Single-crystal growth of multicomponent silicon clathrate compounds by using sodium-tin fluxes

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Silicon (Si) clathrate compounds are composed of host Si atoms organized in cage-like frameworks and guest atoms enclosed in the Si cages. The clathrate compounds exhibit various physical properties depending on the combination of Si cages and inclusion atoms. Si clathrates were generally prepared by thermal decomposition of the precursor compounds. For example, the binary Si clathrates containing Na were synthesized by thermal decomposition of Na_4Si_4 Zintl compound [1]. The clathrate samples obtained by this method were powdery due to the solid state of the precursor compounds. Therefore, it is difficult to prepare the bulk crystal of the Si clathrates. In our previous study, the single crystals of the Na-Si binary clathrate were successfully grown by using Na-Sn flux [2]. In the present study, the single crystals of the multicomponent clathrates were grown by using the Na-Sn flux.

Single crystals of ternary Na-Ga-Si type-I clathrate, $Na_8Ga_xSi_{46-x}$ (x = 4.94–5.52, a = 10.3020(2)–10.3210(3) Å), with the maximum size over 4 mm, were obtained via Na evaporation from Na-Ga-Si melt (molar ratio, Na : Ga : Si : Sn = 6 : 1 : 2 : 1) at 723–873 K. The Si/Ga site, constituting six-membered rings of the $[Si/Ga]_{24}$ cage, was preferentially occupied by Ga atoms with occupancies in the range 64.8(3)–73.0(4) %. The volume increasing rate of the $[Si/Ga]_{24}$ cage is larger than that of the $[Si/Ga]_{20}$ cage. The metallic temperature dependences of the electrical resistivities expected from the formula of $Na_8Ga_xSi_{46-x}$ (x = 4.94–5.52) were confirmed for the single crystals. By heating the Na–Ga–Si–Sn mixture with Sr metal at 773 K, the single crystals of quaternary Si/Ga cage clathrate compounds in which monovalent Na and divalent Sr are mixed in a Si/Ga cage were grown. The occupancies of the Sr atoms for the Na/Sr(2a) sites in the $[Si/Ga]_{20}$ cages (0.605(3)–0.734(3)) were larger than those for the Na/Sr(6d) sites in the $[Si/Ga]_{24}$ cages (0.291(3)–0.435(3)). The Ga occupancies in the $[Si/Ga]_{24}$ cages increased with increasing the Sr composition. It was also shown that increasing the Sr and Ga contents increased the electrical resistivity of the crystal. Single crystals of type-II clathrate $Na_{16}Ba_8Si_{136}$ were synthesized by evaporating Na from a solution of Na_2BaSi_4 and Na_9Sn_4 at 823 K. Na and Ba atoms were full-occupied in Si_{20} and Si_{28} cages, respectively. The electrical resistivity of the single crystal increased with increasing temperature.

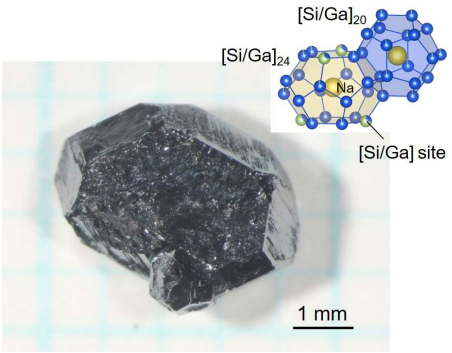

Fig. 1 Single crystal of Na-Ga-Si clathrate grown by Na evaporation from the Na-Ga-Si-Sn solution at 873 K.

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References

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