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## An unknown phase transition in $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ and $\text{PrBa}_2\text{Cu}_3\text{O}_{7-x}$ cuprates

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**Abstract.** By means of differential scanning calorimetry, thermogravimetry, and high-temperature x-ray diffraction in different atmospheres, an opposite thermal dynamic change in superconducting and semiconducting cuprates of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  (Y-123) and  $\text{PrBa}_2\text{Cu}_3\text{O}_{7-x}$  (Pr-123) is observed. At about 300 °C the superconducting Y-123 polycrystals show an endothermal anomaly and a weight loss, while the semiconducting Pr-123 polycrystals show an exothermal anomaly and weight gain. Similar phenomena are also observed in the superconducting and semiconducting Y-123 single crystals at about 450 °C. High-temperature x-ray diffraction reveals that the lattice parameters of the Y-123 increase significantly at this temperature. We argue that this can be attributed to an unknown phase transition and a thermal instability, which is important for understanding the difference in properties between superconducting and semiconducting cuprates.

It is well known that substitution of Pr for Y in the  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  (Y-123) compound can form a single-phase compound  $\text{PrBa}_2\text{Cu}_3\text{O}_{7-x}$  (Pr-123). The Pr-123 phase is a semiconductor [1, 2], but it is quite similar to the Y-123 phase in structure and oxygen content, undergoing an orthorhombic-to-tetragonal (O-T) structure transition at a temperature and oxygen content close to those for the Y-123 phase [3, 4]. The Pr-123 has been extensively studied by many groups [5–7] in an attempt to understand the high- $T_c$  superconductivity mechanism of cuprates on the basis of the absence of superconductivity in this material.

However, it is noticeable that few detailed reports on the thermal behaviours of the Y-123 and Pr-123 phases at temperatures from 20 to 500 °C are available. In this paper, therefore, the focus is on the thermal behaviour of these materials in this temperature range; we aim to find out the possible differences between the Y-123 and the Pr-123 phases as regards thermal dynamics. The reason that pure Pr-123 and Y-123 single phases other than (Y, Pr) $\text{Ba}_2\text{Cu}_3\text{O}_{7-y}$  alloy are chosen as the samples for this study is to avoid possible phase separation in (Y, Pr) $\text{Ba}_2\text{Cu}_3\text{O}_{7-y}$ , which may complicate the interpretation of experimental results. Large-size single crystals of the Y-123 phase with both superconducting and semiconducting behaviours are also examined to exclude the possible influence of grain boundaries in polycrystalline samples. From comparing the behaviours of the superconducting and semiconducting cuprates of Y-123 and Pr-123, it is evident that thermal dynamics in the superconducting and semiconducting cuprates are

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quite different. We believe that this is an unknown characteristic, which might shed light on the high- $T_c$  superconductivity.

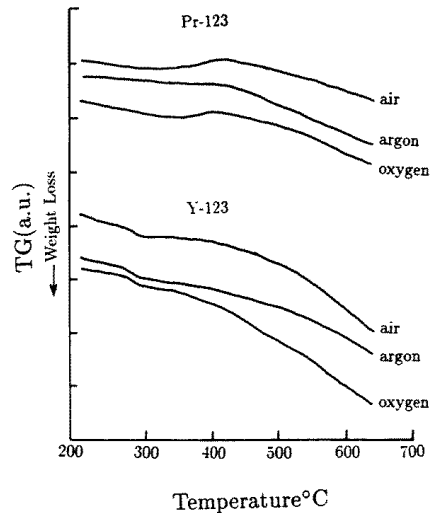
The polycrystalline samples of the Y-123 phase were, for the sake of comparison, obtained from two sources: one was prepared in our laboratory by the conventional solid-state reaction technique, while another was bought from the Hoest AG Germany. Both types are superconducting, with the critical temperature of 90 K. The Pr-123 polycrystalline samples were also prepared in our laboratory, using the conventional solid-state reaction technique. The Pr-123 samples are non-superconducting, showing a semiconductive resistance-temperature behaviour. The Y-123 single crystals were grown by a flux method in a zirconia crucible. BaO and CuO were used as the flux. The single crystal selected for the experiment weighed 99 mg; its dimensions were approximately  $2.5 \times 2.5 \times 1.5 \text{ mm}^3$ . X-ray diffraction showed a single-crystal pattern. Five faces of the crystal were very smooth and glossy; one face was not, due to the damage in the process of extraction from the flux.

