

High-pressure and high-temperature crystallographic study of the gillespite I-II phase transition

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Abstract

Crystal structures of gillespite, $\text{BaFeSi}_4\text{O}_{10}$, which has a reversible first-order phase transition at 18 kbar, were refined from data collected at 1 bar and 9, 21, and 45 kbar. Silicate-layer topology is constant through the transition, but coordination of barium increases from 8 to 10. The almost perfect square-planar coordination group of iron in gillespite I ($\text{Fe}-\text{O} = 1.98\text{\AA}$) changes to a flattened tetrahedron with two additional long $\text{Fe}-\text{O}$ bonds ($\sim 3\text{\AA}$) in gillespite II. The volume discontinuity at the gillespite I-II transition is best described as a consequence of the increased coordination of barium and iron.

Unit-cell parameters of gillespite were measured under nine high-pressure and fourteen combined high-pressure, high-temperature (PT) conditions. The Clausius-Clapeyron slope of the transition is $27 \pm 9 \text{ bar}/^\circ\text{C}$, which is similar to the slope of gillespite-I isochores. On the basis of these observations, the behavior of the gillespite I-II transition is consistent with a geometrically controlled phase transformation, in which the size of the barium site is the critical dimensional factor.

Introduction

The barium-iron silicate gillespite ($\text{BaFeSi}_4\text{O}_{10}$), though a rare mineral, has been the subject of much research, due to both an unusual square-planar coordination of ferrous iron and to a high-pressure phase transition, the latter characterized by a striking red-to-blue color change. Strens (1966) first described the transition, which was subsequently examined by absorption spectroscopy (Abu-Eid *et al.*, 1973) and Mössbauer spectroscopy (Huggins *et al.*, 1975, 1976). Hazen and Burnham (1974, 1975) and Hazen (1977), employing high-pressure, single-crystal X-ray diffraction techniques, were successful in identifying a change from tetragonal to orthorhombic symmetry at the phase transition and an associated distortion of the iron site from ideal square-planar coordination. Hazen (1977) also discussed mechanisms of the first-order transition ($\Delta V = 1\%$) and modes of twinning induced by the reduction of symmetry at high pressure.

Gillespite I is tetragonal, $P4/ncc$, $a = 7.516$, $c = 16.076\text{\AA}$, $Z = 4$. The structure (Fig. 1) has an 8\AA subcell parallel to c , but alternate left- and right-handed rotations of four-membered silicate tetrahedral rings cause the c -dimension to be doubled to 16\AA (Hazen and Burnham, 1974). Four nonbridging oxygen ($\text{O}3$) atoms surround each ferrous iron in almost perfect square-planar coordination. The layers of tetrahedrally coordinated silicon are linked by barium atoms in eight-fold distorted cubic coordination.

"Gillespite II"¹ is orthorhombic, $P2_12_12$, $a \approx b \approx 7.4\text{\AA}$, $c \approx 7.9\text{\AA}$, $Z = 2$, and differs from the room-pressure phase in that all four-membered rings in adjacent silicate layers have the same rotational sense. One consequence of the change in relative layer orientation is that the coordination polyhedra of both iron and barium are altered. Details of these changes were poorly resolved in the previous study of the structure at high pressure, due to the low precision of the refinement.

Several questions regarding the gillespite I-II transition remain unresolved. Hazen and Burnham's single high-pressure refinement of gillespite II, which was the first silicate structure to be determined from single-crystal, high-pressure data, is inadequate both in precision and in the number of pressures studied for calculation of polyhedral distortions and compressibilities. The pressure of the natural gillespite transition was uncertain, because internal pressure standards were not available to them. All previous experiments were performed at room temperature; thus the Clausius-Clapeyron slope of the gillespite I-II transition is also unknown. Other unresolved aspects of gillespite at high pressure are the origin of an extra absorption doublet in Mössbauer spectra of synthetic

¹ "Gillespite II," the high-pressure form of $\text{BaFeSi}_4\text{O}_{10}$, has not been observed in nature and thus is not a proper mineral name. This name has been used for convenience only.

