.0301 | 302.84 | 215.52 |
| 5.1172 | 0.078697 | 31.843 | 9.6435 | | |
| 5.3387 | 0.086146 | 34.802 | 11.517 | | |
| 5.5776 | 0.094097 | 38.040 | 13.646 | | |
| 5.8260 | 0.10301 | 41.568 | 16.065 | | |
| 6.0851 | 0.11534 | 45.426 | 18.850 | | |
| 6.3544 | 0.12829 | 49.642 | 21.855 | | |
| 6.6335 | 0.14150 | 54.247 | 25.261 | | |
| 6.9276 | 0.15754 | 59.282 | 29.261 | | |
| 7.2334 | 0.17546 | 64.781 | 33.651 | | |
| 7.5543 | 0.19742 | 70.790 | 38.496 | | |

**Table S6.** Parameters for low $T$ (< 11 K), mid $T$ (5 K < $T$ < 60 K), and high $T$ ($T$ > 40 K) fits of heat capacity data (in J· K$^{-1}$· mol$^{-1}$) for LDH 1, LDH 2, and LDH 3.

| | Parameter | LDH 1 | LDH 2 | LDH 3 |
|---|---|---|---|---|
| Low $T$ Fits | $\gamma$ (J·K$^{-2}$·mol$^{-1}$) | $2.0531 \cdot 10^{-3}$ | $1.8317 \cdot 10^{-3}$ | $1.8619 \cdot 10^{-3}$ |
| | $B_3$ (J·K$^{-4}$·mol$^{-1}$) | $5.4000 \cdot 10^{-4}$ | $3.9455 \cdot 10^{-4}$ | $4.5268 \cdot 10^{-4}$ |
| | $B_5$ (J·K$^{-6}$·mol$^{-1}$) | $1.8032 \cdot 10^{-6}$ | $-2.6343 \cdot 10^{-7}$ | $2.8756 \cdot 10^{-6}$ |
| | $B_7$ (J·K$^{-8}$·mol$^{-1}$) | $-4.2629 \cdot 10^{-9}$ | $6.4073 \cdot 10^{-9}$ | $-6.9674 \cdot 10^{-9}$ |
| | %RMS | 2.22 | 2.63 | 2.48 |
| | Range (K) | 1.84–9.45 | 1.83–7.53 | 1.85–10.38 |
| Mid $T$ Fits | $A_0$ (J·K$^{-1}$·mol$^{-1}$) | -0.31878 | -0.12228 | -0.19710 |
| | $A_1$ (J·K$^{-2}$·mol$^{-1}$) | 0.19978 | 0.070081 | 0.14741 |
| | $A_2$ (J·K$^{-3}$·mol$^{-1}$) | -0.047198 | -0.012551 | -0.040104 |
| | $A_3$ (J·K$^{-4}$·mol$^{-1}$) | $5.8565 \cdot 10^{-3}$ | $1.0643 \cdot 10^{-3}$ | $5.4544 \cdot 10^{-3}$ |
| | $A_4$ (J·K$^{-5}$·mol$^{-1}$) | $-2.7416 \cdot 10^{-4}$ | $3.2135 \cdot 10^{-5}$ | $-2.6561 \cdot 10^{-4}$ |
| | $A_5$ (J·K$^{-6}$·mol$^{-1}$) | $7.2335 \cdot 10^{-6}$ | $-3.4175 \cdot 10^{-6}$ | $7.2566 \cdot 10^{-6}$ |
| | $A_6$ (J·K$^{-7}$·mol$^{-1}$) | $-1.1077 \cdot 10^{-7}$ | $9.5342 \cdot 10^{-8}$ | $-1.1503 \cdot 10^{-7}$ |
| | $A_7$ (J·K$^{-8}$·mol$^{-1}$) | $9.1549 \cdot 10^{-10}$ | $-1.1631 \cdot 10^{-9}$ | $9.8308 \cdot 10^{-10}$ |
| | $A_8$ (J·K$^{-9}$·mol$^{-1}$) | $-3.1564 \cdot 10^{-12}$ | $5.3436 \cdot 10^{-12}$ | $-3.4961 \cdot 10^{-12}$ |
| | %RMS | 0.439 | 1.15 | 0.393 |
| | Range (K) | 9.45–63.33 | 7.53–56.53 | 10.38–53.08 |
| High $T$ Fits | $m$ (mol) | 4.8569 | 5.3745 | 4.6559 |
| | $\Theta_D$ (K) | 434.16 | 515.11 | 305.64 |
| | $n_1$ (mol) | 9.6376 | 6.1018 | 12.002 |
| | $\Theta_{E,1}$ (K) | 918.70 | 945.92 | 761.46 |
| | $A$ (J·K$^{-2}$·mol$^{-1}$) | 0.35864 | 0.37452 | 0 |
| | %RMS | 0.624 | 0.539 | 3.50 |
| | Range (K) | 63.33–302.59 | 56.53–302.67 | 53.08–201.65 |

**Table S7.** Parameters for low $T$ (< 11 K), mid $T$ (5 K < $T$ < 60 K), and high $T$ ($T$ > 40 K) fits of heat capacity data (in J· $K^{-1}$· $mol^{-1}$) for LDH 4 and LDH 5.

