Structure of (Fe,Ni)₃S₂ under pressure

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1 Introduction
The Earth and planetary cores are composed of iron-nickel alloy and some light elements. Sulfur is a primary candidate of lightening elements alloyed with iron-nickel. Therefore, phase relations and structure of the iron-nickel sulfides at high-pressures and temperatures are fundamental to study formation process and evolution of the planetary cores. Here we focus attention on iron-nickel sulfide (Fe,Ni)₃S₂. Fe₃S₂ is known to be stable above 14 GPa and affect the melting relations in the system Fe-FeS, but its crystal structure is still unknown [1]. On the other hand, Ni₃S₂ is stable even at 1 atm, which has trigonal symmetry with space group R32 (α-Ni₃S₂ heazlewoodite) [2]. This phase is known to transform into the high pressure orthorhombic structure with Cmcm symmetry at high pressures [3]. In this study we examine stability field of high-pressure phase of Ni₃S₂ and alloying effect of iron to its crystal structure.

2 Experiment
High pressure and temperature experiments were conducted at the pressures of 13 to 18 GPa and the temperatures up to 900 K using the MAX III system installed at PF-AR NE7. X-ray diffraction patterns were taken by an energy dispersive method using a Ge-SSD at Bragg angle of 6 degree. Pressure was evaluated by the unit cell volume of NaCl pressure marker. X-ray profiles were analyzed using the PD Indexer software package provided by Seto Y.

3 Results and Discussion
We observed the phase transformation from α-Ni₃S₂ to the orthorhombic structured Ni₃S₂ between 300 K and 500 K around 15 GPa (Fig. 1). This is close to the phase boundary determined by the first-principle calculation [4]. It is, therefore, though to be reasonable that the high-pressure phase of Ni₃S₂ is stable above 15 GPa. The orthorhombic phase can be quenched to room temperature at high pressures, but it backs into α-Ni₃S₂ after decompression. We also observed (Fe₀.₅Ni₀.₅)₃S₂ under pressure and found the orthorhombic structure stabilized above 700 K around 15 GPa (Fig. 2). Thus about 50 % Fe₃S₂ can dissolve into the high pressure Ni₁S₂ phase. This implies that Fe₃S₂ which is stable above 14 GPa may also take the orthorhombic structure with Cmcm symmetry.

Fig. 1: The P-T path of in-situ observation of Ni₃S₂. Solid squares are the orthorhombic phase and open symbols are α-Ni₃S₂. Dashed line is a phase boundary evaluated by the first-principle calculation [4].

Fig. 2: Energy-dispersive X-ray diffraction profiles of (FeₐNi₁₋ₐ)₃S₂.

References

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