Superconductivity in oxygen-added Zr$_5$Pt$_3$

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Keywords: Mn$_5$Si$_3$-type, oxygen addition, superconductivity, microstructure, composition effect

Abstract

Mn$_5$Si$_3$-type structure has been offering an interstitial chemistry. Recent report of enhancement of superconductivity in a Nb-based Mn$_5$Si$_3$-type compound by addition of an interstitial atom motivated us to investigate the effect of oxygen-addition in Mn$_5$Si$_3$-type Zr$_5$Pt$_3$. The superconducting critical temperature of 6.4 K in the parent Zr$_5$Pt$_3$ is monotonously reduced to 3.2 K in Zr$_5$Pt$_3$O$_x$ ($x = 0.6$) with increasing oxygen-content. As $x$ is further increased from 0.6 to 2.5, exceeding the full occupancy of oxygen site ($x = 1.0$), samples become multi-phases composed of Zr$_5$Pt$_3$O$_{0.5-0.6}$, ZrPt and ZrO$_2$. However, the superconducting critical temperature slightly increases to 4.8 K at $x = 2.5$. The metallographic observation has revealed a change of microstructure at $x \geq 1.0$. The change of microstructure and/or the composition effect would be responsible for the enhancement of superconductivity.

1. Introduction

A wide variety of atoms form the hexagonal Mn$_5$Si$_3$-type structure [1], represented as A$_5$B$_3$, with the space group P6$_3$/mcm (No.193). There are three crystallographic sites in A$_5$B$_3$. The A atoms occupy the 4d (for A1 atom) and 6g (for A2 atom) sites and the B atom occupies another 6g site. The A atoms mainly consist of early transition metals, rare earth elements and alkaline earth elements. Metalloid elements and post-transition metals are usually responsible for B atoms. The extensive electron-number of A$_5$B$_3$ allows various interstitial atoms such as oxygen, boron and carbon. These interstitial atoms, denoted by X, occupy the 2b site in P6$_3$/mcm and A$_5$B$_3$X is called as the Ti$_5$Ga$_4$ or Hf$_5$CuSn$_3$-type structure. Figure 1 shows the crystal structure of A$_5$B$_3$X compound. The added X atom is surrounded by A$_2$ atoms in the octahedral site, which forms a face-sharing A$_2$ chain along the c-axis. Another octahedral B atoms enclose the A1 atom which also forms a one-dimensional atomic chain along the c-axis. Therefore an expansion of lattice parameter a would enhance the one-dimensional nature of octahedral A$_2$ and A1 atomic chains.

Although physical properties of numerous Mn$_5$Si$_3$ or Ti$_5$Ga$_4$-type compounds are investigated [2–5], the superconductivity is reported only in several compounds. The Nb-based system Nb$_3$Ir$_2$O is attractive as a rather high superconducting critical temperature $T_c$ compound. In Nb$_3$Ir$_2$O, the parent Mn$_5$Si$_3$-type Nb$_3$Ir$_2$ exhibits superconductivity at 9.3 K. As the oxygen atoms are added, $T_c$ progressively increases to 10.5 K in Nb$_3$Ir$_2$O, which possesses two kinds of superconducting gaps revealed by the specific heat measurement [6].

As for Zr$_5$Ge$_3$-type compounds, Lv et al have reported the superconducting Zr$_5$Sb$_3$ with $T_c$ of 2.3 K [7]. Zr$_5$Sb$_3$ allows interstitial oxygen atoms fully occupying the 2b site. Contrary to the enhancement of $T_c$ in Nb$_3$Ir$_2$O, the addition of oxygen atoms reduces $T_c$ and Zr$_5$Sb$_3$O is a normal metal down to 1.8 K [7]. Recently it has been discovered [8] that a Ru substitution into the Ge site in non-superconducting Zr$_5$Ge$_3$ induces a superconducting behavior at 5.7 K. About 30 years ago, Waterstrat et al reported [9] that Zr$_5$Pt$_3$ is a superconductor with $T_c$ of 7.2 K. Furthermore, oxygen-added Zr$_5$Pt$_3$O is reported to crystallize in the Ti$_5$Ga$_4$-type structure [10], however, the physical properties of Zr$_5$Pt$_3$O have not been investigated. We have focused on the effect of oxygen-addition in superconducting Zr$_5$Pt$_3$. In this paper, we report the synthesis and metallographic characterization of Zr$_5$Pt$_3$O$_x$ and the oxygen-content dependence of $T_c$. 
2. Materials and methods

