Phase stabilities and spin transitions of Fe$_3$(S$_{1-x}$P$_x$) at high pressure and its implications in meteorites

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ABSTRACT

Fe-S-P compounds have been observed in many meteorites and could be the important components in planetary cores. Here we investigated the phase stability of Fe$_3$(S,P) solid solutions and synthesized high-quality Fe$_3$(S$_{1-x}$P$_x$) high-pressure phases in the multi-anvil press. The physical properties of Fe$_3$(S$_{0.5}$P$_{0.5}$) were further studied in the diamond-anvil cell by synchrotron X-ray diffraction and emission spectroscopy. The solubility of S in the Fe$_3$(S,P) solid solution increases with increasing pressure. The minimum pressure to synthesize the pure Fe$_3$S and Fe$_3$(S$_{0.13}$P$_{0.87}$) is about 21 and 8 GPa, respectively. The observed discontinuity in unit-cell parameters at about 18 GPa is caused by the high-spin to low-spin transition of iron, supported by X-ray emission spectroscopy data. The sulfur solubility in Fe$_3$(S,P) solid solutions could be an excellent pressure indicator if such solid solutions are found in nature.

Keywords: Iron sulfides, iron phosphides, high pressure, meteorites, spin transition

INTRODUCTION

Iron phosphides have been commonly found in iron meteorites, chondrites, and lunar rocks. Early studies reported that phosphorus-bearing Fe-Ni-Cr sulfides, the so-called O-phase in the Murchison and Murray CM chondrites (Bunch and Chang 1980) and in carbonaceous chondrite clasts from the Jodzie howardite (Bunch et al. 1979; Bunch and Chang 1980), could host xenon (Lewis et al. 1975). They can crystallize to a single phase alloyed with one or several metallic elements, such as schreibersite (Fe,P) (Clarke and Goldstein 1978) and barringerite [(Fe,Ni),P$_3$] (Buseck 1969), or combined with other non-metallic elements to form much more complex minerals such as perryite [(Fe,Ni)$_4$((S)$_3$P)$_3$] (Okada et al. 1991). The occurrence of iron phosphides is often found to accompany with iron sulfides and considered to record the thermal dynamic history of the host meteorite. Fe-Ni-S-P phases from the Erevan howardite (Nazarov et al. 2009) and in Lovina meteorite with IIE group (Teplyakova 2011) were generally considered to be a high-temperature product (Nazarov et al. 2009) or a production that undergoes melting when phosphides and sulfides melt locally in metals as a result of impact events with subsequent fast cooling (Teplyakova 2011). Some iron meteorites groups (IIAB, IIIAB, IVA, and IVB) are believed to have evolved in the Fe-Ni-S-P system (Jones and Drake 1983). In IIIAB type meteorite, schreibersite was found to coexist with troilite (Buchwald 1975; Goldstein et al. 2009), which was interpreted as immiscible Fe-S and Fe-P molten phases (Goldstein et al. 2009). In contrast, in Elga meteorite with IIE type, schreibersite and Fe-Ni-P-S alloy forms rims and spheres around silicate inclusions, with S and P nearly evenly distributed (Osadchii et al. 1981). Such feature was interpreted as the meteorite experiencing a dynamic pressure process.

Knowledge of phase relations in the Fe-S-P system at high pressure and temperature is essential to interpret the observations and understand the impact history of the meteorites that host the P-bearing iron sulfides. Although the Fe-S-P system shows a large liquid immiscibility field (Raghavan 1988a, 1988b), high-pressure experiments show complete miscibility between Fe-S and Fe-P (Stewart et al. 2007), which could lead to extensive solid solutions such as Fe$_3$(S,P), Fe$_4$(S,P), and Fe$_5$(S,P). However, the effect of pressure and temperature on the S/P proportion of these solid solutions is largely unknown. For example, Fe$_3$P with $I$ structure is stable at ambient condition, whereas Fe$_3$S with the same structure can only form at pressures above 21 GPa (Fei et al. 2000). The solid solutions between Fe$_3$P and Fe$_3$S would therefore be sensitive to pressure, and the proportion of sulfur (S) and phosphorus (P) in the solid solution would potentially indicate the P-T path of the mineral formation.

Sulfur and phosphorus have also been considered as potential “light elements” that present in planetary cores. Due to the abundance of iron phosphides and iron sulfides in meteorites and the high partition coefficient of sulfur and phosphorus between metal and silicate, they could dissolve into the primary metallic cores of terrestrial planets during early differentiation. Therefore, measurements of the physical properties of the Fe-P-S phases at high pressure will provide constraints on core properties. Previous studies have been focused on iron phosphides, such as (Fe,Ni)$_4$P (Dera et al. 2008, 2009), FeP (Gu et al. 2011), and Fe$_3$P(Gu et al. 2014). In this study, we determine the stability field of the high-pressure Fe$_3$(S$_{1-x}$P$_x$) solid solutions in the Fe-S-P system and measure the physical properties of Fe$_3$(S$_{0.5}$P$_{0.5}$) up to 40 GPa.

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