Synchrotron Powder Diffraction Study of Phase Transitions in Rutile Type Halides

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The structures of $CaBr_2$, $CaCl_2$ and $CrCl_2$ have been investigated, using high-resolution synchrotron X-ray powder diffraction methods, at temperature of up to 800 °C. At room temperature all have an orthorhombic $CaCl_2$-type structure (*Pnnm* Z= 2). Heating $CaBr_2$ through 560 °C results in a continuous transition to a tetragonal rutile type structure ($P4_2/mnm$ Z = 2). Investigation, via either spontaneous strain or octahedral tilt angle, suggests that the transition is close to second order in nature, although the contribution from the sixth order term in the Landau potential cannot be neglected [1]. $CaCl_2$ shows a very similar transition, albeit at the lower temperature of 240 °C. By contrast the structure of $CrCl_2$ remains orthorhombic to 800 °C, and even at this temperature shows no signs of reversion toward the higher symmetry rutile structure. We observe strongly anisotropic thermal expansion in this material and, surprisingly, an increasing distortion of the $CrCl_6$ octahedron with increase in temperature.

[1] Kennedy B.J., Howard C.J., *Phys. Rev.* B, 2004, **70**, 144102.

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