

Supporting Information Material

Tab 1 Comparison of the unit cells of different water rich magnesium halide hydrates

| | MgCl₂·12 H₂O | MgI₂·9 H₂O | MgBr₂·9 H₂O | MgI₂·8 H₂O | MgCl₂·8 H₂O | MgBr₂·6 H₂O |
|---------------------|---|---|--|---|--|--|
| SG | P 2 ₁ /n | P 2 ₁ /c | C 2/c | C m c a | P c a b | C 2/m |
| a (Å) | 7.3496 (16) | 15.0768 (13) | 11.835 (4) | 8.5256 (7) | 6.7482 (3) | 10.2299 (16) |
| b (Å) | 14.419 (3) | 6.6334 (3) | 6.4314 (14) | 15.6980 (17) | 11.9153 (4) | 7.2642 (9) |
| c (Å) | 8.570 (3) | 16.7964 (15) | 16.290 (4) | 9.8671 (12) | 13.6052 (5) | 6.1964 (9) |
| α (°) | 90 | 90 | 90 | 90 | 90 | 90 |
| β (°) | 113.44 (2) | 125.447 (6) | 92.04 (3) | 90 | 90 | 93.025 (12) |
| γ (°) | 90 | 90 | 90 | 90 | 90 | 90 |
| V (Å ³) | 833.25 (40) | 1368.47 (21) | 1239.66 (58) | 1320.56 (24) | 1093.95 (7) | 459.83 (11) |
| T (K) | 150 | 200 | 200 | 200 | 230 | 200 |

Tab 2 Mean distances and angles in the Mg-O octahedra of the different magnesium-halide hydrates

| | mean distance Mg ²⁺ -O (Å) | octahedral angles (°) |
|---|---------------------------------------|-----------------------|
| MgCl₂·12 H₂O | 2.059±0.004 | 89.662(63) |
| | | 90.338(62) |
| | | 91.701(63) |
| | | 88.299(63) |
| | | 90.28(6) |
| | | 89.720(59) |
| MgCl₂·8 H₂O | 2.056±0.028 | 89.579(32) |
| | | 90.421(32) |
| | | 90.519(30) |
| | | 89.481(30) |
| | | 89.688(28) |
| | | 90.312(28) |
| MgBr₂·6 H₂O | 2.055±0.002 | 91.557(87) |
| | | 88.443(87) |
| | | 91.425(143) |
| | | 88.575(143) |
| MgBr₂·9 H₂O | 2.058±0.033 | 89.593(98) |
| | | 90.407(98) |
| | | 88.975(93) |
| | | 91.025(93) |
| | | 89.124(82) |
| | | 90.876(82) |
| MgI₂·8 H₂O | 2.054±0.010 | 90.704(109) |
| | | 89.296(109) |
| | | 90.000(2) |
| | | 90.000(2) |
| | | 90.000(2) |
| | | 90.000(2) |
| MgI₂·9 H₂O | 2.061±0.029 | 88.506(123) |
| | | 90.290(123) |
| | | 90.276(118) |
| | | 90.905(118) |
| | | 92.002(116) |
| | | 89.634(121) |
| | | 89.804(119) |
| | | 88.589(124) |
| | | 90.463(110) |
| | | 89.028(108) |
| | | 90.195(107) |
| 90.319(111) | | |

Tab 3 Conversion of the unit cell of $\text{MgCl}_2 \cdot 12 \text{H}_2\text{O}$ to the comparable spacegroup $P2_1/c$

| | $P 2_1/n$ | Converted in $P 2_1/c$ | Sasvari ^[2] |
|--------------------------------|-----------------------|------------------------|------------------------|
| a (Å) | 7.3496 (16) | 8.573(3) | 8.59 (5) |
| b (Å) | 14.419 (3) | 14.420(3) | 14.40 (3) |
| c (Å) | 8.570 (3) | 8.796(3) | 8.75 (5) |
| α (°) | 90 | 90 | 90 |
| β (°) | 113.44 (3) | 129.949(18) | 129.6 (2) |
| γ (°) | 90 | 90 | 90 |
| Pos Mg | 0; 0; 0.5 | 0; 0; 0 | 0; 0; 0 |
| Pos Cl | 0.249; 0.190; 0.012 | 0.263; 0.310; 0.250 | 0.263; 0.310; 0.250 |
| Pos O | -0.022; 0.049; 0.717 | 0.239; 0.049; 0.022 | 0.239; 0.049; 0.022 |
| | -0.114; 0.122; 0.3754 | -0.010; 0.123; 0.114 | -0.008; 0.122; 0.117 |
| | 0.841; 0.290; 0.9073 | 0.203; .0.057; 0.278 | 0.206; -0.056; 0.279 |
| | 0.679; 0.151; 0.032 | 0.435; -0.210; 0.342 | 0.435; -0.210; 0.342 |
| | 0.337; 0.988; 0.190 | 0.352; -0.489; 0.162 | 0.351; -0.488; 0.162 |
| | 0.278; 0.056; 0.574 | 0.147; -0.348; 0.180 | 0.147; -0.348; 0.181 |