Polycrystalline samples were prepared using Zr pieces (or powder) (99%), Pt wire (99.9%) and ZrO₂ powder (98%). Zr₅Pt₃ was synthesized by arc melting the Zr pieces and Pt wire with the stoichiometric composition. To synthesize oxygen-added Zr₅Pt₃Oₓ, Zr₅Oₓ was initially prepared as follows. Zr and ZrO₂ powders were mixed in an agate mortar and pressed into a pellet. The pelletized sample was arc melted and then Zr₅Oₓ was remelted with added Pt wire to form the stoichiometric composition. The samples were remelted several times to ensure the homogeneity of the samples. The weight loss during the arc melting was negligible. Each as-cast sample was annealed in an evacuated quartz tube at 800 °C for 4 days. The samples were evaluated using a powder x-ray diffractometer (Shimadzu, XRD-7000L) with Cu-Kα radiation. The metallographic characterization was carried out by observing back-scattered electron images obtained by a field emission scanning electron microscope (FE-SEM; JEOL, JSM-7100F). The atomic composition of sample was checked by using an energy dispersive x-ray (EDX) spectrometer that was equipped with the FE-SEM.

The temperature dependence of ac magnetic susceptibility χac(T) in an alternating field of 5 Oe at 800 Hz, between 2.8 K and 300 K, was measured using a closed-cycle He gas cryostat. The temperature dependence of electrical resistivity ρ(T) between 2.8 K and 300 K was measured by the conventional DC four-probe method using the cryostat.

3. Results and discussion

Figure 2(a) shows the x-ray diffraction (XRD) patterns of Zr₅Pt₃Oₓ (x = 0, 0.2, 0.6 and 1.0). The simulated patterns of Zr₅Pt₃ (Mn₅Si₃-type) and Zr₅Pt₃O (Ti₅Ga₄-type) are also presented. The diffraction peaks of parent compound Zr₅Pt₃ and oxygen-added Zr₅Pt₃Oₓ with x = 0.2 and 0.6 samples can be well indexed by the Mn₅Si₃-type and the Ti₅Ga₄-type structure, respectively. Although the XRD pattern of Ti₅Ga₄-type structure is contained in Zr₅Pt₃Oₓ, impurity phases of ZrPt (filled triangle) and ZrO₂ (filled circle) appear. The ideal uppermost oxygen content is 1.0 by taking into account the full occupancy of 2b site, however, we prepared the samples with x exceeding 1.0. The peak intensity of impurity phases grows with increasing x from 1.0 (see figure 2(b)). In Zr₅Pt₃Oₓ, the maximum peak intensity of ZrPt surpasses that of the Ti₅Ga₄-type structure. The lattice parameters of prepared samples were refined by the least square method using XRD data and listed in table 1. The x dependences of a and c, and c/a-ratio are displayed in figures 3(a) and (b), respectively. In both figures, the nominal oxygen-content is employed as x. Both a and c systematically decrease with increasing x from 0 to 1.0. Above x = 1.0, c steeply increases, while a shows a slight increase. A monotonous increase of c/a-ratio with increasing x is confirmed in figure 3(b).

