Stability and bulk modulus of Ni$_3$S, a new nickel sulfur compound, and the melting relations of the system Ni-NiS up to 10 GPa

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**ABSTRACT**

We found a new nickel sulfide that is isostructural with Fe$_3$S. The synthesized nickel sulfide is a non-stoichiometric compound with a Ni deficiency and its composition is Ni$_{2.96±0.1}$S$_{3.9±0.1}$. In situ synchrotron X-ray observations indicate that Ni$_3$S forms above 5.1 GPa and melts incongruently into Ni+liquid up to 10 GPa. The bulk modulus of Ni$_3$S at 300 K was determined to be 140 ± 2 GPa with a fixed $K’=4$ by static compression with a liquid pressure medium. The eutectic point of the Ni-NiS system lies between Ni$_3$S and Ni$_2$S$_3$ up to 10 GPa and its composition changes from Ni$_{0.94±0.05}$S$_{1.57±0.07}$ at 0.1 MPa to Ni$_{3.30±0.05}$S$_{2.83±0.05}$ at 10 GPa. The eutectic melting temperature of the Ni-NiS system decreases to 5.1 GPa and 720 K as the pressure increases where Ni and α-Ni$_3$S$_2$ are the eutectic solids. On the other hand, the eutectic melting temperature increases with a positive slope above 5.1 GPa where Ni$_3$S+α-Ni$_3$S$_2$ is stable under subsolidus conditions. Intermediate compounds appear at a lower pressure in the Ni-NiS system than that for the Fe-FeS system. Ni$_3$S$_2$ is stable at atmospheric pressure and Ni$_3$S forms at 5.1 GPa, whereas Fe$_3$S$_2$ and Fe$_3$S form at 14 and 20 GPa, respectively. The addition of Ni complicates the melting relationship in the Fe-FeS system at high pressure because of the wider stability field of Ni$_3$S. The low-melting temperature of the Fe-Ni-S system plays an important role in the percolative core-formation of planetesimals during planetary accretion.

**Keywords:** Nickel, sulfur, light element, melting, high pressure, core

**INTRODUCTION**

The Earth’s core is thought to consist of iron, nickel, and 5–10 wt% light elements such as sulfur, silicon, oxygen, carbon, and hydrogen (e.g., Poirier 1994). A larger fraction of nickel is partitioned into the core than into the mantle compared with iron (e.g., Urakawa 1991). Nickel is estimated to substitute for at least 5% of the iron in the core based on the solar abundance of the elements. The phase relationships of iron-nickel alloys and light elements are critically important to understand the core formation process during the evolutionary stage of the Earth as well as the chemical composition of the Earth’s core. Among the light elements, sulfur has been intensively investigated as a candidate for light element incorporation into the core and experimental studies have revealed the phase relationships of sulfur-bearing iron systems. The evolution of the eutectic temperature and composition as a function of pressure and the effects of the intermediate compounds, which are stable under high pressures, as well as the effect of the electronic spin transition of FeS on the phase relationships have also been studied (e.g., Usselmann 1975; Urakawa et al. 1987, 2004; Fei et al. 1995, 1997, 2000; Li et al. 2001; Campbell et al. 2007; Chudinovskikh and Boehler 2007; Stewart et al. 2007; Morard et al. 2007; Zhang and Fei 2008; Tsuno and Ohtani 2009; Kamada et al. 2010).

The evolution of phase relationships in the Fe-rich side of an Fe-S system as a function of pressure is affected by intermediate compounds. Fe$_3$S$_2$ forms above 14 GPa and Fe$_3$S$_2$ forms above 20 GPa (Fei et al. 1997, 2000). The eutectic point of the Fe-S system is always located between Fe and the intermediate compound and it continuously shifts toward the Fe-rich side as the pressure increases. On the other hand, the eutectic temperature shows a complex pathway dependent on the pressure and it is nearly constant at up to about 5 GPa (Ryzhenko and Kennedy 1973; Fei et al. 1997). It then decreases to the pressure at which Fe$_3$S$_2$ forms and finally increases with pressure (e.g., Fei et al. 1997, 2000; Morard et al. 2007; Tsuno and Ohtani 2009).

The addition of Ni to a sulfur-bearing iron system shows a remarkable change in phase relationships especially over the eutectic melting temperature (e.g., Urakawa et al. 1987). The addition of Ni should also affect the stability fields of the intermediate compounds of the Fe-S system (Zhang and Fei 2008) but our knowledge about the phase relationships of the Fe-Ni-S system under high pressure is quite limited. Therefore, it is important to investigate the high-pressure phase relationships of the Ni-NiS system to clarify the effects of Ni addition on the phase relationships of the FeS system.

We found that a new sulfide phase with a composition of Ni$_3$S, as a liquidus phase, coexists with the Ni-S liquid while carrying out melting experiments on the Ni-NiS system at 10 GPa. We