Evidence for an $I2/a$ to $Imab$ phase transition in the silica polymorph moganite at $\sim570$ K

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ABSTRACT

Rietveld analysis of synchrotron X-ray powder diffraction data for the silica mineral moganite from 100 K to 1354 K has revealed a reversible phase transition from space group $I2/a$ to $Imab$ at approximately 570 K. The thermal expansion behavior of the lattice parameters alters sharply at the transition point, and the monoclinic $\beta$ angle decreases to 90°. The displacive transition from $\alpha$- to $\beta$-moganite is effected by the rotation of apparently rigid tetrahedra about the [010] axis, and the linear temperature dependence of the volume strain and of the non-symmetry-breaking $e_{11}$ and $e_{22}$ strains indicates that the character of the transition is second-order. The continuous increase in the $b$ axis over the entire temperature range reveals a concomitant rotation of tetrahedra about [100] that does not affect the overall symmetry. In addition, we present a refinement without structural constraints for $\alpha$-moganite at room temperature using time-of-flight neutron diffraction data.

INTRODUCTION

The silica minerals have yielded some of our most profound insights into the mechanisms that drive displacive phase transitions in solid materials. The chemical simplicity of the system allows an unfettered examination of the interaction between structure and transition behavior, and the full polymerization of the silica network promotes a long-range coupling between the order parameter and the spontaneous strain. This interaction generates a rich diversity of transition behaviors in silica minerals, which have served as models for the complex transformation processes that attend temperature and pressure variations in a multiplicity of mineral classes. Soft modes, for example, were first discovered during C.V. Raman’s investigations of the $\alpha$-$\beta$ quartz transition (Raman and Nedungadi 1940), and the silica polymorphs have played an important role in the development of the rigid unit mode (RUM) theory of phase transitions (Dove et al. 2000). Consequently, scientists have extensively documented the displacive transformations that occur in the low-pressure polymorphs quartz, tridymite, and cristobalite (reviewed in Heaney 1994). In this paper, we present evidence for a structural transition in the fourth species of crystalline silica common in crustal environments—the mineral moganite.

Despite initial skepticism regarding the distinction between moganite and quartz, the International Commission on New Minerals and Mineral Names approved moganite as a mineral species in 1999. First described from chert-like nodules within rhyolitic ignimbrites of the Mogán Formation, Gran Canaria, Spain (Flörke et al. 1976, 1984), moganite apparently lacks a stability field in the pure SiO$_2$ system. Although some molecular dynamical simulations have suggested that moganite is more stable than quartz at ambient conditions (Murashov and Svisshchev 1998), calorimetric studies yield an enthalpy for moganite relative to quartz at 298 K of 3.4±0.7 kJ/mol, slightly higher than those of tridymite and cristobalite (Petrovic et al. 1996). To date, no one has reported a procedure for the synthesis of moganite.

Moganite is a widespread and significant indicator mineral. Heaney and Post (1992) have demonstrated that moganite is extensively intergrown with quartz in microcrystalline silica varieties that are less than ~100 Ma in age. Over longer time scales it diagenetically transforms to quartz. Moganite appears to precipitate most readily from alkaline brines, and high concentrations (>20 wt%) of moganite in chert signify formation in evaporitic paleo-environments (Heaney 1995). Gislason et al. (1997) have shown that the solubility of moganite (44 mg/kg) is significantly greater than that of quartz (6 mg/kg). Consequently, geothermometers for hydrothermal fluids that are based on the concentration of dissolved silica (Fournier and Rowe 1966; Fournier 1977) must account for the presence of moganite within the chalcedony that co-exists with the solution.

The structure of moganite (Miehe et al. 1988; Miehe and Graetsch 1992) can be visualized as quartz that is Brazil twinned along (101) at the unit-cell scale: right-handed slabs of quartz alternate regularly with left-handed slabs to generate a structure that is distinct from quartz (Fig. 1). Miehe and Graetsch (1992) refined the structure in the non-conventional space group $I2/a$, which they selected in order to maintain the relationship with the trigonal cell of quartz: $a_{\text{mog}} = 2a_{\text{qtz}}$, $b_{\text{mog}} = b_{\text{qtz}}$, and $c_{\text{mog}} = 2c_{\text{qtz}}$. X-ray structure analysis of natural moganite is challenging, because no crystals suitable for single-crystal X-ray diffraction studies have been discovered. More-

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