Figure 1. Crystal structure of Ti₅Ga₄-type A₅B₃X compound (a) along the c-axis and (b) in the a-b plane, respectively.
Back-scattered electron images obtained by FE-SEM with electron beams of 15 keV are shown in figure 4. The atomic composition obtained by EDX measurement of each sample is listed in table 2. For each sample with $x \leq 0.2$, non-contrast image means almost single phase. In Zr$_5$Pt$_3$, Zr$_5$Pt$_3$O$_{0.2}$ and Zr$_5$Pt$_3$O$_{0.6}$, the respective sample shows the atomic composition being near to the starting one. As $x$ is further increased from 1.0, the sample decomposes into three phases Zr$_5$Pt$_3$O$_{\sim 0.5 - 0.6}$, ZrPt and ZrO$_2$. Although the composition ratios between Zr and Pt atoms in Zr$_5$Pt$_3$O$_x$ ($x \leq 1.0$) are close to Zr$_5$Pt$_3$, the oxygen-contents are far less than the nominal ones, which means a solubility limit of oxygen atoms ($x \sim 0.6$) in Zr$_5$Pt$_3$. The dark islands observed in Zr$_5$Pt$_3$O$_x$ ($x \geq 1.0$) are ZrO$_2$ phases, which begin to appear in Zr$_5$Pt$_3$O$_{0.6}$ as a small amount of point-like structure. The

![Figure 4](image-url)

Figure 2. (a) XRD patterns of Zr$_5$Pt$_3$O$_x$ with $x = 0, 0.2, 0.6$ and 1.0. The simulated patterns of Zr$_5$Pt$_3$ and Zr$_5$Pt$_3$O are also shown. The origin of each pattern is shifted by an integer value for clarity. The filled triangle and circle denote impurity phases of ZrPt and ZrO$_2$, respectively. (b) XRD patterns of Zr$_5$Pt$_3$O$_x$ with $x = 1.0, 1.5$ and 2.5. The simulated patterns of ZrPt and ZrO$_2$ are also shown. The origin of each pattern is shifted by an integer value for clarity.

Table 1. Lattice parameters ($a$ and $c$), $c/a$-ratio and $T_c$’s determined by $\chi$ ac and $\rho$ measurements for Zr$_5$Pt$_3$O$_x$ and Zr$_4.9$Pt$_3.1$O$_{0.67}$.

| Sample          | $a$ (Å)  | $c$ (Å)  | $c/a$  | $\chi_{ac}$ (K) | $\rho$ (K) |
|-----------------|----------|----------|--------|-----------------|-------------|
| Zr$_5$Pt$_3$    | 8.182(3) | 5.384(2) | 0.6380 | 6.4             | 6.4         |
| Zr$_5$Pt$_3$O$_{0.2}$ | 8.167(2) | 5.375(1) | 0.6381 | 4.1             | 4.0         |
| Zr$_5$Pt$_3$O$_{0.6}$ | 8.156(2) | 5.372(2) | 0.6387 | 3.2             | 3.1         |
| Zr$_5$Pt$_3$O   | 8.151(3) | 5.369(2) | 0.6387 | 3.8             | 3.2         |
| Zr$_5$Pt$_3$O$_{1.5}$ | 8.159(3) | 5.376(2) | 0.6390 | 4.1             | 3.7         |
| Zr$_5$Pt$_3$O$_{2.5}$ | 8.175(3) | 5.384(2) | 0.6401 | 4.8             | 4.8         |
| Zr$_4$Pt$_3$O$_{0.67}$ | 8.159(2) | 5.379(1) | 0.6393 | 3.7             | 3.3         |
brighter images in figures 4(d), (e) and (f) are ZrPt phases. It is remarkable that Zr5Pt3O0.5−0.6 and ZrPt partially forms a eutectic-like structure, for example, denoted by red elliptic closed-curves as in figures 4(d) and (e). On going from x = 1.0, 1.5 to 2.5, the area of eutectic-like structure seems to increase. We note here that it is important to investigate a phase relation, a homogeneity range and so on, for example, using a differential thermal analysis method. However, even for the binary Zr-Pt system, the phase diagrams in the vicinity of Zr5Pt3 differ from literature to literature [11–13], which indicates some difficulties in obtaining a precise phase relation or homogeneity range for Zr5Pt3Ox system. Therefore, a thermal analysis study would require a long time and careful experiment, and remains an issue.

