Origin of the difference between the high and low-$T_c$ phases in the yttrium sesquicarbide system

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Abstract

The fabrication conditions of a high-pressure synthesis using a BN crucible have been established for the high-$T_c$ ($T_c \approx 14$ K) and the low-$T_c$ ($T_c \approx 12$ K) phases of the yttrium sesquicarbide (Y$_2$C$_3$). The single-phase sample was synthesized from an arc-melted precursor. In contrast, Y$_2$C$_3$ samples made from a powder precursor were not single-phase, although the reproducibilities of the high-$T_c$ phase and the highest value of $T_c$ were higher.

The refinement results of neutron powder diffraction data for the high- and low-$T_c$ phases indicate a small difference between the two phases in the interatomic distance of the C–C dimer, while the lattice parameter was constant for all samples. The values of $dT_c/dP$ were measured for the high-$T_c$ phases ($T_c \approx 15$ K) and low-$T_c$ phases ($T_c \approx 11$ K) by a clamp cell technique detecting the AC susceptibility of the sample. The $T_c$ of Y$_2$C$_3$ systematically changes with applied hydrostatic pressure for both phases. However, the trends for the $dT_c/dP$ are opposite: the value for the high-$T_c$ phase is positive, and that for the low-$T_c$ phase is negative. From these results, we concluded that the difference between the high-$T_c$ and low-$T_c$ phases in our Y$_2$C$_3$ samples did not originate in a simple contraction of the unit cell, but in the difference in the interatomic distances of the C–C dimers.

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1. Introduction

Yttrium sesquicarbide, Y$_2$C$_3$, has long been recognized as a metallic superconductor with a high, over 10 K, superconducting transition temperature, $T_c$ [1]. The highest $T_c$ of pure Y$_2$C$_3$ was long ago determined as 11.5 K, while a higher $T_c$ (over 15 K, which was a very high value at that time) was reported for several related phases [1–3]. However, Amano et al. [4] recently found a high $T_c$ of 18 K for a pure unsubstituted Y$_2$C$_3$ phase. We attempted to confirm the reproducibility of this phenomenon, and discovered from the resistivity data that the upper critical magnetic field, $B_{c2}$, of this phase is over 30 T [5]. However, obtaining further precise information for this high-$T_c$ phase in Y$_2$C$_3$ has been difficult, since the preparation of the single-phase sample is quite challenging. Additionally, the phase instability of this high-$T_c$ phase in air complicated our investigation. Consequently, the origins of the high- and low-$T_c$ phases in the Y$_2$C$_3$ system are still unclear.

According to the report by Amano et al. [4], the lattice parameter of the high-$T_c$ phase is quite a bit shorter than that of the low-$T_c$ phases. Hence, we can expect that the
high-$T_c$ phase could be obtained by applying pressure to the low-$T_c$ phase, if the difference between the phases is simply due to a change in the size of the unit cell. Moreover, we can expect that the differences between the high-$T_c$ and low-$T_c$ phases can be explained from the structural data.

In this paper, we discuss our experimental results with respect to single-phase fabrication, neutron powder diffraction (NPD), and the effect of pressure on $T_c$. Based on these results, we evaluate the origin of the difference between the high-$T_c$ and low-$T_c$ phases.

2. Experiments

The samples were fabricated using a cubic-anvil-type high-pressure apparatus. The synthesis conditions were $3.5\text{ GPa at } 1400 ^\circ C$ for $30\text{ min in a BN crucible}$ [6]. For this high-pressure synthesis, we prepared two types of precursors: first was a mixture powder of yttrium ($99.9\%$: Kojundo Chemical Lab.) and carbon (graphite: $99.9\%$: Rare Metallic Co., Ltd.) with a nominal composition of $Y_2C_3$, and the second was a melted bulk of $Y_2C_3$. The melted bulk was prepared from bulk yttrium metal ($99.99\%$: Rare Metallic Co., Ltd.) and carbon (graphite $99.999\%$: Rare Metallic Co., Ltd.) by the arc-melting technique.

The samples’ $T_c$ values were characterized at ambient pressure with a SQUID magnetometer (MPMS-XL: Quantum Design) in $10\text{ Oe of applied magnetic field}$, and for the phase content by X-ray diffraction (XRD, RINT2500: RIGAKU) at room temperature.

