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In-situ observation of formation of Si clathrates

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Introduction

Type-I Si clathrates, whose general chemical formula is A_8Si_{46}, have a unique structure. In the compounds, Si atoms form Si_{20} dodecahedra and Si_{24} tetrakaidehedra, and these polyhedra are linked by shared faces. The A atoms are located in the center of the polyhedra. A search on the superconducting materials has been conducted in Si clathrates since discovery of superconducting fullerides because these polyhedra are isostructural with the fullerene C_{20} and C_{24}. Yamanaka and his coworkers synthesized the superconducting Si clathrate $(Na,Ba)_8Si_{46}$ by removing Na atoms from Na_2BaSi_4 at high temperatures under vacuum [1]. They, furthermore, succeeded in a synthesis of Ba_8Si_{46} from a mixture of Si and orthorhombic $BaSi_2$ at pressures ranging from 3 to 5GPa and temperatures ranging from 1073 to 1673K [2,3]. On the other hand, $BaSi_2$ has been reported to undergo two structural phase transitions, the orthorhombic-to-trigonal, and the trigonal-to-cubic transitions, in this pressure-temperature region [4]. It is, therefore, interesting to see which kind of phases (the orothorhombic, the trigonal or the cubic) of $BaSi_2$ is responsible for the formation of Ba_8Si_{46} from the mixture of $BaSi_2$ and Si at high pressures and high temperatures.

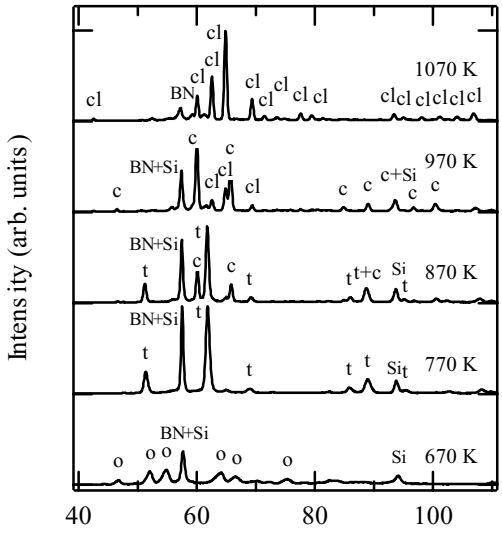
In this research, we have tried to observe the formation of Ba_8Si_{46} from the mixture of $BaSi_2$ and Si in-situ at high pressures and high temperatures.

Experimental

High Pressures were applied using the multianvil high-pressure apparatus MAX80, installed in the beam line PF-AR NE5C. Samples were prepared by arc-melting of an 8:30 molar mixture of orthorhombic $BaSi_2$ and Si. The powdered samples were loaded in a h-BN capsule. Pressure was evaluated from the lattice constant of an NaCl internal pressure marker. The sample was compressed up to 4.3 GPa at room temperature then heated up to 1270 K at this pressure. X-ray diffraction patterns were measured during this process.

Results and Discussion

Figure 1 shows x-ray diffraction patterns of $8BaSi_2$+30Si observed during heating up to 1270 K at about 4.3 GPa. At room temperature at 4.3 GPa, the sample consists of orthorhombic $BaSi_2$ and Si. On heating



up to 870K, only $BaSi_2$ undergoes two structural phase transitions: the orthorhombic-to-trigonal and the trigonal-to-cubic transitions. Si undergoes no structural transition at these temperatures. On further heating, the cubic $BaSi_2$ and Si start to react and the Si clathrate Ba_8Si_{46} appears at 970 K. The formation of Ba_8Si_{46} is completed at 1070 K.

Fig. 1 X-ray diffraction patterns of $8BaSi_2$+30Si observed during heating up to 1270 K at about 4.3 GPa. The symbols “o”, “t”, “c” and “cl” represent reflections from the orthorhombic $BaSi_2$, the trigonal $BaSi_2$, the cubic $BaSi_2$, and the Si clathrate Ba_8Si_{46}.

References

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