| | Parameter | LDH 4 | LDH 5 |
|---|---|---|---|
| Low $T$ Fits | $\gamma$ ($J{\cdot}K^{-2}{\cdot}mol^{-1}$) | $1.8338{\cdot}10^{-3}$ | $5.8660{\cdot}10^{-3}$ |
| | $B_3$ ($J{\cdot}K^{-4}{\cdot}mol^{-1}$) | $3.5949{\cdot}10^{-4}$ | $3.2984{\cdot}10^{-4}$ |
| | $B_5$ ($J{\cdot}K^{-6}{\cdot}mol^{-1}$) | $-6.4087{\cdot}10^{-8}$ | $3.5323{\cdot}10^{-7}$ |
| | $B_7$ ($J{\cdot}K^{-8}{\cdot}mol^{-1}$) | $2.9992{\cdot}10^{-9}$ | $6.8696{\cdot}10^{-10}$ |
| | $n$ (mol) | $8.4226{\cdot}10^{-3}$ | $6.2266{\cdot}10^{-3}$ |
| | g | 1 | 1 |
| | $\theta_{sch}$ (K) | 2.5475 | 2.3755 |
| | %RMS | 1.62 | 1.09 |
| | Range (K) | 1.85–9.09 | 1.85–10.03 |
| Mid $T$ Fits | $A_0$ ($J{\cdot}K^{-1}{\cdot}mol^{-1}$) | -0.064662 | -0.11303 |
| | $A_1$ ($J{\cdot}K^{-2}{\cdot}mol^{-1}$) | 0.030877 | 0.061953 |
| | $A_2$ ($J{\cdot}K^{-3}{\cdot}mol^{-1}$) | $-1.5460{\cdot}10^{-3}$ | $-8.0956{\cdot}10^{-3}$ |
| | $A_3$ ($J{\cdot}K^{-4}{\cdot}mol^{-1}$) | $-4.3304{\cdot}10^{-4}$ | $3.8340{\cdot}10^{-4}$ |
| | $A_4$ ($J{\cdot}K^{-5}{\cdot}mol^{-1}$) | $1.2904{\cdot}10^{-4}$ | $7.2237{\cdot}10^{-5}$ |
| | $A_5$ ($J{\cdot}K^{-6}{\cdot}mol^{-1}$) | $-6.8917{\cdot}10^{-6}$ | $-4.7865{\cdot}10^{-6}$ |
| | $A_6$ ($J{\cdot}K^{-7}{\cdot}mol^{-1}$) | $1.6345{\cdot}10^{-7}$ | $1.2116{\cdot}10^{-7}$ |
| | $A_7$ ($J{\cdot}K^{-8}{\cdot}mol^{-1}$) | $-1.8495{\cdot}10^{-9}$ | $-1.4131{\cdot}10^{-9}$ |
| | $A_8$ ($J{\cdot}K^{-9}{\cdot}mol^{-1}$) | $8.1307{\cdot}10^{-12}$ | $6.3166{\cdot}10^{-12}$ |
| | %RMS | 0.874 | 0.600 |
| | Range (K) | 9.09–44.48 | 10.03–45.03 |
| High $T$ Fits | $m$ (mol) | 6.1587 | 3.0331 |
| | $\Theta_D$ (K) | 901.82 | 425.80 |
| | $n_1$ (mol) | 1.3653 | 4.4812 |
| | $\Theta_{E,1}$ (K) | 268.82 | 760.72 |
| | $A$ ($J{\cdot}K^{-2}{\cdot}mol^{-1}$) | 0.32059 | 0.26156 |
| | %RMS | 0.380 | 0.331 |
| | Range (K) | 44.48–302.81 | 45.03–302.84 |

**Table S8.** Standard thermodynamic functions of LDH 1 using the formula $LiAl_2(OH)_6Cl{\cdot}3.20H_2O$. All calculated thermodynamic values have an estimated standard uncertainty of about 0.02 X below 10 K and 0.01 X above 10 K where X represents the thermodynamic property.

| $T$ (K) | $C_{p,m}$(J·K$^{-1}$·mol$^{-1}$) | $\Delta^T_{\circ}S^{\circ}_m$(J·K$^{-1}$·mol$^{-1}$) | $\Delta^T_{\circ}H^{\circ}_m$(kJ·mol$^{-1}$) | $\Phi^{\circ}_m$ (J·K$^{-1}$·mol$^{-1}$) |
|---|---|---|---|---|
| 0 | 0 | 0 | 0 | 0 |
| 1 | $2.595{\cdot}10^{-3}$ | $2.233{\cdot}10^{-3}$ | $1.162{\cdot}10^{-6}$ | $1.072{\cdot}10^{-3}$ |
| 2 | $8.483{\cdot}10^{-3}$ | $5.558{\cdot}10^{-3}$ | $6.285{\cdot}10^{-6}$ | $2.415{\cdot}10^{-3}$ |
| 3 | 0.02117 | 0.01111 | $2.039{\cdot}10^{-5}$ | $4.309{\cdot}10^{-3}$ |
| 4 | 0.04455 | 0.02009 | $5.218{\cdot}10^{-5}$ | $7.046{\cdot}10^{-3}$ |
| 5 | 0.08307 | 0.03384 | $1.145{\cdot}10^{-4}$ | 0.01094 |
| 6 | 0.14179 | 0.05383 | $2.250{\cdot}10^{-4}$ | 0.01633 |
| 7 | 0.22639 | 0.08167 | $4.067{\cdot}10^{-4}$ | 0.02357 |
| 8 | 0.34305 | 0.11912 | $6.885{\cdot}10^{-4}$ | 0.03306 |
| 9 | 0.49822 | 0.16808 | $1.106{\cdot}10^{-3}$ | 0.04523 |
| 10 | 0.69549 | 0.23044 | $1.699{\cdot}10^{-3}$ | 0.06051 |
| 15 | 2.3242 | 0.78430 | $8.801{\cdot}10^{-3}$ | 0.19754 |
| 20 | 4.9332 | 1.7895 | 0.02658 | 0.46030 |
| 25 | 8.2944 | 3.2393 | 0.05938 | 0.86402 |
| 30 | 12.229 | 5.0916 | 0.11048 | 1.4090 |
| 35 | 16.636 | 7.3021 | 0.18246 | 2.0890 |
| 40 | 21.443 | 9.8334 | 0.27751 | 2.8956 |
| 45 | 26.565 | 12.652 | 0.39742 | 3.8206 |
| 50 | 31.914 | 15.726 | 0.54354 | 4.8554 |
| 60 | 43.126 | 22.526 | 0.91817 | 7.2227 |
| 70 | 55.278 | 30.070 | 1.4091 | 9.9392 |
| 80 | 67.887 | 38.274 | 2.0249 | 12.962 |
| 90 | 80.453 | 46.996 | 2.7667 | 16.255 |
| 100 | 92.908 | 56.118 | 3.6336 | 19.782 |
| 110 | 105.32 | 65.555 | 4.6247 | 23.512 |
| 120 | 117.78 | 75.253 | 5.7401 | 27.418 |
| 130 | 130.38 | 85.176 | 6.9808 | 31.478 |
| 140 | 143.13 | 95.304 | 8.3482 | 35.674 |
| 150 | 156.04 | 105.62 | 9.8439 | 39.992 |
| 160 | 169.05 | 116.10 | 11.469 | 44.421 |
| 170 | 182.12 | 126.74 | 13.225 | 48.950 |
| 180 | 195.16 | 137.52 | 15.112 | 53.570 |
| 190 | 208.10 | 148.42 | 17.128 | 58.275 |
| 200 | 220.89 | 159.42 | 19.273 | 63.057 |
| 210 | 233.48 | 170.51 | 21.545 | 67.910 |
| 220 | 245.80 | 181.65 | 23.942 | 72.826 |
| 230 | 257.85 | 192.85 | 26.460 | 77.801 |
| 240 | 269.58 | 204.07 | 29.098 | 82.828 |
| 250 | 280.99 | 215.31 | 31.851 | 87.903 |
| 260 | 292.06 | 226.54 | 34.716 | 93.019 |
| 270 | 302.79 | 237.77 | 37.691 | 98.172 |
| 273.15 | 306.10 | 241.30 | 38.650 | 99.802 |
| 280 | 313.19 | 248.97 | 40.771 | 103.36 |
| 290 | 323.26 | 260.14 | 43.953 | 108.57 |
| 298.15 | 331.23 | 269.20 | 46.621 | 112.84 |
| 300 | 333.01 | 271.26 | 47.235 | 113.81 |

