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CHEMISTRY AND MINERALOGY OF EARTH'S MANTLE

Optical properties of siderite ($FeCO_3$) 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 10 325 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 15 629 cm^{-1} (88 cm^{-1}/GPa) appears in the spectrum. Tanabe-Sugano diagram analysis allowed assigning the observed absorption bands to $^5T_{2g} \rightarrow {}^5E_g$ and $^1A_{1g} \rightarrow {}^1T_{1g}$ electronic transitions in high- and low-spin siderite, respectively. Similarly, we evaluate the crystal field splitting energy of low-spin siderite 10Dq = 17 600 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 $^1A_g \rightarrow {}^1T_{1g}$ absorption band and the Fe-O charge transfer.

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