CHEMISTRY AND MINERALOGY OF EARTH’S MANTLE

Raman spectroscopy of siderite at high pressure: Evidence for a sharp spin transition

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ABSTRACT

We have measured high-pressure Raman spectra of both siderite single-crystalline and polycrystalline powder samples in diamond-anvil cell experiments across the pressure-induced high-spin (HS) to low-spin (LS) transition of Fe2+. Between 43.3 and 45.5 GPa, we observed a color change from transparent to green, which is associated to the spin transition. Furthermore, we calibrated the position of the Raman active ν₁ mode with pressure. In a second diamond-anvil cell experiment, we observed the color change from transparent to green in the form of a transition front passing through the single crystal and collected Raman spectra across the transition front. We were able to constrain the stress variation across this transition front to about 0.2 GPa, well below the resolution of our Raman-based pressure/stress calibration. In contrast to the single crystal, the powder sample shows the spin transition over a pressure range of 5 GPa, which we attribute to intergranular stresses. We conclude that within the resolution of our stress/pressure calibration the spin transition of iron in single-crystalline siderite is sharp.

Keywords: Siderite, high pressure, carbonates, spin transition

INTRODUCTION

Carbonates are the most frequent carbon carriers in the Earth’s mantle. Therefore their behavior at high pressure promotes our understanding of the processes involved in the deep carbon cycle. Carbonates have been found as inclusions in diamonds, thus proving their existence in Earth’s mantle (e.g., Kaminsky 2012). Furthermore, the proof from natural samples is backed by various experimental studies, which show that various carbonates can be stable under mantle conditions. Examples include Merlini et al. (2012) who studied some of the polymorphs of CaCO₃ up to 40 GPa and Ishiki et al. (2004) who showed that magnesite is stable up to conditions resembling 2600 km depth in the Earth.

It has been shown that the major lower mantle minerals ferropericlase and bridgmanite undergo a pressure-induced transition of Fe²⁺ from high spin (HS) to low spin (LS) state (Badro et al. 2003; Lin et al. 2012), which changes the physical and chemical behavior of these minerals in terms of, for example, sound velocities and thermal conductivities (e.g., Lin et al. 2013).

A spin transition at high pressure can also be expected in Fe²⁺-bearing carbonates. Therefore, either the pure end-member siderite (FeCO₃) or Fe-rich magnesite (MgCO₃), rhodochrosite (MnCO₃), and calcite (CaCO₃) are the ideal materials to study the fine details of such effect on carbonates (e.g., Lavina et al. 2010; Liu et al. 2014). In the following paragraphs, we refer to both the siderite end-member and siderite solid solutions as siderite.

Siderite crystalizes in the calcite structure at ambient conditions. It has been shown by single-crystal X-ray diffraction (XRD) at high pressure that a sharp and isostructural volume collapse ranging from 6.5 to 10% (Lavina et al. 2009, 2010; Nagai et al. 2010; Farfan et al. 2012) takes place between 40 and 50 GPa depending on the composition of siderite (Table 1). The volume collapse is assigned to the HS to LS electronic transition of the octahedrally coordinated Fe²⁺ in siderite. The phenomenon is also accompanied by a sudden change of color from transparent to green (e.g., Lobanov et al. 2015). Depending on the experimental methods and the exact composition of the sample material (Table 1), however, a general inconsistency about the exact pressure and, especially, about the pressure range of the spin transition exists. Studies that used Raman spectroscopy place the spin transition over a sizeable pressure range (4–7 GPa), where the two configurations are thought coexist as micro-domains (Spivak et al. 2014; Cerantola et al. 2015). On the contrary, single-crystal XRD studies observe a sharp spin transition (1–2 GPa).

Lavina et al. (2010), who performed single-crystal XRD on siderite, observe the coexistence of HS and LS state within a narrow pressure range, which they interpret as measuring both HS and LS domains in their sample. A similar behavior was observed in a single-crystal optical absorption study (Lobanov et al. 2015). In particular, Lobanov et al. (2015) report the appearance of a green (LS) domain progressively extending to the whole sample at the expense of the original (HS) transparent domain between 44 and 45 GPa and propose that a stress gradient is responsible for the coexistence of both HS and LS configurations. Domains of high-pressure phases passing through the low-pressure phase have been previously observed. For example Arlt and Angel (2000) see the phase transition of spodumene from the P2₁/c structure to the C2/c structure in the form of a transient domain progressing through a single crystal.