**Table S9.** Standard thermodynamic functions of LDH 2. All calculated thermodynamic values have an estimated standard uncertainty of about 0.02 X below 10 K and 0.01 X above 10 K where X represents the thermodynamic property.

| $T$ (K) | $C_{p,m}$(J·K$^{-1}$·mol$^{-1}$) | $\Delta^T_0 S^\circ_m$(J·K$^{-1}$·mol$^{-1}$) | $\Delta^T_0 H^\circ_m$(kJ·mol$^{-1}$) | $\Phi^\circ_m$ (J·K$^{-1}$·mol$^{-1}$) |
|---|---|---|---|---|
| 0 | 0 | 0 | 0 | 0 |
| 1 | $2.226\cdot10^{-3}$ | $1.963\cdot10^{-3}$ | $1.014\cdot10^{-6}$ | $9.487\cdot10^{-4}$ |
| 2 | $6.812\cdot10^{-3}$ | $4.714\cdot10^{-3}$ | $5.239\cdot10^{-6}$ | $2.094\cdot10^{-3}$ |
| 3 | 0.01610 | $9.035\cdot10^{-3}$ | $1.621\cdot10^{-5}$ | $3.633\cdot10^{-3}$ |
| 4 | 0.03241 | 0.01570 | $3.978\cdot10^{-5}$ | $5.761\cdot10^{-3}$ |
| 5 | 0.05815 | 0.02550 | $8.417\cdot10^{-5}$ | $8.671\cdot10^{-3}$ |
| 6 | 0.09596 | 0.03924 | $1.601\cdot10^{-4}$ | 0.01256 |
| 7 | 0.14900 | 0.05780 | $2.812\cdot10^{-4}$ | 0.01764 |
| 8 | 0.22237 | 0.08221 | $4.648\cdot10^{-4}$ | 0.02411 |
| 9 | 0.32214 | 0.11389 | $7.347\cdot10^{-4}$ | 0.03225 |
| 10 | 0.45168 | 0.15426 | $1.119\cdot10^{-3}$ | 0.04236 |
| 15 | 1.6299 | 0.52900 | $5.936\cdot10^{-3}$ | 0.13325 |
| 20 | 3.7296 | 1.2645 | 0.01897 | 0.31600 |
| 25 | 6.5885 | 2.3920 | 0.04450 | 0.61203 |
| 30 | 9.9808 | 3.8864 | 0.08574 | 1.0284 |
| 35 | 13.787 | 5.7056 | 0.14499 | 1.5630 |
| 40 | 18.018 | 7.8177 | 0.22431 | 2.2099 |
| 45 | 22.706 | 10.206 | 0.32594 | 2.9632 |
| 50 | 27.735 | 12.857 | 0.45195 | 3.8179 |
| 60 | 37.908 | 18.810 | 0.78000 | 5.8100 |
| 70 | 49.012 | 25.474 | 1.2137 | 8.1350 |
| 80 | 60.905 | 32.789 | 1.7629 | 10.753 |
| 90 | 73.180 | 40.669 | 2.4331 | 13.635 |
| 100 | 85.576 | 49.021 | 3.2269 | 16.752 |
| 110 | 97.955 | 57.758 | 4.1446 | 20.080 |
| 120 | 110.26 | 66.809 | 5.1857 | 23.595 |
| 130 | 122.46 | 76.117 | 6.3494 | 27.276 |
| 140 | 134.56 | 85.636 | 7.6346 | 31.103 |
| 150 | 146.54 | 95.329 | 9.0402 | 35.061 |
| 160 | 158.37 | 105.17 | 10.565 | 39.134 |
| 170 | 170.05 | 115.12 | 12.207 | 43.311 |
| 180 | 181.53 | 125.16 | 13.965 | 47.579 |
| 190 | 192.79 | 135.28 | 15.837 | 51.928 |
| 200 | 203.82 | 145.45 | 17.820 | 56.350 |
| 210 | 214.60 | 155.66 | 19.913 | 60.836 |
| 220 | 225.10 | 165.88 | 22.111 | 65.378 |
| 230 | 235.33 | 176.12 | 24.414 | 69.970 |
| 240 | 245.27 | 186.34 | 26.817 | 74.606 |
| 250 | 254.92 | 196.55 | 29.318 | 79.280 |
| 260 | 264.30 | 206.73 | 31.914 | 83.986 |
| 270 | 273.39 | 216.88 | 34.603 | 88.721 |
| 273.15 | 276.20 | 220.07 | 35.469 | 90.217 |
| 280 | 282.22 | 226.98 | 37.381 | 93.478 |
| 290 | 290.79 | 237.04 | 40.247 | 98.255 |
| 298.15 | 297.58 | 245.19 | 42.644 | 102.16 |
| 300 | 299.10 | 247.04 | 43.196 | 103.05 |

