

Bonding and structural changes in siderite at high pressure

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ABSTRACT

Understanding the physical and chemical properties of carbonate minerals at extreme conditions is important for modeling the deep carbon cycle, because they represent likely hosts for carbon in the lower mantle. Previous high-pressure studies have identified a structural and electronic phase transition in siderite using X-ray diffraction and X-ray emission spectroscopy. The Fe end-member of the carbonate group, siderite (FeCO₃), exhibits unique high-pressure behavior that we investigated using a combination of in situ Raman spectroscopy, synchrotron X-ray diffraction, and theoretical methods. In this Raman spectroscopy study, we observed the appearance of a new CO₃ symmetric stretching mode at 20 cm⁻¹ lower frequency beginning at approximately 46 GPa. This softening is due to the lengthening of the C-O bonds as a result of a combination of rotation and volume shrinkage of the FeO₆ octahedra while siderite undergoes the isostructural volume collapse and electronic spin transition.

Keywords: High pressure, diamond-anvil cell, Raman spectroscopy, deep carbon cycle, siderite