Quartz: structural and thermodynamic analyses across the $\alpha \leftrightarrow \beta$ transition with origin of negative thermal expansion (NTE) in $\beta$ quartz and calcite

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The temperature, $T$, variation of the crystal structure of quartz, SiO$_2$, from 298 to 1235 K was obtained with synchrotron powder X-ray diffraction data and Rietveld structure refinements. The polymorphic transformation from $P3_21$ (low-$T$, $\alpha$ quartz) to $P6_22$ (high-$T$, $\beta$ quartz) occurs at a transition temperature, $T_{tr} = 847$ K. The $T$ variations of spontaneous strains and several structural parameters are fitted to an order parameter, $Q$, using Landau theory. The change in Si atom coordinate, $Si_x$, gives $T_{tr} - T_c = 0.49$ K, which indicates an $\alpha \leftrightarrow \beta$ transition that is weakly first order and nearly tricritical in character ($Q^4 \propto T$). Strains give higher $T_{tr} - T_c$ values ($\approx 7$ K). Other fitted parameters are oxygen O$_z$ coordinate, Si-Si distance, Si-O-Si and $\phi$ angles, and intensity of the (111) reflection, $I_{111}$. In $\alpha$ quartz, the Si-Si distance increases with $T$ because of cation repulsion, so the Si-O-Si angle increases (and $\phi$ decreases) and cause the thermal expansion of the framework structure that consists of corner-sharing distorted rigid SiO$_4$ tetrahedra. The Si-Si distances contract with $T$ and cause negative thermal expansion (NTE) in $\beta$ quartz because of increasing thermal librations of the O atom in the Si-O-Si linkage that occur nearly perpendicular to the Si-Si contraction. In calcite, CaCO$_3$, the short Ca-Ca distance expands with $T$, but the next-nearest Ca-Ca distance, which is of equal length to the $a$ axis, contracts with $T$ and causes NTE along the $a$ axis. The thermal librations of the atoms in the rigid CO$_3$ group increase with $T$ along the $c$ axis.