**Table S10.** Standard thermodynamic functions of LDH 3 (including spline values). All calculated thermodynamic values have an estimated standard uncertainty of about 0.02 X below 10 K and 0.01 X above 10 K where X represents the thermodynamic property.

| $T$ (K) | $C_{p,m}$(J·K$^{-1}$·mol$^{-1}$) | $\Delta^T_0 S^\circ_m$(J·K$^{-1}$·mol$^{-1}$) | $\Delta^T_0 H^\circ_m$(kJ·mol$^{-1}$) | $\Phi^\circ_m$ (J·K$^{-1}$·mol$^{-1}$) |
|---|---|---|---|---|
| 0 | 0 | 0 | 0 | 0 |
| 1 | $2.035\cdot10^{-3}$ | $1.652\cdot10^{-3}$ | $8.740\cdot10^{-7}$ | $7.779\cdot10^{-4}$ |
| 2 | $7.356\cdot10^{-3}$ | $4.427\cdot10^{-3}$ | $5.174\cdot10^{-6}$ | $1.840\cdot10^{-3}$ |
| 3 | 0.01868 | $9.307\cdot10^{-3}$ | $1.759\cdot10^{-5}$ | $3.445\cdot10^{-3}$ |
| 4 | 0.03907 | 0.01721 | $4.553\cdot10^{-5}$ | $5.824\cdot10^{-3}$ |
| 5 | 0.07343 | 0.02930 | $1.004\cdot10^{-4}$ | $9.228\cdot10^{-3}$ |
| 6 | 0.12849 | 0.04719 | $1.993\cdot10^{-4}$ | 0.01397 |
| 7 | 0.21146 | 0.07282 | $3.667\cdot10^{-4}$ | 0.02044 |
| 8 | 0.32886 | 0.10831 | $6.337\cdot10^{-4}$ | 0.02909 |
| 9 | 0.48557 | 0.15569 | $1.037\cdot10^{-3}$ | 0.04041 |
| 10 | 0.68456 | 0.21677 | $1.619\cdot10^{-3}$ | 0.05487 |
| 15 | 2.3117 | 0.76709 | $8.677\cdot10^{-3}$ | 0.18859 |
| 20 | 4.8743 | 1.7635 | 0.02630 | 0.44842 |
| 25 | 8.1403 | 3.1909 | 0.05859 | 0.84735 |
| 30 | 11.935 | 5.0034 | 0.10858 | 1.3840 |
| 35 | 16.151 | 7.1549 | 0.17864 | 2.0509 |
| 40 | 20.696 | 9.6052 | 0.27064 | 2.8391 |
| 45 | 25.468 | 12.317 | 0.38598 | 3.7393 |
| 50 | 30.377 | 15.253 | 0.52555 | 4.7421 |
| 60 | 41.681 | 21.756 | 0.88395 | 7.0233 |
| 70 | 52.962 | 29.038 | 1.3578 | 9.6407 |
| 80 | 63.577 | 36.809 | 1.9409 | 12.547 |
| 90 | 73.928 | 44.895 | 2.6285 | 15.690 |
| 100 | 84.450 | 53.226 | 3.4201 | 19.025 |
| 110 | 95.424 | 61.785 | 4.3190 | 22.521 |
| 120 | 106.95 | 70.578 | 5.3304 | 26.158 |
| 130 | 118.97 | 79.610 | 6.4597 | 29.921 |
| 140 | 131.37 | 88.879 | 7.7111 | 33.800 |
| 150 | 143.96 | 98.372 | 9.0877 | 37.787 |
| 160 | 156.57 | 108.07 | 10.590 | 41.875 |
| 170 | 169.04 | 117.93 | 12.219 | 46.058 |
| 180 | 181.24 | 127.94 | 13.970 | 50.329 |
| 190 | 193.06 | 138.06 | 15.842 | 54.679 |
| 200 | 204.43 | 148.25 | 17.830 | 59.103 |
| 210 | 219.9613 | 158.6473 | 22.31585 | 65.01163 |
| 220 | 233.4615 | 169.1936 | 26.86996 | 71.00387 |
| 230 | 246.0031 | 179.8529 | 31.48925 | 77.04386 |
| 240 | 257.0678 | 190.562 | 36.16901 | 83.0732 |
| 250 | 266.6905 | 201.2555 | 40.90264 | 89.03307 |
| 260 | 275.2242 | 211.8844 | 45.68232 | 94.88234 |
| 270 | 283.026 | 222.4198 | 50.49994 | 100.6 |
| 273.15 | 285.3525 | 225.7162 | 52.0241 | 102.3723 |
| 280 | 290.1166 | 232.8437 | 55.34777 | 106.1761 |
| 290 | 295.8712 | 243.1295 | 60.21844 | 111.5913 |
| 298.15 | 299.3539 | 251.38 | 64.19967 | 115.8605 |
| 300 | 300.0427 | 253.2339 | 65.10435 | 116.8097 |