The thermal analysis was carried out on two different machines: a NETZSCH SAT and a SHIMAZA thermal analyser. Both of them are capable of simultaneous differential scanning calorimetry (DSC) and thermogravimetry (TG). For powder samples, each group with a weight of about 60 mg was analysed in air, oxygen, and argon, respectively. The results obtained from the two machines are consistent with each other. High-temperature x-ray diffraction (HTXRD) analysis was performed on a SIEMENS x-ray diffraction system with Cu  $K\alpha$  radiation source. A Ta sheet was used as the hot stage. A Cr-Al thermal couple was spot welded on the hot stage in the centre to monitor the temperature. The high-temperature x-ray diffraction was carried out in an argon atmosphere. The heating rate was  $5 \text{ }^\circ\text{C min}^{-1}$ , and temperature was kept stable during scanning. The scanning degree was from  $5^\circ$  to  $60^\circ$  in  $2\theta$ . The integrated intensities were collected by the use of a step scan with the step height and scanning time of  $0.02^\circ$  and  $1000 \text{ s deg}^{-1}$ , respectively. The lattice parameters were calculated using a modified APPLEMAN index program. Twelve reflection peaks were used for determining the lattice parameters of each pattern. The resistance and the critical temperature were measured by the standard four-probe technique. An a.c. susceptibility technique was also used to determine the critical temperature.

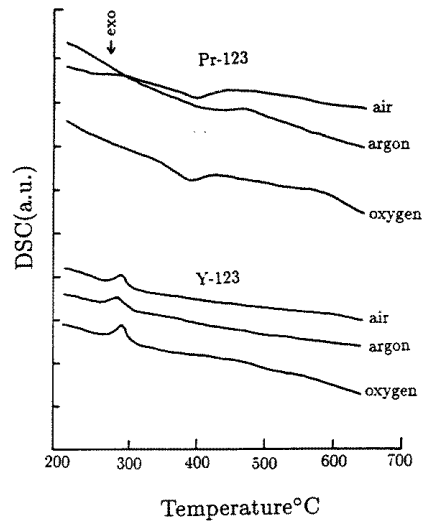
Figure 1 shows the TG curves of the Y-123 and the Pr-123 polycrystalline samples in the heating process in air, argon, and oxygen atmospheres, respectively. For the Y-123 phase, a significant weight loss appears at about  $300 \text{ }^\circ\text{C}$ , no matter what atmospheres are applied during the analyses. However, for the Pr-123 phase, a significant weight gain—rather than weight loss—appears at about  $350 \text{ }^\circ\text{C}$ , in which the weight gain is more obvious in air and oxygen than in argon. Figure 2 shows the DSC curves of the Y-123 and the Pr-123 polycrystals which were heated in different atmospheres. An endothermic anomaly was observed at about  $300 \text{ }^\circ\text{C}$  in the Y-123 phase, but an exothermic anomaly was found at about  $350 \text{ }^\circ\text{C}$  in the Pr-123 phase. It has been noted that the exothermic anomaly is not very obvious in argon; the reason for this will be discussed below.

A thermal analysis-mass spectroscopy connecting system was used to detect the element which escapes from the Y-123 sample during the weight loss at about  $300 \text{ }^\circ\text{C}$ . It was found that some oxygen atoms came out of the sample at this temperature, indicating that the weight loss and the endothermic anomaly at about  $300 \text{ }^\circ\text{C}$  are correlated with the loss of oxygen. In the case of the Pr-123 phase (see figure 1 and figure 2) the weight gain and the exothermic anomaly in argon atmosphere are not as significant as in oxygen or in air, indicating that the weight gain and the exothermic anomaly in the Pr-123 phase are correlated with the increase of the oxygen content.

The high-temperature x-ray diffraction analysis was carried out in argon for the Y-123 phase; the scanning range was from  $5\text{--}60^\circ$  in  $2\theta$ . Because the changes in weight and heat



**Figure 1.** TG curves of the Y-123 and the Pr-123 polycrystals for heating in air, argon and oxygen atmospheres. The Y-123 sample shows a significant weight loss in all of the atmospheres at about 300 °C; the Pr-123 sample shows a significant weight gain at about 350 °C in air and oxygen, but the weight gain in argon is not as significant as that in air and oxygen.



**Figure 2.** DSC curves of the Y-123 and the Pr-123 polycrystals for heating in different atmospheres. The Y-123 sample shows a significant endothermic anomaly in all of the atmospheres at about 300 °C; the Pr-123 phase shows a significant exothermic anomaly in air and oxygen at about 350 °C.