Shown in figures 5(a) and (b) are χac(T) of Zr5Pt3Ox with 0 ≤ x ≤ 0.6 and those with 1.0 ≤ x ≤ 2.5, respectively. All Zr5Pt3Ox samples exhibit diamagnetic signals. In each sample, Tc was determined as being the intercept of the linearly extrapolated diamagnetic slope with the normal state signal (see the broken lines in the figures), and listed in table 1. Tc of Zr5Pt3 is slightly lower than the literature [9] value 7.2 K. As x is increased from 0 to 0.6, Tc systematically decreases to 3.2 K. However, further increase of x enhances Tc up to 4.8 K at x = 2.5. As mentioned above, the samples with x ≥ 1.0 contain well known insulating ZrO2 and ZrPt. In order to check whether ZrPt is a superconductor or not, χac of ZrPt was measured and no diamagnetic signal down to 2.8 K is observed as shown in figure 5(b). Therefore the observed superconductivities are intrinsic for Zr5Pt3O0.5−0.6 phases in Zr5Pt3Ox with x ≥ 1.0.

Figures 6(a) (b) summarizes ρ(T) of Zr5Pt3Ox with 0 ≤ x ≤ 0.6 (1.0 ≤ x ≤ 2.5). In a few samples with low Tc, zero resistivity could not be observed at the lowest achievable temperature. Each Tc determined by following the same manner as in χac(T) roughly corresponds to that obtained by χac(T) measurement (see table 1). The sample with x = 0 (also with 0.2 and 0.6) shows ρ(T) largely deviating from the linearity above Tc. The similar deviation is observed in A15 superconductors such as Nb3Sn or a pyrochloa superconductor of KO8S8O, which is ascribed to an existence of additional scattering source [14, 15]. Although the origin of scattering source might be controversial, Woodward and Cody [14] have presented a well-known empirical formula as follows:
where the first term means a residual resistivity, the second one phonon part of $\rho$ and the third one describes anomalous temperature dependence. In Nb$_3$Sn and KO$_3$O$_6$, the equation well reproduces respective $\rho(T)$. We have also fitted $\rho(T)$ of Zr$_3$Pt$_3$ using equation (1). If the linear term $\rho_l T$ is taken into account, the fitting accuracy is not satisfactory. The well reproducibility as depicted by the solid curve in figure 6 can be obtained by eliminating the linear term, which suggests a dominance of anomalous temperature dependence. The parameters were determined to be $\rho_0 = 183 \mu\Omega$cm, $\rho_2 = 234 \mu\Omega$cm and $T_0 = 56$ K. The large deviation from the linearity is not discernible in $\rho(T)$ of samples with $x \geq 1.0$ partially due to the contamination by ZrPt.

Zr$_3$Pt$_3$O$_x$ with $x = 0.2$ and 0.6 can be regarded as the almost single-phased Ti$_5$Ga$_4$-type with the 2b site partially filled by oxygen atoms. The oxygen addition up to $x = 0.6$ systematically reduces $T_c$. The similar systems of Nb$_3$Ir$_3$O and Zr$_3$Sb$_3$O also exhibit some interstitial-atom concentration dependences of $T_c$ [6, 7]. The

$$\rho = \rho_0 + \rho_1 T + \rho_2 \exp \left( -\frac{T}{T_0} \right).$$  (1)

Table 2. Atomic composition of Zr$_3$Pt$_3$O$_x$ and Zr$_{4.8}$Pt$_{3.1}$O$_{0.67}$ determined by EDX measurement.

| Sample      | Atomic composition                                      |
|-------------|---------------------------------------------------------|
| Zr$_3$Pt$_3$ | Zr$_{5.1(2)}$Pt$_{2.9(2)}$                              |
| Zr$_3$Pt$_3$O$_{0.2}$ | Zr$_{4.9(1)}$Pt$_{3.1(1)}$O$_{0.2(9)}$               |
| Zr$_3$Pt$_3$O$_{0.6}$ | Zr$_{5.1(1)}$Pt$_{2.9(1)}$O$_{0.6(6)}$           |
| Zr$_3$Pt$_3$O$_{1.0}$ | Zr$_{5.2(2)}$Pt$_{2.8(1)}$O$_{0.4(5)}$, Zr$_{1.0(2)}$Pt$_{1.0(2)}$, Zr$_{1.0(2)}$O$_{1.0(0)}$ |
| Zr$_3$Pt$_3$O$_{1.5}$ | Zr$_{4.9(1)}$Pt$_{3.1(1)}$O$_{0.8(7)}$, Zr$_{0.9(9)}$Pt$_{1.0(1)}$, Zr$_{0.9(9)}$O$_{0.2(9)}$ |
| Zr$_3$Pt$_3$O$_{2.5}$ | Zr$_{4.9(1)}$Pt$_{3.1(1)}$O$_{0.7(7)}$, Zr$_{0.9(9)}$Pt$_{1.0(1)}$, Zr$_{0.9(9)}$O$_{0.2(8)}$ |
| Zr$_{4.8}$Pt$_{3.1}$O$_{0.67}$ | Zr$_{4.9(1)}$Pt$_{3.2(2)}$O$_{0.4(2)}$, Zr$_{0.9(9)}$Pt$_{1.0(1)}$, Zr$_{0.9(9)}$O$_{0.2(0)}$ |