**Table S11.** Standard thermodynamic functions of LDH 4. All calculated thermodynamic values have an estimated standard uncertainty of about 0.02 X below 10 K and 0.01 X above 10 K where X represents the thermodynamic property.

| $T$ (K) | $C_{p,m}$(J·K$^{-1}$·mol$^{-1}$) | $\Delta^T_0 S^\circ_m$(J·K$^{-1}$·mol$^{-1}$) | $\Delta^T_0 H^\circ_m$(kJ·mol$^{-1}$) | $\Phi^\circ_m$ (J·K$^{-1}$·mol$^{-1}$) |
|---|---|---|---|---|
| 0 | 0 | 0 | 0 | 0 |
| 1 | 0.03279 | 0.02018 | $1.396\cdot10^{-5}$ | $6.226\cdot10^{-3}$ |
| 2 | 0.02595 | 0.04140 | $4.410\cdot10^{-5}$ | 0.01935 |
| 3 | 0.02579 | 0.05149 | $6.897\cdot10^{-5}$ | 0.02850 |
| 4 | 0.03675 | 0.06016 | $9.937\cdot10^{-5}$ | 0.03532 |
| 5 | 0.05840 | 0.07048 | $1.460\cdot10^{-4}$ | 0.04128 |
| 6 | 0.09201 | 0.08390 | $2.202\cdot10^{-4}$ | 0.04721 |
| 7 | 0.13978 | 0.10148 | $3.348\cdot10^{-4}$ | 0.05365 |
| 8 | 0.20465 | 0.12417 | $5.054\cdot10^{-4}$ | 0.06099 |
| 9 | 0.29051 | 0.15300 | $7.510\cdot10^{-4}$ | 0.06955 |
| 10 | 0.40350 | 0.18920 | $1.096\cdot10^{-3}$ | 0.07964 |
| 15 | 1.4552 | 0.52273 | $5.383\cdot10^{-3}$ | 0.16384 |
| 20 | 3.3653 | 1.1837 | 0.01710 | 0.32873 |
| 25 | 5.9379 | 2.2015 | 0.04015 | 0.59572 |
| 30 | 8.8772 | 3.5402 | 0.07708 | 0.97086 |
| 35 | 12.018 | 5.1421 | 0.12924 | 1.4495 |
| 40 | 15.384 | 6.9635 | 0.19763 | 2.0228 |
| 45 | 19.022 | 8.9844 | 0.28360 | 2.6822 |
| 50 | 22.664 | 11.174 | 0.38769 | 3.4207 |
| 60 | 30.682 | 16.003 | 0.65376 | 5.1073 |
| 70 | 39.290 | 21.374 | 1.0033 | 7.0415 |
| 80 | 48.239 | 27.201 | 1.4407 | 9.1930 |
| 90 | 57.433 | 33.412 | 1.9689 | 11.536 |
| 100 | 66.829 | 39.948 | 2.5900 | 14.048 |
| 110 | 76.385 | 46.764 | 3.3060 | 16.710 |
| 120 | 86.045 | 53.824 | 4.1181 | 19.507 |
| 130 | 95.741 | 61.094 | 5.0270 | 22.425 |
| 140 | 105.40 | 68.544 | 6.0328 | 25.452 |
| 150 | 114.96 | 76.142 | 7.1347 | 28.578 |
| 160 | 124.37 | 83.863 | 8.3315 | 31.791 |
| 170 | 133.56 | 91.680 | 9.6213 | 35.084 |
| 180 | 142.53 | 99.569 | 11.002 | 38.447 |
| 190 | 151.23 | 107.51 | 12.471 | 41.873 |
| 200 | 159.65 | 115.48 | 14.026 | 45.354 |
| 210 | 167.80 | 123.47 | 15.663 | 48.883 |
| 220 | 175.67 | 131.46 | 17.381 | 52.455 |
| 230 | 183.27 | 139.44 | 19.176 | 56.063 |
| 240 | 190.60 | 147.39 | 21.045 | 59.703 |
| 250 | 197.68 | 155.32 | 22.987 | 63.369 |
| 260 | 204.52 | 163.20 | 24.998 | 67.058 |
| 270 | 211.12 | 171.05 | 27.076 | 70.764 |
| 273.15 | 213.16 | 173.51 | 27.745 | 71.935 |
| 280 | 217.51 | 178.84 | 29.220 | 74.485 |
| 290 | 223.70 | 186.58 | 31.426 | 78.217 |
| 298.15 | 228.60 | 192.85 | 33.269 | 81.265 |
| 300 | 229.70 | 194.27 | 33.693 | 81.957 |

**Table S12.** Standard thermodynamic functions of LDH 5. All calculated thermodynamic values have an estimated standard uncertainty of about 0.02 X below 10 K and 0.01 X above 10 K where X represents the thermodynamic property.

