Compressibility and pressure-induced amorphization of guest-free melanophlogite: 
An in-situ synchrotron X-ray diffraction study

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ABSTRACT

Melanophlogite, a clathrasil, possesses a framework of corner-linked silica tetrahedra forming framework cavities that can enclose small guest molecules. Synchrotron X-ray diffraction experiments of the guest-free melanophlogite have been conducted at pressures up to 12 GPa and temperatures up to 1473 K. Upon compression at room temperature, melanophlogite gradually lost its crystallinity and became completely X-ray amorphous at ~8 GPa. The amorphization process was similar to those of denser silica polymorphs, but it reached completion at a much lower pressure (e.g., quartz becomes X-ray amorphous at ~30 GPa). The decreased amorphization pressure of melanophlogite may be attributed to its lower framework density and the ease of bending of its Si-O-Si linkages, thereby accelerating the collapse of the structure under high pressure. Determination of cell volumes of melanophlogite prior to its amorphization yielded a room-temperature bulk modulus of 26.3 ± 1.7 GPa, which is consistent with the relatively large compressibilities reported for the structurally similar zeolites. When heated at ~8 GPa, the amorphous phase started to crystallize at 873 K into coesite, the stable silica phase at these pressure and temperature conditions. Thus the occurrence of pressure-induced amorphization in melanophlogite appears to result from the kinetic hindrance to its transformation to the thermodynamically stable coesite.

Keywords: Melanophlogite, clathrasil, pressure-induced amorphization, compressibility, synchrotron X-ray diffraction

INTRODUCTION

Melanophlogite, 46SiO₂·6M¹⁴·2M¹² (M¹⁴ = CO₂, N₂; M¹² = CH₄, N₂), belongs to a family of silicas called “clathrasils” that possess a framework of corner-linked [SiO₄] tetrahedra surrounding isolated pores and cages (Liebau 1983). Because their openings are small, these cavities can encage certain sizes of polyatomic ions and/or molecules (such as CH₄, N₂, and CO₂ gas molecules in melanophlogite) that cannot diffuse through the crystal. Though rare in nature, melanophlogite is of considerable interest due to its ability to store up to 8 wt% (~15 mol%) volatile molecules (Skinner and Appleman 1963). Thus melanophlogite, which has been successfully synthesized in the laboratory (Gies et al. 1982), may potentially serve as a host for greenhouse gases and radon.

Melanophlogite is also interesting from the viewpoint of crystal chemistry. At ambient condition, melanophlogite is tetragonal with space group P4₁/nbc (Nakagawa et al. 2001). On heating, however, it transforms displacively to the cubic phase (Pm₃n), which is isostructural with hydrate clathrate sI, at 338 K (Gies 1983). Upon further heating, the cubic framework expands, as do the openings of its cavities. As a result, the trapped gases can be completely released above 873 K (Liu et al. 1997). On cooling to room temperature, the framework contracts but maintains its integrity (though its symmetry probably changes), resulting in the so-called “guest-free melanophlogite.” This phase is essentially a polymorph of silica, but has a much larger molar volume (or lower framework density) than common silica phases (such as quartz and tridymite). Since crystalline silica is one of the most comprehensively studied systems for its various applications (Heaney et al. 1994), investigating this microporous silica phase and comparing it with other, denser polymorphs will provide important insights into the effects that structure can exert on physical properties, including compressibility and pressure-induced amorphization, which are the topics of this study.

High-pressure behavior of silica has been an active research area not only for its geophysical significance but also for its materials applications (Hemley et al. 1994). One of the most distinctive properties of the silica system is its richness in polymorphism as a function of pressure, temperature, and synthesis conditions; the reported silica phases include low-pressure polymorphs such as quartz, cristobalite and pure-silica zeolites, and high-pressure polymorphs, including coesite and stishovite. Upon compression, the structures of these phases (except stishovite whose framework is composed of [SiO₄] octahedra) decrease in volume via the following mechanisms with increasing pressure: (1) a rigid rotation of [SiO₄] tetrahedra, reflected by decreases in the intertetrahedral Si-O-Si angles; (2) a distortion of tetrahedra due to changes in the O-Si-O angles; and (3) a decrease in the Si-O bond lengths (Jorgensen 1978; Hemley et al. 1994; Ovsyuk

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