Pressure-induced C23–C37 transition and compression behavior of orthorhombic Fe$_2$S to Earth’s core pressures and high temperatures

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Abstract

The phase stability of orthorhombic Fe$_2$S was explored to 194 GPa and 2500 K using powder and multigrain synchrotron X-ray diffraction techniques. Between 30 and 120 GPa, a C23-like (Co$_2$P, Pnma, Z = 4) Fe$_2$S structure is observed and determined to exhibit a highly compressible a axis. A softening of the a axis occurs between 120 and 150 GPa and a relative stiffening of the b and c axes accompanies this compressibility change. Above 150 GPa, the a axis stiffens as the b and c axes soften, and a C37-like (Co$_2$Si, Pnma, Z = 4) Fe$_2$S unit cell is measured. On the basis of these changes in unit cell geometry, a pressure-induced C23–C37 Fe$_2$S phase transition is inferred between 120–150 GPa. The C23 and C37 (Pnma, Z = 4) structures are closely related and share the same site symmetries. Forming the C37 structure from the C23 structure requires a shortening of the a axis and lengthening of the b and c axes accompanied by a four- to fivefold coordination change. The softening of the a axis above 120 GPa may therefore indicate the onset of a coordination change, and the final compressibility change above 150 GPa may mark the completion of this phase transition. The presented pressure-temperature (P-T) stabilities of C23 and C37 structures of Fe$_2$S are in agreement with and resolve the differing observations of two previous studies (Tateno et al. 2019; Zurkowski et al. 2022). As C37 Fe$_2$S is observed to core-mantle boundary pressures and high temperatures, the C37 Fe$_2$S density profile through Earth’s outer core was determined by fitting the C23 Fe$_2$S equation of state (<120 GPa) and applying a 1.6% volume reduction based on the C37 Fe$_2$S volume residuals to this fit. Comparing the density of liquid C37 Fe$_2$S with that of liquid hcp-Fe (Dewaele et al. 2006) and the seismologically determined density deficit of Earth’s core (Irving et al. 2018), 13.9 ± 1.5 wt% and 8.6 ± 0.8 wt% sulfur are required to match the densities at the CMB and ICB, respectively, for a purely Fe-S core.

Keywords: Fe-sulfide, Earth’s core, high pressure, diamond anvil cell, equation of state, phase transition, iron alloys, high temperature

Introduction

Earth’s seismologically determined density profile and geomagnetic field indicate that its core is likely iron rich, and chemical analysis of mantle materials compared to meteorite compositions suggests that the density deficit measured in Earth’s core compared to iron is a result of a light element component (e.g., Birch 1952; Jephcoat and Olson 1987; McDonough and Sun 1995; Scott and Wasson 1975). Earth’s core is a complex, natural system, and cosmochemically abundant elements such as S, O, Si, C, and H are primary core alloying candidates. Investigating the densities of these core-relevant Fe-alloys at high pressures and temperatures is critical for assessing the multi-component composition of Earth’s liquid outer and solid inner core (Birch 1952; McDonough and Sun 1995). Fe-S alloys are of particular importance because sulfur is a significant component of the iron-rich meteorites thought to originate in the cores of planetesimals. As Earth likely formed from collision and aggregation of planetesimals, iron meteorites may be relic of the building blocks of terrestrial planets like Earth. Sulfur also significantly lowers the melting point of pure iron (e.g., Campbell et al. 2007; Chen et al. 2008; Fei et al. 1997, 2000; Morard et al. 2008), and during Earth’s differentiation, the presence of sulfur would have facilitated metal melt formation and core segregation (e.g., Murthy and Hall 1970; Shannon and Agee 1996; Stevenson 1988; Yoshino et al. 2003).

The Fe-S system is characterized by intricate phase and melting relations. Several high-P-T sulfide phases have been reported in Fe-rich systems. At low pressures, Fe and FeS form a binary eutectic with Fe$_2$S$_2$ stabilizing as an intermediate compound above 14 GPa. Fe$_2$S$_2$ melts at a peritectic to FeS plus liquid at 14 GPa (Fei et al. 1997), and a non-ideal Fe-rich liquidus curve is observed between 14 and 21 GPa (Chen et al. 2008; Tao and Fei 2021). Above 21 GPa, several other sulfides have been identified: Fe$_3$S is observed to melt incongruently to FeS$_2$ plus liquid, and Fe$_2$S is observed over a limited subsolidus temperature and composition range (Fei et al. 2000). The

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