CHEMISTRY AND MINERALOGY OF EARTH’S MANTLE

Optical properties of siderite (FeCO₃) across the spin transition: Crossover to iron-rich carbonates in the lower mantle†

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ABSTRACT

Upper mantle carbonates are thought to be iron poor and magnesium rich. However, at lower mantle conditions spin-pairing transitions in iron-bearing phases may trigger iron redistribution between the minerals. Here, using visible and near infrared absorption measurements, we examine the siderite crystal field up to 65 GPa. Optical spectrum of siderite at 1 bar has an absorption band at 10325 cm⁻¹ corresponding to the crystal field splitting energy (10Dq) of ferrous iron in an octahedral field. This band intensifies and blue-shifts (86 cm⁻¹/GPa) with pressure, but disappears abruptly at 44 GPa signaling the spin transition. Simultaneously, a new absorption band centered at 15629 cm⁻¹ (88 cm⁻¹/GPa) appears in the spectrum. Tanabe-Sugano diagram analysis allowed assigning the observed absorption bands to ⁵T₂g → ³Eₗ and ¹A₄g → ¹T₁g electronic transitions in high- and low-spin siderite, respectively. Similarly, we evaluate the crystal field splitting energy of low-spin siderite 10Dq = 17600 cm⁻¹ (45 GPa), as well as the Racah parameters B = 747 cm⁻¹ and C = 3080 cm⁻¹. We find that the crystal field stabilization energy (CFSE) of ferrous iron in low-spin siderite (45 700 cm⁻¹ at 45 GPa) is an order of magnitude higher than that in the high-spin phase (4130 cm⁻¹ at 1 bar). From the derived CFSE values we estimate the iron-partitioning coefficient for the carbonate-perovskite system and show that low-spin carbonates are iron rich and magnesium poor. We also show that the color of siderite is governed by the ¹A₄g → ¹T₁g absorption band and the Fe-O charge transfer.

Keywords: Crystal field, high pressure, crystal chemistry, Tanabe-Sugano diagram, iron partitioning

INTRODUCTION

Carbonates are involved in the deep carbon cycle with subduction being the major process in transportation of carbon to the mantle (Dasgupta and Hirschmann 2010; Dobretsov and Shatskiy 2012). Chemical interaction of Ca-rich carbonates with silicate minerals in subducting slabs ultimately results in the formation of iron-bearing magnesite (Biellmann et al. 1993; Grassi and Schmidt 2011; Litasov 2011; Seto et al. 2008). Magnesite (MgCO₃) is isosstructural with siderite (FeCO₃) with a continuous range of compositions established for natural and synthetic samples (Bouland et al. 2012; Rividi et al. 2010; Shatskiy et al. 2014). Laboratory experiments (Figuet et al. 2002; Ishihiki et al. 2004), together with findings of carbonates as inclusions in transition zone and lower mantle diamonds (Brenker et al. 2007; Bulanova et al. 2010), indicate that Mg,Fe-bearing carbonates may withstand high-pressure high-temperature conditions of subducting slabs, penetrate into the lower mantle, and experience structural transformations (Bouland et al. 2011; Mao et al. 2011; Oganov et al. 2013; Skorodumova et al. 2005). If so, the electronic structure of iron in lower mantle carbonates may undergo a high-spin (HS) to low-spin (LS) transformation resulting in abrupt changes of carbonate physical properties.

The spin transition in siderite was first reported to occur at approximately 30 GPa by Battila et al. (2007) who employed X-ray emission spectroscopy to measure the spin state of iron in siderite upon compression. Subsequently, the structures of HS and LS siderite were studied by synchrotron X-ray diffraction, and the spin transition pressure was established to be at 43–49 GPa (Lavina et al. 2009, 2010b). Discontinuities in vibrational properties over the spin transition were revealed by Raman spectroscopy; it was found that the Raman shift of lattice modes increases abruptly, whereas C-O symmetric stretching vibration softens at the spin transition pressure indicating a collapse of the FeO₆ octahedra (Farfan et al. 2012; Lin et al. 2012). This is in agreement with the structural model of HS to LS transformation, where the atomic displacements upon the spin transition do not result in a space-group change, and the symmetry of LS siderite is the same as the HS phase (Lavina et al. 2010b). Elastic constants have been reported for a wide range of magnesite-siderite solid solutions both for the HS and LS states (Lavina et al. 2009, 2010a, 2010b; Lin et al. 2012; Litasov et al. 2013; Liu et al. 2014). It was established that the LS phase is denser and has a higher bulk modulus than HS siderite (Lavina et al. 2009;