For the evaluation of the crystal structures, we took NPD data for the high-$T_c$ and low-$T_c$ phases with a time-of-flight versatile neutron diffractometer (VEGA) [6] at the Neutron Science Laboratory (KENS) in the High Energy Accelerator Research Organization. The details of the NPD measurements and the Rietveld refinements [7] are described elsewhere [8].

For the measurement of the hydrostatic-pressure effect on $T_c$, we utilized the clamp cell technique [9], and measured the value of the $T_c$ from the AC susceptibility data [10]. A pickup-coil (outer: $\phi = 3\text{ mm}$; inner: $\phi = 2\text{ mm}$, length $5\text{ mm}$) filled with the sample, Pb, and MgB$_2$ as references for the temperature-calibrations using the known $P$–$T_c$ dependence for these materials [11,12] was put into the clamp cell (outer: $\phi = 25\text{ mm}$; inner: $\phi = 7\text{ mm}$, length $70\text{ mm}$). In order to observe the superconducting transition curve of the $Y_2C_3$ sample as clearly as possible, we separated the sample and reference materials; their directions of superconducting transition curves become to be opposite. The pickup-coil plus sample was put into the clamp cell with a pressure-transmitting medium (Daphne Oil 7373: Idemitsu Kosan company). The clamp cell was pressurized in the range from 0.16 to 2 GPa. The values of $T_c$ were determined by drawing two extrapolated lines for the data around it and the results were checked from estimated onset $T_c$ values in the data plotted with the same scale. The details of the $T_c$ determination are described elsewhere [10].

3. Results and discussion

The superconducting phase of $Y_2C_3$ was successfully synthesized from both the powder and the arc-melted precursors. The lattice parameter, $a$, of the $Y_2C_3$ was almost constant at $a \approx 8.235\text{ Å}$ for all samples, even though the $T_s$s were different. On the basis of the $T_c$ values, we roughly classified the samples obtained into two groups: one has a $T_c$ of 9–12 K (“low-$T_c$ phase”) and the other has a $T_c$ of 14–18 K (“high-$T_c$ phase”). According to the report in 1969 by Krupka et al. [1], the $T_c$ of $Y_2C_3$ strongly depended on the synthesis conditions, and the highest value noted then was 11.5 K. Therefore, our low-$T_c$ phase samples appear to be the same as the conventional $Y_2C_3$ sample investigated in the 1970s. The results of sample fabrications for $Y_2C_3$ from each precursor are summarized in Table 1. In the sample made from the powder precursors, we noted many impurities, as shown by the peaks in the XRD patterns of Fig. 1; however, we consistently obtained the high-$T_c$ phase from the powder. The $T_c$ was always larger than 15 K (around 18 K). On the other hand, samples made from the arc-melted precursor always showed an XRD pattern assigned as single-phase $Y_2C_3$ (see Fig. 1). However, the $T_c$ of such a sample was not reproducible (i.e. the $T_c$ varied from run to run, sometimes high and sometimes low); the $T_c$ of the high-$T_c$ phase made from an arc-melted precursor was approximately 14.5 K (i.e. less than 15 K). The reason for the difference between the powder and arc-melted precursors has not yet been clarified. It does seem to imply important information about the origin of the high-$T_c$ phase, but requires further investigation.

Fig. 2 shows the Rietveld refinement for the high- and low-$T_c$ phases of the $Y_2C_3$ fabricated from arc-melted precursors, and Table 2 summarizes the interatomic distances and the value of $a$ determined from the refinement results for these samples. More extensive data are described elsewhere [8]. According to the results, the value of $a$ is the same for both types of samples. However, the interatomic distances change slightly, except for the

| Precursor | XRD result | SQUID result |
|-----------|------------|--------------|
| Powder    | Impurities | • Major superconducting phase is high $T_c$ ($\geq 18\text{ K}$). |
|           |            | • Minor phase is low $T_c$ ($9\text{ K} < T_c < 12\text{ K}$). |
| Arc-melt  | Single-phase | • The $T_c$ varied from run to run, sometimes high and sometimes low. |
|           |            | • High $T_c$ ($\geq 14.5\text{ K}$) and/or low $T_c$ ($9\text{ K} < T_c < 12\text{ K}$) phases. |
Y–Y\textsuperscript{iv} distances, which are the lengths of the Y–Y bond along the [1 1 1] direction. The relative change in the Y–Y\textsuperscript{iv} distances (Δl/l = −2.80 \times 10^{-5}) is much lower than others, and is almost the same as that of the lattice parameter (Δa/a = −2.43 \times 10^{-5}). The C–C\textsuperscript{iv} distance is shorter than the other distances, and is the parameter that varies most between the high-\textit{Tc} and low-\textit{Tc} phases. This distance is the length of the C–C dimer threefold symmetry axis around the Y–Y\textsuperscript{iv} bond when viewed from the [1 1 1] direction. These data suggest that \textit{a} depends on the Y–Y bond length along the [1 1 1] direction, but, for our samples, this bond length seems to be a constant parameter in which we can observe no variation. However, the distances associated with the C position are different, and thus, the interatomic distances of the C–C dimer vary between the high-\textit{Tc} and low-\textit{Tc} phases. The electronic structure, which affects the superconductivity, strongly depends on the atomic positions of the elements constituting the material. Therefore, we believe that the superconductivity of Y\textsubscript{2}C\textsubscript{3} correlates with the length of the C–C dimer.

