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Study of superconducting Ba–Ge–Co compounds

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Abstract

We prepared samples with starting composition Ba_8–Ge_{46-x}–Co_x ($x = 0$, 4 and 6) by direct melting. These Ge-based compounds were characterized by X-ray diffraction and WDS, and we found two superconducting transitions at $T_C = 10$ and 4 K in the Co-free sample. Co-doping results in the suppression of T_C to 7 K. The superconducting volume fraction also decreases with increasing Co-doping. For Co-doped samples, there is no 4 K superconducting transition. X-ray refinement shows that the compounds are mixtures of several phases. The dominant phase is diamond Ge, and we found no Ge-clathrate phases. Besides diamond Ge, there are also several weak diffractions from an unknown Ba–Ge phase, and most of them were indexed on the basis of a monoclinic unit cell. Diffraction peaks for Ba_2Ge, BaGe, $BaGe_2$, $BaGe_2O_5$, $BaGeO_3$, Ba_3GeO_5, α-$BaGeO_3$, $BaGe_2O_5$, $Ba_2Ge_5O_{12}$, β-$BaGeO_3$, Ba_2GeO_4 and $BaGe_4O_9$ were carefully searched for but not seen in the samples. For the Co-doped sample, besides the main diamond Ge phase, there is also a semiconducting phase $CoGe_2$. With increasing Co content, the $CoGe_2$ content increases. The WDS results agree with this result. The main phase composition for the Co-free sample is $Ba_{0.01}Ge_{99.9}$. We also discuss the origin of two superconducting transitions in Ge-based compounds.

Keywords: Ge–Ba compounds; Superconductivity; Co-doping; Clathrate

Ge- and Si-based compounds present variegated polymorphs of the same stoichiometric composition that differ in the germanium and silicon metal coordination. The different bonding possibilities of Ge and Si give rise to slightly different structural phases that can differ very much in their physical behaviour. For semiconducting Si- and Ge-based compounds, such as materials with clathrate structure, superconductivity could realize by doping and modify their bonding coordinations and electron structures [1–4]. It is intriguing in theoretical and practical interest although there are some controversies for Ge-based clathrates [2,3]. Superconductivity in these materials has not been so exhaustively explored. In order to help clarify the controversy on these problems, we research transport and magnetic properties on (Ge, Ba)-based compounds. Here, we report two Type II superconducting transitions with $T_C \sim 10$ K and $T_C \sim 4$ K, respectively, in (Ge, Ba)-based compounds. We also report Co-doping effect on superconductivity for (Ge, Ba)-based compounds.

Ba–Ge–Co compounds with starting compositions $Ba_8Ge_{46-x}Co_x$ ($x = 0$, 4 and 6) were synthesized by directly high temperature reaction of elements, and also investigated by X-ray diffractions. Samples are comprised of mixtures of Ge (diamond) and several unknown phases. A high percentage of Ge with diamond structure can be produced for all the samples. Diffraction peaks for Ba_2Ge, BaGe, $BaGe_2$, $BaGe_2O_5$, $BaGeO_3$, Ba_3GeO_5, α-$BaGeO_3$, $BaGe_2O_5$, $Ba_2Ge_5O_{12}$, β-$BaGeO_3$, Ba_2GeO_4 and $BaGe_4O_9$ were carefully searched for but not seen in the samples. For Co-free Ba–Ge sample, several weak diffractions from an unknown Ba–Ge phase were indexed on the basis of a monoclinic unit cell. For Co-doped samples, there is no such unknown phase, but there is $CoGe_2$ phase with the $PdSn_2$ structure. With increasing Co content, the $CoGe_2$ content

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increases. Our composition analyses by using WDS microscopic technique also confirm these results. The main phase composition for the Co-free sample is $Ba_{0.01}Ge_{99.9}$. For the Co-doped samples, besides diamond Ge phase, there is $CoGe_2$ phase, and the content increases with Co-doping increasing.

