Magnesium sulfate trihydrate: an elusive mineral on Earth and Mars?

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Magnesium sulfate trihydrate was, hitherto, one of the last MgSO₄ hydrates with an unknown structure. Amongst the M²⁺SO₄ hydrates, only two other trihydrates are known, the mineral bonattite (CuSO₄·3H₂O) and CrSO₄·3H₂O, which are isostructural in space-group Cc. We have grown large (order 1 mm³) single crystals, with a flat bladed morphology [forms {100}, {010}, {102}], which are comparatively stable in air at room temperature for periods of at least several days. Our synthesis method suggests to us that MgSO₄·3H₂O may be formed commonly in low-T hydrothermal systems, but will transform over time to pseudomorphs composed of hexahydrite (MgSO₄·6H₂O) and/or epsomite (MgSO₄·7H₂O). However, on Mars, the hydration process may be inhibited by the low atmospheric water abundance and the low temperatures.

We report the crystal structure of MgSO₄·3H₂O, determined from neutron single-crystal diffraction measurements made using the VIVALDI diffractometer at the Institut Laue Langevin, and X-ray single-crystal measurements. We also report complementary measurements of the thermal expansion of MgSO₄·3H₂O powder in the range 8 < T < 295 K made using the High Resolution Powder Diffractometer (HRPD) at the ISIS neutron spallation source, as well as CP and TGA data. MgSO₄·3H₂O undergoes a first-order phase transition at 245 K from the high-T Pbca structure to a low-T monoclinic structure (P₂₁/c after permutation of the axes into a standard monoclinic setting); the transition is apparently caused by orientational ordering of the disordered hydrogen bonds in the structure. Unit-cell dimensions are

\[ a = 8.1925(2) \text{ Å}, \ b = 10.9210(2) \text{ Å}, \ c = 12.3866(4) \text{ Å} \] at 295 K, and

\[ a = 12.3616(5) \text{ Å}, \ b = 8.1414(3) \text{ Å}, \ c = 10.8324(2) \text{ Å}, \beta = 91.131(3)° \] at 8 K.

The axial thermal expansion is highly anisotropic, being largest along the b-axis (the direction perpendicular to the plane of the h-bonded sheets in the structure) and smallest along the c-axis. The volume thermal expansion at room temperature is comparable to that of hexahydrite, and much larger than that of epsomite, suggesting that MgSO₄·3H₂O may exert large (i.e., damaging) pore pressures in natural or manmade materials wherever hot aqueous fluids are able to precipitate.

Synthetic MgSO₄·3H₂O typically forms small clusters of blades (each shown here is ~ 1mm across the 010 face). These may occur in nature as hexahydrite or epsomite pseudomorphs.