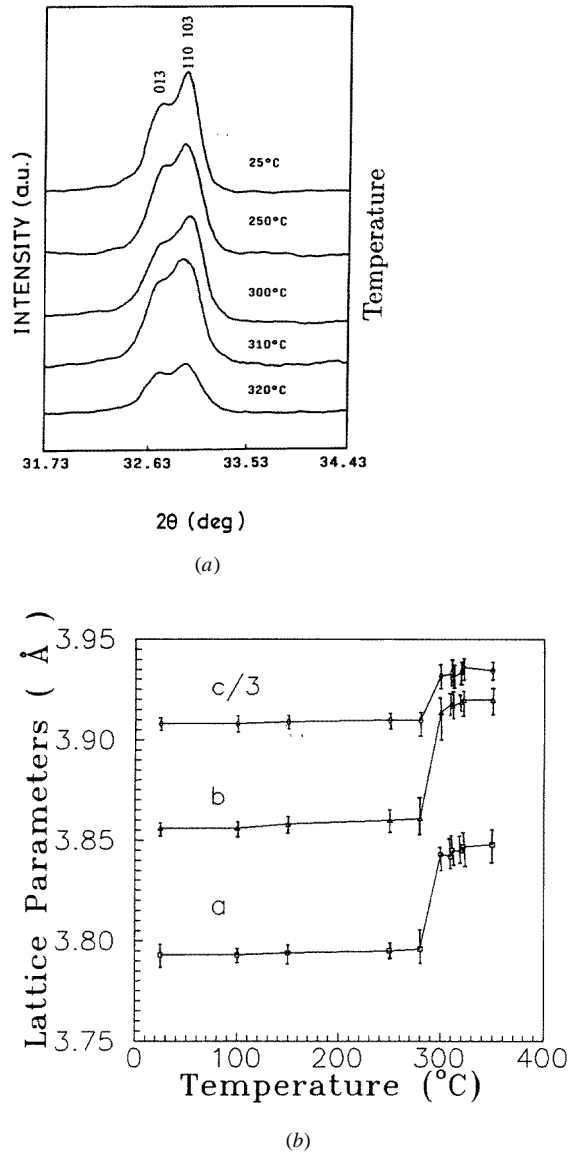
for the Pr-123 phase in argon are not significant, and high-temperature diffraction in air and oxygen cannot be studied with our instruments, the Pr-123 phase was not x-rayed at high temperature. Some significant changes can be seen in the high-temperature x-ray diffraction patterns for the Y-123 at about 300 °C. The typical changes in peaks 013, 110, and 103 are shown in figure 3(a). Furthermore, the calculation of lattice parameters demonstrates that there is a jump of the lattice parameters at about 300 °C (see figure 3(b)), indicating a discontinuous thermal expansion at this temperature.

As has been reported by Jorgensen *et al* [8], there is an O–T structural transition at about 700 °C in the Y-123 phase. By comparing the characteristics of the O–T transition and the anomaly at 300 °C for the Y-123 described above, some interesting differences and similarities can be seen as listed below.

(1) Both the O–T transition and the anomaly at 300 °C involve the loss of weight—in fact, loss of oxygen.

(2) The anomaly at 300 °C shows a heat change, which has never been observed in the O–T transition.

(3) The O–T transition originates from the order–disorder transition of oxygen located in the Cu(1)–O chain layer. The space group of the orthorhombic structure is  $Pmmm$ , whereas the space group of the tetragonal structure is  $P4/mmm$  which is a supergroup of  $Pmmm$ . Combining the characteristics of the O–T transition as regards structure and heat, it is evident that it is a second-order phase transition. This is different from the anomaly at 300 °C which is a first-order phase transition as shown by the heat change during the transition (see figure 2). Moreover, no detectable changes can be found in the crystal symmetry in the anomaly at 300 °C.



**Figure 3.** (a) The of 013, 110, and 103 peaks of the *in situ* high-temperature x-ray diffraction patterns for the Y-123 polycrystals. (b) The temperature dependence of the lattice parameters for Y-123; a jump can be seen at about 300 °C.

(4) The O–T transition shows an increase in the *a* and *c* axes, and a decrease in *b* [8], but the anomaly at 300 °C shows an increase in *a*, *b* and *c*, indicating a thermal expansion of the lattice.

