American Mineralogist, Volume 87, pages 642–647, 2002

High-pressure single-crystal X-ray diffraction study of katoite hydrogarnet: Evidence for a phase transition from $Ia3d \rightarrow I\bar{4}3d$ symmetry at 5 GPa

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ABSTRACT

The crystal structure of katoite hydrogarnet has been refined at 0.0001, 2.15, 4.21, 5.09, 6.00, 7.09, and 7.78 GPa from single-crystal X-ray diffraction data using a 4:1 methanol:ethanol mixture as pressure medium in a Merrill-Bassett diamond-anvil cell. Below ~5 GPa, the katoite structure has $Ia3d$ symmetry and compresses by bond shortening rather than bond bending, in agreement with recent quantum mechanical calculations. An unconstrained third-order Birch-Murnaghan fit to the unit-cell volumes and pressures for $Ia3d$ symmetry gave the following equation of state parameters: $V_o = 1987.6(1)$ Å^3, $K_o = 58(1)$ GPa and $K' = 4.0(7)$. Above this pressure, the structure undergoes a phase transition to space group $I\bar{4}3d$, a non-centric subgroup of $Ia3d$. In the $I\bar{4}3d$ structure, there are two non-equivalent (O_4H_4) groups. Both the Ca and Al atoms are displaced along ***a*** relative to their positions in $Ia3d$. It is proposed that compression of the short H-H distance between (O_4H_4) groups destabilizes the structure and may initiate the observed phase transition. Corroboration of this model will require accurate information on the hydrogen atom positions at pressures above 5 GPa.