Figure 4. Back-scattered electron (15 keV) images of Zr$_3$Pt$_3$O$_x$ for nominal $x$ values of (a) 0 (b) 0.2 (c) 0.6 (d) 1.0 (e) 1.5 and (f) 2.5, respectively.
reported dependences, combined with the variations of lattice parameters by atom additions, are summarized in table 3. In Nb$_4$Ir$_3$O, $T_c$ enhancement occurs with the addition of oxygen atoms, which shrinks $c$ and expands $a$. The expansion of $a$ would bring octahedral Nb$_{26}$ and Nb$_{13}$ atomic chains closer to a one-dimensional system, and the shrinkage of $c$ leads to a shorter Nb-Nb distance. These might cause the $T_c$ enhancement. On the other hand, Zr$_5$Sb$_3$O and Zr$_5$Pt$_3$O$_x$ ($x \approx 0.6$) show the reduction of $T_c$ by adding oxygen atoms. In Zr$_5$Pt$_3$O$_x$ ($x \approx 0.6$), both $a$ and $c$ decrease by oxygen addition, while the opposite trends are reported [7, 16] in Zr$_5$Sb$_3$O, suggesting the weak correlation between lattice parameters and $T_c$. In Zr compounds with the Mn$_5$Si$_3$-type structure, for example, the superconductivity appears [8] by substituting Ru into the Ge site in Zr$_5$Ge$_3$. The substitution of atoms would be effective for the enhancement (appearance) of superconductivity in Zr based Mn$_5$Si$_3$ or Ti$_5$Ga$_4$-type structure.

We discuss here the $T_c$ enhancement in Zr$_5$Pt$_3$O$_x$ with $x \geq 1.0$, in which the superconducting Zr$_5$Pt$_3$O$_{0.5–0.6}$ phase coexists with ZrO$_2$ and ZrPt phases. Once the phase decomposition occurs at $x = 1.0$, the oxygen content is reduced to approximately 0.45. The increase of $x$ from 1.0 again gradually adds oxygen atoms. Contrary to the above mentioned results of Zr$_5$Pt$_3$O$_x$ ($x \leq 0.6$), the oxygen addition causes the $T_c$ enhancement. As shown in figures 3(a) and (b), $a$, $c$ and $c/a$ might have some correlation with $T_c$ of samples with $x \geq 1.0$; the expansion of both $a$ and $c$ with increased $c/a$-ratio possibly leads to the enhancement of $T_c$. In order to elucidate the correlation between lattice parameters and $T_c$, we prepared a sample with the starting composition of Zr$_{4.9}$Pt$_{3.1}$O$_{0.67}$. The compound, containing ZrPt impurity phase detected as the brighter image in figure 7, shows $a$, $c$ and $c/a$-ratio, which are between those of the sample with $x = 1.5$ and $x = 2.5$ (see table 1). Nonetheless $T_c$,