(5) The critical temperature of the O–T transition is strongly atmosphere dependent [9], but the anomaly at 300 °C is independent of the atmosphere. The latter can be seen from figures 1 and 2: the changes always take place at about the same temperature no matter what kind of atmospheres are applied.

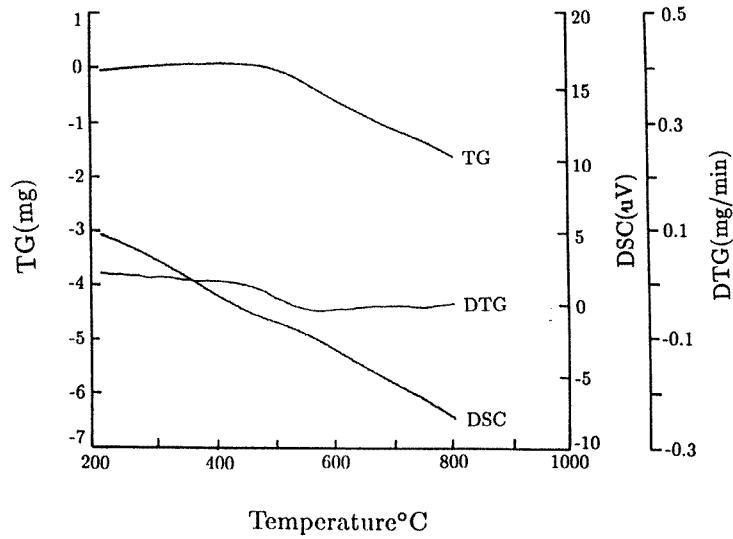
From the comparison described above, it can be seen that the anomaly at 300 °C is probably an intrinsic transition in the Y-123 crystal lattice. The O–T transition originates from the changes in the Cu(1)–O chain layer, but the anomaly at 300 °C is possibly present throughout the lattice, which means that the oxygen comes out not only from the Cu(1)–O chain layer, but also from other planes. Perhaps this change is associated with some unknown characteristics.

From figure 1 and figure 2 it is evident that both the weight and the heat changes at about 300 °C also take place in the Pr-123 phase, indicating that the transition at 300 °C may be a feature common to the 123-compounds. We try to attribute the change to a thermal instability and an unknown phase transition. We know from the high-temperature x-ray diffraction (figure 3) that there is a change of parameters in the the Y-123 phase at about 300 °C; thermal analysis also shows a weight and heat change at this temperature (figure 1, figure 2). It is known that an endothermal change increases the internal energy in a crystal lattice, and makes the lattice more unstable. But the Pr-123 phase shows a weight increase and an exothermal anomaly that decreases the internal energy and makes the lattice more stable. It is worth pointing out that in a previous report [8] some authors observed that a fully oxygenated Y-123 sample at 321 °C in 2% oxygen showed clear evidence for structural variation during data collection. Unfortunately, they did not give any more information and explanation as regards this phenomenon.

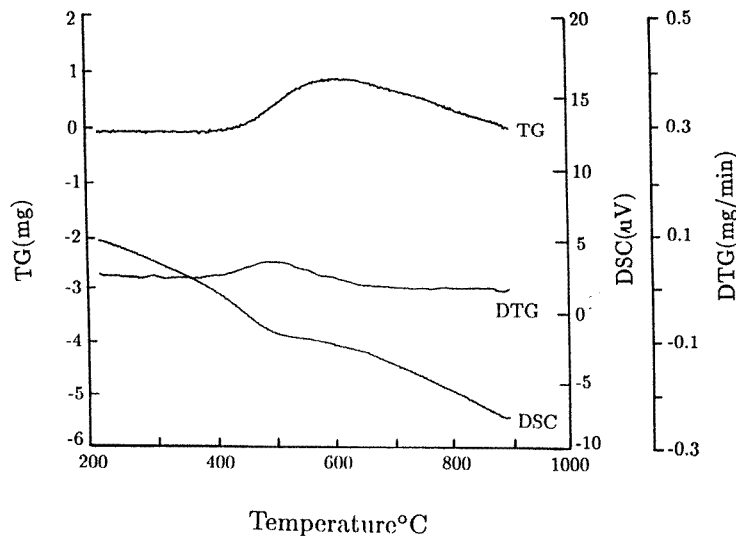
From figure 1 and figure 2 we also noted that the heat and weight changes in the Pr-123 phase are completely opposite to those in the Y-123 phase. There are many explanations [10–12] for the  $T_c$ -depression in a Y-123 phase with partial Pr substitution, most of them involving the localization of holes through the hybridization of the valence electrons with the 4f band. We think that the opposite behaviours of the Y-123 phase and the Pr-123 phase at about 300 °C may provide another clue as regards understanding the difference in superconductivity between them.