| $T$ (K) | $C_{p,m}$ (J·K$^{-1}$·mol$^{-1}$) | $\Delta_0^T S_m^\circ$ (J·K$^{-1}$·mol$^{-1}$) | $\Delta_0^T H_m^\circ$ (kJ·mol$^{-1}$) | $\Phi_m^\circ$ (J·K$^{-1}$·mol$^{-1}$) |
|---|---|---|---|---|
| 0 | 0 | 0 | 0 | 0 |
| 1 | 0.02893 | 0.02088 | $1.347\cdot10^{-5}$ | $7.406\cdot10^{-3}$ |
| 2 | 0.02746 | 0.04060 | $4.179\cdot10^{-5}$ | 0.01971 |
| 3 | 0.03356 | 0.05255 | $7.146\cdot10^{-5}$ | 0.02873 |
| 4 | 0.04913 | 0.06411 | $1.120\cdot10^{-4}$ | 0.03611 |
| 5 | 0.07448 | 0.07760 | $1.730\cdot10^{-4}$ | 0.04301 |
| 6 | 0.11133 | 0.09425 | $2.648\cdot10^{-4}$ | 0.05011 |
| 7 | 0.16215 | 0.11503 | $4.003\cdot10^{-4}$ | 0.05785 |
| 8 | 0.22994 | 0.14090 | $5.948\cdot10^{-4}$ | 0.06655 |
| 9 | 0.31827 | 0.17286 | $8.670\cdot10^{-4}$ | 0.07653 |
| 10 | 0.43172 | 0.21202 | $1.240\cdot10^{-3}$ | 0.08806 |
| 15 | 1.4658 | 0.55523 | $5.644\cdot10^{-3}$ | 0.17896 |
| 20 | 3.3033 | 1.2107 | 0.01725 | 0.34791 |
| 25 | 5.7602 | 2.2027 | 0.03971 | 0.61422 |
| 30 | 8.5770 | 3.4980 | 0.07545 | 0.98306 |
| 35 | 11.612 | 5.0455 | 0.12584 | 1.4501 |
| 40 | 14.886 | 6.8067 | 0.19197 | 2.0075 |
| 45 | 18.466 | 8.7713 | 0.27555 | 2.6481 |
| 50 | 21.981 | 10.896 | 0.37654 | 3.3654 |
| 60 | 29.740 | 15.577 | 0.63447 | 5.0029 |
| 70 | 38.112 | 20.785 | 0.97336 | 6.8797 |
| 80 | 46.794 | 26.438 | 1.3977 | 8.9669 |
| 90 | 55.639 | 32.459 | 1.9098 | 11.240 |
| 100 | 64.591 | 38.784 | 2.5108 | 13.676 |
| 110 | 73.621 | 45.363 | 3.2018 | 16.255 |
| 120 | 82.695 | 52.158 | 3.9834 | 18.963 |
| 130 | 91.766 | 59.135 | 4.8557 | 21.784 |
| 140 | 100.78 | 66.266 | 5.8185 | 24.705 |
| 150 | 109.68 | 73.523 | 6.8709 | 27.717 |
| 160 | 118.40 | 80.881 | 8.0115 | 30.810 |
| 170 | 126.93 | 88.316 | 9.2383 | 33.973 |
| 180 | 135.21 | 95.807 | 10.549 | 37.200 |
| 190 | 143.22 | 103.33 | 11.942 | 40.483 |
| 200 | 150.96 | 110.88 | 13.413 | 43.814 |
| 210 | 158.43 | 118.42 | 14.960 | 47.187 |
| 220 | 165.61 | 125.96 | 16.580 | 50.597 |
| 230 | 172.52 | 133.48 | 18.271 | 54.037 |
| 240 | 179.16 | 140.96 | 20.030 | 57.503 |
| 250 | 185.55 | 148.40 | 21.853 | 60.990 |
| 260 | 191.70 | 155.80 | 23.740 | 64.495 |
| 270 | 197.62 | 163.15 | 25.687 | 68.013 |
| 273.15 | 199.44 | 165.45 | 26.312 | 69.123 |
| 280 | 203.33 | 170.44 | 27.692 | 71.541 |
| 290 | 208.84 | 177.67 | 29.753 | 75.076 |
| 298.15 | 213.19 | 183.52 | 31.473 | 77.960 |
| 300 | 214.16 | 184.84 | 31.868 | 78.615 |

**Table S13.** Thermodynamic parameters for [Li-Al-Cl] LDHs at $T$ = 298.15 K from binary oxy-hydroxide and binary hydroxide.

| LDH | $\Delta H°_{f,ox\text{-}hyd}$ (kJ·mol$^{-1}$) | $\Delta S°_{f,ox\text{-}hyd}$ (J·K$^{-1}$·mol$^{-1}$) | $\Delta G°_{f,ox\text{-}hyd}$ (kJ·mol$^{-1}$) | $\Delta H°_{f,hyd}$ (kJ·mol$^{-1}$) | $\Delta S°_{f,hyd}$ (J·K$^{-1}$·mol$^{-1}$) | $\Delta G°_{f,hyd}$ (kJ·mol$^{-1}$) |
|---|---|---|---|---|---|---|
| LDH1 | -37.76±3.30 | -205.72±5.38 | 23.58±3.30 | -24.68±2.20 | -131.72±.5.38 | 14.59±2.20 |
| LDH2 | -69.42±3.45 | -182.25±4.90 | -15.08±3.45 | -56.34±2.42 | -108.25±4.90 | -24.06±2.42 |
| LDH3 | -56.35±3.23 | -122.42±5.03 | -19.85±3.23 | -43.29±2.09 | -48.42±5.03 | -28.85±2.09 |
| LDH4 | -33.99±3.33 | -99.99±3.91 | -4.18±3.33 | -23.59±2.25 | -42.27±3.91 | -10.99±2.25 |
| LDH5 | -72.96±3.42 | -109.25±3.73 | -40.39±3.42 | -61.28±2.37 | -43.76±3.73 | -48.23±2.37 |

**Table S14**. Thermochemical cycle used to calculate the reaction enthalpies of [Li-Al-Cl] LDHs from binary oxides, binary hydroxides, and binary ox-hydroxides.