The pressure dependence of \textit{Tc} was measured for Y\textsubscript{2}C\textsubscript{3} samples prepared from both powder and arc-melted precursors, and the results are plotted in Fig. 3. The values of \textit{Tc} for all samples change linearly with the applied pressure; however, the values of d\textit{Tc}/d\textit{P} are not the same. For the high-\textit{Tc} phases, these values are positive, but for the low-\textit{Tc} phase, they are negative. This result indicates that obtaining the high-\textit{Tc} phase of Y\textsubscript{2}C\textsubscript{3} is impossible by simply compressing the unit cell of the low-\textit{Tc} phase. In this case, the pressure applied to the sample was not an anisotropic pressure, such as a chemical pressure, but a hydrostatic pressure via an oil medium. Therefore, the applied pressure must have changed not only the length of the C–C dimer, but also all the other interatomic distances in Y\textsubscript{2}C\textsubscript{3}. Thus, the electronic structure of the pressurized low-\textit{Tc} phase could not resemble that of the high-\textit{Tc} phase.

The absolute value of d\textit{Tc}/d\textit{P} is plotted in Fig. 4 as a function of the \textit{Tc} at ambient pressure. Though there are too few data points for Y\textsubscript{2}C\textsubscript{3} to allow for quantitative discussion, we may still say that there is a linear relationship. In that case, the McMillan equation is applicable [13], and the slope of the line depends on the interatomic electron–phonon coupling. The slope of the line changes in...
will result in an increase in the $T_c$. Our $Y_2C_3$ samples were fabricated via a high-pressure synthesis, and the samples were in direct contact with the BN crucible. Therefore, some N may have substituted for the C, and electron doping could occur. The substitution of N for the C of $Y_2C_3$ intuitively seems difficult. However, the reactive surface area between the starting material and BN is larger for the powder precursor than the arc-melted precursor. Thus, the powder precursor, which is likely to react more easily with BN than the arc-melted precursor, readily produced the high-$T_c$ phase in our case. This result also may support our speculations, although there is no evidence for the N substitution, and no quantitative analyses of the difference between the high-$T_c$ and the low-$T_c$ phases have yet been done. Thus, $Y_2C_3$ requires further investigation.

4. Conclusions

To compare the high- and low-$T_c$ phases in the $Y_2C_3$ system, we fabricated single-phase samples of this compound. The sample prepared from an arc-melted precursor was identified as a single-phase sample of $Y_2C_3$; however, the maximum $T_c$ of the high-$T_c$ phase was low ($T_c \approx 14.5$ K). At the same time, the sample prepared from a mixture powder of Y and C included a certain amount of impurity phases; however, the maximum $T_c$ of the high-$T_c$ phase was high ($15 < T_c < 18$ K). In order to evaluate the precise crystal structure, we performed NPD measurements for the high- and low-$T_c$ phases. The two phases differed in the interatomic distance of the C–C dimer. We suspect that this structural change affected the electronic structure of the $Y_2C_3$ samples and is the reason for the difference between the phases. Moreover, the experimental result for the hydrostatic pressure dependence of $T_c$ shows that the gradients, $dT_c/dP$, show opposite trends: a positive value for high-$T_c$ and a negative value for low-$T_c$ phases. Our preparative technique applies isotropic pressure to the sample, thereby compressing all bond distances equally. From our results, we conclude that the difference between the high-$T_c$ and low-$T_c$ phases in our $Y_2C_3$ samples did not originate in a simple contraction of the unit cell, but in the varying interatomic distances of the C–C dimer.

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