Fig. 1 presents the magnetizations of Ba_8–Ge_{46-x}–Co_x ($x = 0$, 4 and 6) compounds as a function of temperature, under conditions of zero field cooling (ZFC) at 100 Oe. In the Ge–Ba compound, there are two superconducting phases, and the superconducting transitions is observed at $T_{C1} = 10$ K and $T_{C2} = 3.5$ K, respectively. Resistivity measurement also revealed that there are two superconducting transitions, respectively, originating from so-called the 10 K phase and the 4 K phase. In addition, the irreversibility behaviour of the samples in ZFC and FC procedures show both two transitions belong to the type II superconductors. Under applied field 100 Oe, diamagnetic signals are rather week below T_C, magnetic field suppress the magnitude of superconducting response easily, as shown in Fig. 2, which indicating that superconductivity is not bulk in nature. According to the measurement under a magnetic field of 100 Oe at 2 K for Ba_8Ge_{46}, we estimated the volume fraction of the 4 K phase is ~1% of that expected for a bulk ideal superconductor, while the volume of the 10 K phase is even smaller than that of the 4 K phase, just only about 1/10 of the 4 K phase. This result is in agreement with the X-ray diffraction analysis, in which the 10 K phase and the 4 K phase exist in sample Ba_8–Ge_{46} while in the Co-doped samples there only is the 10 K phase. We take into consideration that there exists no clathrate phases in our Ba_8–Ge_{46} sample, so we can exclude a possibility for the superconducting transition at 10 K originating clathrates. Moreover, our pure-phase germanium clathrates also have shown no sign of the

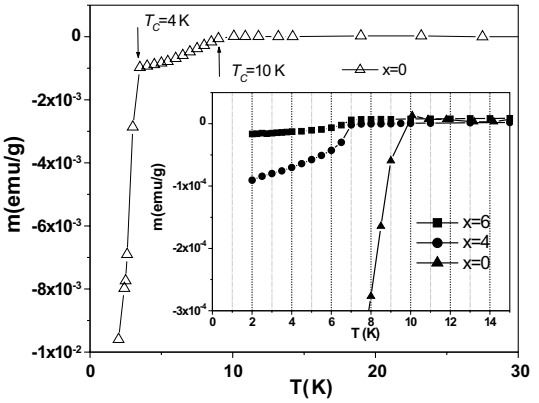

Fig. 1. Diamagnetic behaviour of Ba_8–Ge_{46-x}–Co_x ($x = 0$, 4 and 6) samples under 100 Oe (ZFC). Inset is a magnified view of the temperature region near superconducting transition.

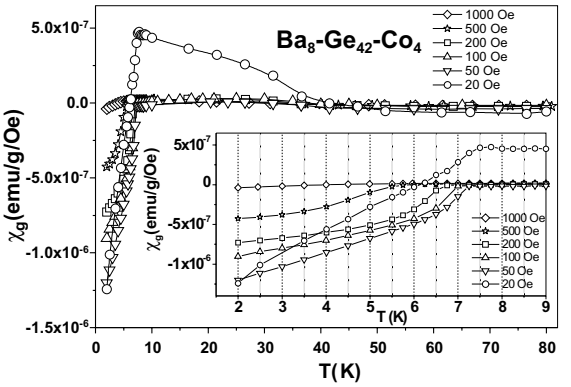

Fig. 2. Temperature dependence of the susceptibility $\chi = M/H$ of the Ba_8–Ge_{42}–Co_4 sample for several applied magnetic fields. Inset shows the detail of M–T curve near T_C.

superconductivity [5]. So our result does not support germanium clathrate with superconductivity [2] at ambient condition.

When Co is doped in Ba–Ge compounds, we found that Co-doping result in a suppression effect on superconducting transition in the 10 K phase. As shown in Fig. 1, the onset superconducting transition temperature is shifted to 7 K. It is clear that Co dopant has entered into lattice of the 10 K phase to suppress superconductivity because of its magnetic moment. The possible pair-breaking effects of the magnetic Co dopant cannot be overlooked simply. On the other hand, one has not observed a second superconducting transition around 4 K yet, which implies that Co doping gives rise to a restraint effect on the 4 K phase producing.

We notice that no sign of the superconductivity was found in our pristine germanium powder and barium lump, and the highest $T_C = 4.93$ K in $BaGe_2$ [6]. We speculate that the superconductivity in Ge–Ba composites originates from a new phase or germanium–barium interaction at the diamond germanium similar to the effect of C–S composite [7], in which a hybridization between carbon and sulfur can increase the local charge density and therefore trigger the superconductivity.

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