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Mechanisms of Cr and H incorporation in stishovite determined by single-crystal EPR spectroscopy and DFT calculations

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ABSTRACT

Synthetic stishovite before and after electron- and γ-ray irradiation has been investigated by single-crystal electron paramagnetic resonance (EPR) spectroscopy for the first time. Room-temperature single-crystal EPR spectra of as-is stishovite reveal two high-spin (S = 3/2) Cr^{3+} centers: one with D_{2h} symmetry and another of triclinic symmetry. Quantitatively determined spin Hamiltonian parameters, including matrices **g**, **D**, and **A**(^{53}Cr) and high-spin Zeeman term BS^3, suggest that the D_{2h} center represents a substitutional Cr^{3+} ion at the Si site without an immediate charge compensator. The triclinic center, which is characterized by a well-resolved ^{1}H superhyperfine structure, also arises from a substitutional Cr^{3+} ion at the Si site but has an H^+ charge compensator bonded to one of the four equatorial oxygen atoms. The magnitude and orientation of the ^{1}H superhyperfine structure yield the location of the H atom at (0.46, 0.12, 0). These structural models for Cr and H in stishovite also have been corroborated by periodic density functional theory (DFT) calculations using the Vienna ab initio simulation package (VASP), with $2 \times 2 \times 4$ supercells, plane-wave basis sets and the projector augmented wave (PAW) potentials. In addition, 85 K EPR spectra of irradiated stishovite show that the two Cr^{3+} centers are both converted to an S = 1/2 Cr^{5+} center characterized by two ^{29}Si superhyperfine structures arising from interactions with two nearest and eight second-nearest Si atoms, respectively. The spin Hamiltonian parameters of this Cr^{5+} center provide further support for the location of the two Cr^{3+} centers at the Si site.

Keywords: Stishovite, single-crystal EPR, ^{53}Cr hyperfine, ^{29}Si and ^{1}H superhyperfine, site occupancy, local structure, substitution mechanism, periodic DFT calculations