

Evidence for a Frustrated Phase Transition in the Silica Polymorph Moganite Near 500 K

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Moganite is a naturally abundant but little-known member of the silica system. First described by Flörke et al. (1976) from secondary precipitates within ignimbrite flows on the island of Gran Canaria, moganite now is recognized as a common intergrowth within unaltered microcrystalline silica varieties, such as chert and chalcedony (Heaney and Post, 1992). Moganite accounts for the significantly higher solubility of chalcedony relative to quartz (Gislason et al. 1997), and a high concentration of moganite in sedimentary cherts (>20 wt%) is a strong indicator of crystallization in evaporitic environments (Heaney, 1995).

In this study, we refined the structure of moganite at room temperature using combined neutron and synchrotron X-ray powder diffraction data sets collected from nearly pure powders from Gran Canaria, and we examined the thermal expansion of moganite from 77 K to ~1300 K by time-resolved synchrotron XRD. Beginning with the structure solution in space group *I2/a* presented by Mieke and Graetsch (1992), the room temperature structure refined stably without the use of atomic positional constraints. The lattice parameters yielded values of $a = 8.7465(5)\text{Å}$, $b = 4.8694(3)\text{Å}$, $c = 10.7255(6)\text{Å}$, and $\beta = 0.18(1)\text{Å}$ with a final R_{wp} of 2.71%.

The evolution of the structure with temperature reveals an apparently non-symmetry-breaking phase transition near 500 K. From 77 K to the transition temperature, the linear volume expansion coefficient α is $4.09 \times 10^{-5}\text{K}^{-1}$, whereas above T_c α equals $1.54 \times 10^{-5}\text{K}^{-1}$. The a parameter increases linearly up to T_c and registers virtually no change at higher temperatures, and β exhibits a minimum at T_c . We interpret this behavior as a frustrated transition from space group *I2/a* to that of the moganite aristotype, *Imab*. On approaching the critical temperature, the silica tetrahedra rotate about [001] to satisfy the (100) mirror constraint imposed by S.G. *Imab*, but the rigid unit character of the tetrahedra inhibits a transition to orthorhombic symmetry. Consequently, monoclinicity increases above the critical temperature with further structural expansion.

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