Anomalous behavior at the $I2/a$ to $Imab$ phase transition in $\text{SiO}_2$-moganite: An analysis using hard-mode Raman spectroscopy

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ABSTRACT

The silica polymorph moganite is commonly intergrown with quartz in microcrystalline silica varieties that are less than ~100 Ma in age. Synchrotron X-ray diffraction suggests that a displacive phase transition occurs when moganite is heated above ~570 K, with an increase in symmetry from $I2/a$ to $Imab$. In the present study, we employed hard-mode Raman spectroscopy to confirm the existence of the $\alpha$-$\beta$ moganite transformation and to offer complementary insight into the transition mechanism. Our analysis of the displacement of the 501 cm$^{-1}$ symmetric stretching-bending vibration ($B_{2g}$ mode) with changing temperature strongly supports the existence of a monoclinic-to-orthorhombic phase transition between 570 and 590 K. Between 593 and 723 K, however, the mode remained fixed at 496 cm$^{-1}$. This behavior was repeated on cooling, but with a hysteresis of over 100 K. We offer three hypotheses that may explain this observation: (1) the intergrowth of nanoscale quartz lamellae within moganite may exert a strain that inhibits the transition; (2) the transition may exhibit a martensitic character marked by the co-existence of $\alpha$- and $\beta$-moganite over a finite temperature interval; and (3) the $\alpha$- and $\beta$-moganite transition may occur via an intermediate phase.

Keywords: Moganite, phase transition, Raman spectroscopy, silica

INTRODUCTION

Moganite has received less scientific scrutiny than its polymorphic brethren in the silica family because it passed virtually unrecognized until Flörke and colleagues reported its existence within rhyolitic ignimbrites from Gran Canaria, Spain, 30 years ago (Flörke et al. 1976, 1984). More recently, the determination of its structure (Miehe et al. 1988; Miehe and Graetsch 1992) and the discovery of its abundance in most microcrystalline “quartz” varieties (Heaney and Post 1992) have established both the validity of moganite and its importance as a distinct silica phase. Analyses of such silica varieties as chert, flint, chalcedony, and agate from around the world reveal that most of these materials crystallize with between 5 and 20 wt% moganite (Heaney 2001). In low-pressure regimes, moganite precipitates from aqueous fluids that range from room temperature to several hundred degrees Celsius. Heaney (1995) argued that higher moganite concentrations are diagnostic of evaporitic silica deposits, and subsequent studies have substantiated the observation that surficial brines precipitate a significant fraction of moganite along with quartz within microcrystalline silcretes and playa sediments (Bustillo 2001; English 2001; Nash and Hopkinson 2004).

Recent research has demonstrated that moganite also is a common mineral in hydrothermal environments. Parthasarathy et al. (2001) reported that hydrothermal chaledony nodules within the gas cavities of the Deccan flood basalts in Maharashtra, India typically contain 70 ± 10 wt% moganite. These nodules rival the chert seams in Gran Canaria, the type locality for moganite, in their moganite abundance. In addition, Rodgers and coworkers (Herdianita et al. 2000; Rodgers and Cressey 2001; Rodgers and Hampton 2003; Hampton et al. 2004) have shown that moganite is a typical intermediate phase in the diagenesis of geothermal opal-A to quartz. These authors examined microcrystalline quartz-bearing sinters from 13 active and extinct geothermal systems over a range of localities in New Zealand, and they documented the presence of moganite at levels of up to ~13 wt% in samples between 20 000 and 200 000 years in age. With longer maturation times, the concentration of moganite in these sinters decreases as larger fractions of moganite have transformed to quartz. Similarly, moganite is observed as an intermediate phase in the diagenesis of permineralized fossil wood (Witke et al. 2004). The observation that moganite is a metastable transitory phase during silica diagenesis supports inferences presented in Heaney and Post (1992) and Moxon and Rios (2004), who discerned no moganite in microcrystalline “quartz” varieties older than the Devonian.