| | |
|---|---|
| **Undoped Li-Al LDHs** | |
| $xLiCl\ (s) + 2Al(OH)_3(s) + nH_2O(l) \rightarrow Li_xAl_2(OH)_6Cl_x \cdot nH_2O(s)$ | $\Delta H_1$ |
| $xLiCl(s) + 2AlOOH(s) + (2+n)H_2O(l) \rightarrow Li_xAl_2(OH)_6Cl_x \cdot nH_2O(s)$ | $\Delta H_2$ |
| $xLiCl(s) + Al_2O_3(s) + (3+n)H_2O(l) \rightarrow Li_xAl_2(OH)_6Cl_x \cdot nH_2O(s)$ | $\Delta H_3$ |
| **Fe doped Li-Al LDHs** | |
| $xLiCl(s) + (2-y)Al(OH)_3(s) + yFeOOH(s) + (y+n)H_2O(l) \rightarrow Li_xFe_yAl_{2-y}(OH)_6Cl_x \cdot nH_2O(s)$ | $\Delta H_4$ |
| $xLiCl(s) + (2-y)AlOOH(s) + yFeOOH(s) + (2+n)H_2O(l) \rightarrow Li_xFe_yAl_{2-y}(OH)_6Cl_x \cdot nH_2O(s)$ | $\Delta H_5$ |
| $xLiCl(s) + ((2-y)/2)Al_2O_3(s) + (y/2)Fe_2O_3(s) + (3+n)H_2O(l) \rightarrow Li_xFe_yAl_{2-y}(OH)_6Cl_x \cdot nH_2O(s)$ | $\Delta H_6$ |
| $LiCl(s) \rightarrow Li^+(aq) + Cl^-(aq)$ | $\Delta H_7$ |
| $\gamma\text{-}Al(OH)_3(s) + 3H^+ \rightarrow Al^{3+}(aq) + 3H_2O(aq)$ | $\Delta H_8$ |
| $0.5\ \alpha\text{-}Al_2O_3(s) + 1.5H_2O(l) \rightarrow Al(OH)_3(s)$ | $\Delta H_{10} = \Delta H_{rxn}(Al_2O_3)$ |
| $\alpha\text{-}AlOOH(s) + H_2O(l) \rightarrow Al(OH)_3(s)$ | $\Delta H_9 = \Delta H_{rxn}(AlOOH)$ |
| $\alpha\text{-}FeOOH(s) + 3H^+ + \rightarrow Fe^{3+}(aq) + 2H_2O(aq)$ | $\Delta H_{11}$ |
| $0.5\ Fe_2O_3(s) + 0.5H_2O(l) \rightarrow FeOOH(s)$ | $\Delta H_{12} = \Delta H_{rxn}(Fe_2O_3)$ |
| $H_2O(l) \rightarrow H_2O(aq)$ | $\Delta H_{13}$ |
| $Li_xAl_2(OH)_6Cl_x \cdot nH_2O(s) + 3H^+ \rightarrow xLi^+(aq) + xCl^-(aq) + 2Al^{3+}(aq) + (3+n)H_2O(aq)$ | $\Delta H_{14}$ |
| $Li_xFe_yAl_{2-y}(OH)_6Cl_x \cdot nH_2O(s) + 3H^+ \rightarrow xLi^+(aq) + xCl^-(aq) + (2-y)Al^{3+}(aq) + yFe^{3+}(aq) + (3+n)H_2O(aq)$ | $\Delta H_{15}$ |

$\Delta H_1 = x\Delta H_7 + 2\Delta H_8 + n\Delta H_{13} - \Delta H_{14}$
$\Delta H_4 = x\Delta H_7 + (2-y)\Delta H_8 + y\Delta H_{11} + (y+n)\Delta H_{13} - \Delta H_{15}$
$\Delta H_2 = x\Delta H_7 + 2(\Delta H_9 + \Delta H_8) + (2+n)\Delta H_{13} - \Delta H_{14}$
$\Delta H_5 = x\Delta H_7 + (2-y)(\Delta H_9 + \Delta H_8) + y\Delta H_{11} + (2+n)\Delta H_{13} - \Delta H_{15}$
$\Delta H_3 = x\Delta H_7 + 2(\Delta H_{10} + \Delta H_8) + (3+n)\Delta H_{13} - \Delta H_{14}$
$\Delta H_6 = x\Delta H_7 + ((2-y)/2)(\Delta H_{10} + \Delta H_8) + (y/2)(\Delta H_{11} + \Delta H_{12}) + (3+n)\Delta H_{13} - \Delta H_{15}$

$\Delta H_{rxn}(Al_2O_3) = \Delta H_{f,el}(Al(OH)_3(s)) - 0.5\Delta H_{f,el}(\alpha\text{-}Al_2O_3(s)) - 1.5\Delta H_{f,el}(H_2O(l))$
$\Delta H_{rxn}(Fe_2O_3) = \Delta H_{f,el}(FeOOH(s)) - 0.5\Delta H_{f,el}(\alpha\text{-}Fe_2O_3(s)) - 0.5\Delta H_{f,el}(H_2O(l))$
$\Delta H_{rxn}(AlOOH) = \Delta H_{f,el}(Al(OH)_3(s)) - \Delta H_{f,el}(\alpha\text{-}AlOOH(s)) - \Delta H_{f,el}(H_2O(l))$

**Table S15.** Enthalpy of formation and standard entropy of components at $T$ = 298.15 K.

| Binary component | Formula | $\Delta H°_{f,el}$ (kJ·mol$^{-1}$) | $S°_{el,298.15}$ (J·K$^{-1}$·mol$^{-1}$) |
|---|---|---|---|
| LiCl | Lithium chloride | -408.35±0.3 [a] | 59.3±0.2 [a] |
| γ-$Al(OH)_3$ | Gibbsite | -1293.1±1.2 [b] | 68.4±0.1 [b] |
| α-AlO(OH) | Diaspore | -1001.3±2.2 [b] | 35.4±0.1 [b] |
| α-$Al_2O_3$ | Corundum | -1675.7±1.3 [b] | 50.9±0.1 [b] |
| α-FeOOH | Goethite | -562.6±2.1 [b] | 60.4±0.6 [b] |
| α-$Fe_2O_3$ | Hematite | -826.8±1.3 [b] | 87.4±0.2 [b] |
| $H_2O$ | Water | -285.8±0.1 [b] | 70.0±0.1 [b] |

a = Parker, V.B. (1965) Thermal Properties of Aqueous Uni-Univalent Electrolytes, National Standard Reference Data Series, National Bureau of Standards, Washington, D.C., U.S, 2, 66p.
b = R.A. Robie, B.S. Hemingway (1995) Thermodynamic Properties of Minerals and Related Substances at 298.15 K and 1 bar (105 Pascals) and Higher Temperatures. USGS, Menlo Park, CA.