The selected single crystal of the Y-123 phase was placed in an alumina crucible; a smooth face contacted the bottom of the crucible closely for good heat conduction. In general, as-prepared single crystal is not fully oxygenated, especially for a large size. In view of this, the crystal was heated in oxygen from room temperature to 600 °C, then cooled down to room temperature. Then it was heated and cooled in argon, like in oxygen. Both the heating and cooling rates were 10 °C min<sup>-1</sup>. In order to form a fluent channel of oxygen diffusion, this process was repeated about 60 times. Finally, the crystal was annealed in oxygen at 400 °C for 30 h, then cooled also in oxygen to room temperature. The a.c. susceptibility and resistance measurements showed that the crystal is superconducting at 90 K (zero resistance). After it was established that the crystal was superconducting, it was thermally analysed. Because the diffusion of oxygen in a large crystal is very slow, the fully oxygenated crystal was heated in argon to enhance the diffusion of oxygen out of it. We tried heating the crystal in air, but the changes were hardly observable. Figure 4 shows the TG, DTG and DSC curves of the crystal. The changes of three curves at about 450 °C are significant. After analysing the superconducting crystal, the crystal was changed into a semiconducting one by annealing it at 500 °C in argon for 60 h. The a.c. susceptibility and resistance measurements demonstrated that it had become a semiconducting crystal. The semiconducting crystal was thermally analysed in oxygen. Figure 5 shows the TG, DTG and DSC results. The significant changes of the three curves at about 450 °C are also observed. For the same as reason mentioned above, the changes produced by heating the crystal in air were also hardly observable.

Now we discuss the different behaviours, shown in figure 4 and figure 5, of the superconducting and semiconducting crystals. For the superconducting crystal, at about 450 °C,



**Figure 4.** TG, DTG, and DSC curves for the Y-123 superconducting single crystal for heating in argon. At about 450 °C a significant weight loss can be seen in the TG and DTG curves; a small endothermal anomaly can be seen in the DSC curve. For heating in air and oxygen, no such change was observed.



**Figure 5.** TG, DTG, and DSC curves for the Y-123 semiconducting single crystal for heating in oxygen. At about 450 °C a significant weight increase and exothermal anomaly can be seen. For heating in air and argon, no such change was observed.

the TG curve shows a weight loss, and the DTG curve gives further confirmation of this; the DSC curve shows a small endothermal anomaly (figure 4). The case here is similar to that for the Y-123 phase polycrystal sample (figure 1, figure 2). The difference is that in

the single crystal the changes appear at about 450 °C, but in the polycrystals they appear at about 300 °C. We suggest that the changes of weight and heat in the single crystal and polycrystals arise from same source. The higher temperature at which the changes take place in the single crystal is possibly due to the diffusion of oxygen being difficult in a large crystal.

For the semiconducting single crystal, the behaviour is entirely opposite to that of the superconducting one (figure 5), and similar to that of the Pr-123 phase sample. The higher temperature at which the changes take place can also be attributed to the diffusion of oxygen being difficult in a large crystal. The changes of the single crystal at about 450 °C are different from the O–T phase transition in the Y-123 phase and the Pr-123 phase. The O–T transition is of second order, no latent heat change is observed, and the O–T transition has a close relationship with the oxygen content [9]; for the transition at about 450 °C in the single crystal, the latent heat change is significant. For the superconducting crystal, there is an endothermal anomaly; for the semiconducting crystal, there is an exothermal one. This change has nothing to do with oxygen content. Figure 4 and figure 5 show that the curves change at nearly same temperature for both fully oxygenated crystal (superconducting crystal) and poorly oxygenated crystal (semiconducting crystal). We also try to attribute the change at about 450 °C to an unknown phase transition and a thermal instability. The reasoning is the same as that given above in discussing the behaviours of the polycrystal samples.

In summary, a possible unknown phase transition in the Y-123 phase and the Pr-123 phase was observed. The behaviours of the superconducting samples and semiconducting samples are quite different at this transition. This observation may provide a clue to the understanding of the different properties of the superconducting and semiconducting cuprates.

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