Figure 5. (a) Temperature dependence of $\chi_{ac}$ for Zr$_5$Pt$_3$O$_x$ with $x = 0.0, 0.2$ and 0.6. (b) Temperature dependence of $\chi_{ac}$ for Zr$_5$Pt$_3$O$_x$ with $x = 1.0, 1.5$ and 2.5. $\chi_{ac}(T)$ of ZrPt is also shown.
of Zr$_4.9$Pt$_3.1$O$_{0.67}$ is lower than that of the sample with $x = 1.5$ as demonstrated by figure 8. This result suggests that the degree of $T_c$ enhancement is not determined only by the lattice parameters. The important metallographic aspect is that, as $x$ is increased, the microstructure changes at $x \geq 1.0$, showing the $T_c$ enhancement (see also figures 4(d) to (f)). However, the microstructure of Zr$_4.9$Pt$_3.1$O$_{0.67}$ as shown in figure 7 is largely different from those of Zr$_5$Pt$_3$O$_x$ ($x \geq 1.0$). The synthesis with the oxygen content, exceeding the solubility limit, has changed a material’s microstructure, which would play an important role for the $T_c$ enhancement. We note here that in Sr$_2$RuO$_4$ or Ir a change of microstructure also enhances $T_c$ [17, 18]. The
eutectic Sr$_2$RuO$_4$ sample shows a lamellar pattern of Ru metal [17]. Although the lamellar pattern does not affect the lattice parameters of Sr$_2$RuO$_4$, $T_c$ increases from 1.5 K to 3 K. Ir with a small amount of YIr$_2$ forms a lamellar pattern and possesses a small lattice mismatch, leading to the strain-induced lattice softening [18]. This softening contributes to the $T_c$ enhancement from 0.1 K to 2.7 K.

Another scenario of $T_c$ enhancement is a composition effect. For example, if a ternary compound possesses a certain homogeneity range in its ternary phase diagram, $T_c$ or magnetic ordering temperature frequently depends on the composition of compound. Such composition effect is reported for superconducting CeCu$_2$Si$_2$ or antiferromagnetic compound Nd$_3$Pd$_{20}$Ge$_6$. In CeCu$_2$Si$_2$, the lattice parameters do not exhibit clear composition dependence. On the other hand, Nd$_3$Pd$_{20}$Ge$_6$ shows lattice parameters strongly depending on the composition. Although the composition of Zr$_3$Pt$_3$O$_{0.6}$ with $T_c = 3.2$ K is not so different from that of Zr$_3$Pt$_3$O$_{2.5}$ with $T_c = 4.8$ K (see table 2), more precise study of composition effect might be needed.

### 4. Conclusions

We have investigated the oxygen-content dependence of $T_c$ in Zr$_5$Pt$_3$O$_x$ by measuring $\chi_{ac}$ and $\rho$, combined with the metallographic study. Single phase is confirmed for each sample with $x = 0$ and 0.2. A small amount of ZrO$_2$ appear in Zr$_5$Pt$_3$O$_{0.6}$. Thus the oxygen content is limited to approximately 0.6. With further increasing $x$ above
1.0, corresponding to the full occupancy of oxygen atoms, Zr$_5$Pt$_3$O$_x$ shows the decomposition into Zr$_5$Pt$_3$O$_{0.5–0.6}$ ZrPt and ZrO$_2$. The FE-SEM observation has confirmed the change of microstructure at $x \geq 1.0$. The parent Zr$_5$Pt$_3$ shows the superconductivity at $T_c$ of 6.4 K, which is decreased to 3.2 K as the oxygen content is increased to 0.6. The crystallographic consideration is presented by surveying the results of Nb$_3$Ir$_3$O, Zr$_5$Sb$_3$O and Zr$_5$Ge$_{3–x}$Ru$_x$. For Zr-based Mn$_5$Si$_3$-type compounds, oxygen addition would reduce $T_c$, irrespective of the oxygen-content dependence of lattice parameters. The atom substitution like in Zr$_5$Ge$_{3–x}$Ru$_x$ might be effective for the enhancement of superconductivity. In Zr$_5$Pt$_3$O$_x$ ($x \geq 1.0$) showing the change of microstructure, slight enhancement of $T_c$ with increasing $x$ is observed. The fact would be correlated with the change of microstructure and/or the composition effect.

Acknowledgments

JK is grateful for the financial support provided by the Comprehensive Research Organization of Fukuoka Institute of Technology.

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