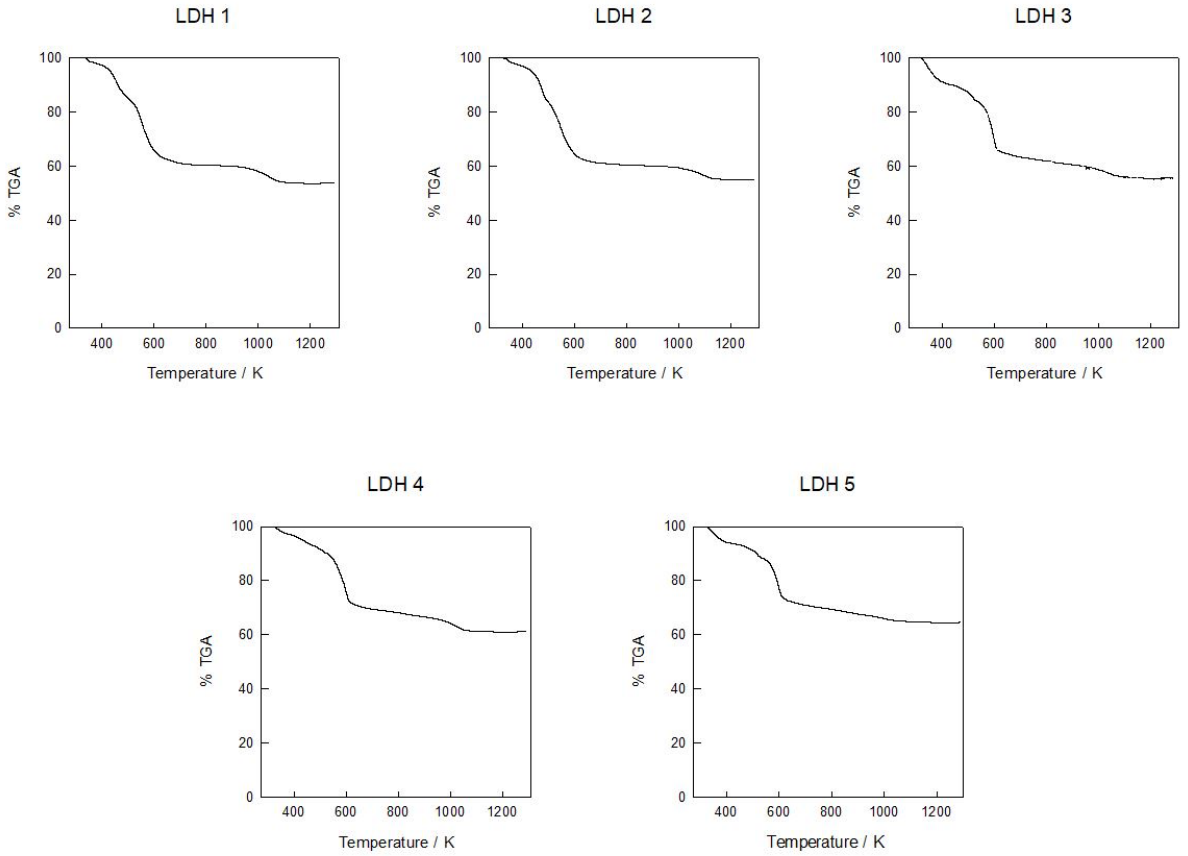


**Figure S1**. TGA curves from 303 K to 1273 K for all [Li-Al-Cl] LDH samples.

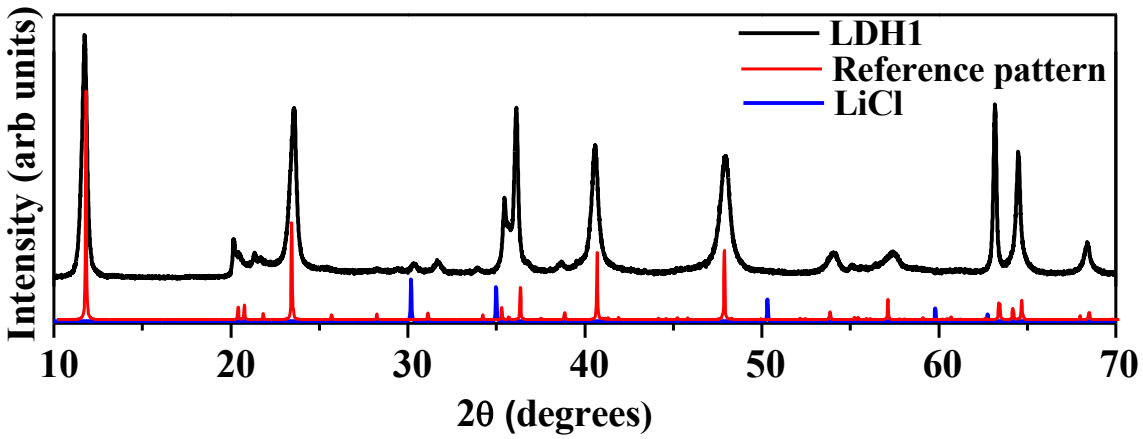


**Figure S2**. PXRD pattern of LDH1 overlaid with reference pattern and secondary phase LiCl. Note the peak at 2θ=30.