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\(^{(5)Cr}\) and high-spin Zeeman term BS\(^{1}\), 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\(^{3+}\) 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\(^{3+}\) 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

INTRODUCTION

Stishovite (\(P_{42}/mnm\) or rotation group D\(_{4h}\)), one of the hardest oxides (Luo et al. 2007; Mohanty et al. 2009), has the rutile-type structure containing two magnetically nonequivalent, distorted [SiO\(_4\)] octahedra of orthorhombic (D\(_{2h}\)) symmetry per unit cell (Fig. 1; Sinclair and Ringwood 1978; Yamanaka et al. 2002). Stishovite is of great geological and geophysical interests, because it may occur in significant amounts in the subducted oceanic crust in the Earth’s upper and lower mantle (~10 and 20 vol%, respectively; Irfune et al. 1994; Ono et al. 2002; Lakshtanov et al. 2005). Also, stishovite and other high-pressure polymorphs of silica present in meteorites and shocked rocks are important indicators of planetary impact processes (Chao et al. 1962; El Goresy et al. 2000, 2008). Furthermore, stishovite is a prototype phase for other lower mantle silicates of octahedrally coordinated silicon.

Stishovite, in particular the Al-bearing variety, is capable of accommodating significant amounts of H (up to 3000 wt. ppm H\(_2\)O) (Pawley et al. 1993; Smyth et al. 1995; Chung and Kagi 2002; Bromiley et al. 2006; Litasov et al. 2007) and has been suggested it to play an important role in the transport of water in the Earth’s interior (Panero et al. 2003). These impurities in stishovite (Smyth et al. 1995; Panero 2006; Liu et al. 2007) are known to exert profound effects on its stability and other properties as well. For example, Ono et al. (2002) and Lakshtanov et al. (2005) reported a reduction in the bulk modulus of Al- and H-bearing stishovite relative to its pure counterpart. Lakshtanov et al. (2007a) showed that Al and associated oxygen vacancies in stishovite have strong effects on its density and elastic properties. Also, Lakshtanov et al. (2007b) demonstrated that incorporation of Al results in a significant reduction in the rutile-CaCl\(_2\) phase transition pressure (see also Bolfan-Casanova et al. 2009). Likewise, incorporation of transition metals in stishovite (Litasov et al. 2007; Liu et al. 2007) is expected to affect its physicochemical properties, particularly electrical conductivity and magnetic properties (Matsumoto et al. 2001; Misra et al. 2009; Dho et al. 2010).

Not surprisingly, numerous studies (Pawley et al. 1993; Smyth et al. 1995; Ross et al. 2003; Gibbs et al. 2003, 2004; Panero and Stixrude 2004; Panero 2006; Bromiley et al. 2006; Stebbins et al. 2006; Brunet et al. 2007; Stebbins et al. 2009; Botis