Variations of superconducting transition temperature in YbBa$_2$Cu$_3$O$_{7-\delta}$ ceramics by Gd substitution

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Abstract. So-called RE-123 superconductors are said to generally exhibit superconductivity at the transition temperature $T_c$ around 90K with RE (rare-earth) ions from Nd to Lu. However there is some tendency that $T_c$ decreases with decrease in RE ionic radius. Especially for Yb-123, $T_c$ often becomes below 90K. We find that the smaller the ionic radius is, the lower the melting temperature becomes for RE-123 ceramics. In fact, Yb-123 ceramics often melt above 910°C, while Gd-123 ceramics can be sintered above 950°C without melting. From this tendency we suppose that such $T_c$ lowering is due to insufficient sintering temperature, resulting in insufficient solid state reaction and poor crystal growth. In this work, we try to raise $T_c$ in Yb-123 ceramics by increasing the sintering temperature through Gd substitution. We find that the optimum sintering temperature is 930°C in Yb$_{0.7}$Gd$_{0.3}$Ba$_2$Cu$_3$O$_{7-\delta}$ ceramics with the highest $T_c$ of 91.8K (zero resistivity).

1. Introduction

It is well known that the cuprate compound of YBa$_2$Cu$_3$O$_{7-\delta}$ is the first superconductor which has been discovered to exhibit superconductivity above liquid-nitrogen temperature [1]. Soon after this discovery, superconductivity in a series of REBa$_2$Cu$_3$O$_{7-\delta}$ (RE-123) compounds (RE = rare-earth element) has been investigated and the transition temperature has been reported to be nearly independent of the rare-earth ion [2]. Then, it seems that not much attention has been paid to the RE substitution effect in comparison to substitution effects of barium or copper ions [3, 4] with rather drastic phenomena.

However, when we look into detail, we find some tendency [5] that $T_c$ decreases with decrease in RE ionic radius as shown in figure 1 (the solid line is for eye-guide). Especially for Yb-123, $T_c$ often becomes below 90K. We find that the smaller the ionic radius is, the lower the melting temperature becomes for RE-123 ceramics. In fact, Yb-123 ceramics often melt above 910°C, while Gd-123 ceramics can be sintered above 950°C without melting. From this tendency we suppose that such $T_c$ lowering is due to insufficient sintering temperature, resulting in insufficient solid state reaction and poor crystal growth.

In this work, we try to raise $T_c$ in Yb-123 ceramics by increasing the sintering temperature through Gd substitution. We find that the optimum sintering temperature is 930°C in Yb$_{0.7}$Gd$_{0.3}$Ba$_2$Cu$_3$O$_{7-\delta}$ ceramics with the highest $T_c$ of 91.8K (zero resistivity).

2. Experimental
Pure and substituted samples were prepared by the solid state reaction method. The raw materials of Yb₂O₃, Gd₂O₃, BaCO₃ and CuO powders (all with 99.99% purity) were weighed to be in the ratio of Yb:Gd:Ba:Cu = 1-x:x:2:3, where x = 0, 0.1, 0.2 and 0.3. The total of 8 g mixture with certain x was ground carefully in the agate mortar, calcined at 880 °C for 24 h in air and repeated this process twice. This makes a single batch of the calcined powder with a given x. Then, weighing about 0.8 g of the calcined powder, ground carefully, pelletized in a disk of 10 mm in diameter and sintered for 24 h in air at certain temperature between 885 °C and 950 °C. During the final cooling down, the intermediate annealing was applied at 500 °C for 10 h in order to take enough oxygen. Thus, we were able to obtain up to 8 pellets of Yb₁₋ₓGdₓBa₂Cu₃O₇₋δ ceramics with different sintering temperatures from a single batch of the calcined powder with a given x. Adherence to such single batch process can avoid possible complication due to undesirable variation in the calcination process.

Obtained pellets were cut into bar shape (typically 1x2x8 mm³) for resistivity measurements with the standard four-probe method. Some other parts from the pellets were used for estimation of sample morphology with the scanning electron microscopy (SEM). Oxygen contents were also estimated by thermogravimetry (TG) measurements.

![Figure 1](image1.png)  
**Figure 1.** Variation of superconducting transition temperature $T_c$ as a function of rare-earth ionic radius.

![Figure 2](image2.png)  
**Figure 2.** Electrical resistivity in the pure YbBa₂Cu₃O₇₋δ (Yb-pure) as a function of temperature.

3. Results and discussion

3.1. pure YbBa₂Cu₃O₇₋δ

Temperature dependent resistivity in the pure YbBa₂Cu₃O₇₋δ (Yb-pure) is shown in figure 2 for ceramics sintered between 885 °C and 920 °C with 5 °C interval. From the results we first estimate the onset point of the superconducting transition by linearly extrapolating resistivity curves just around the onset region. In the sample sintered at 900 °C, for example, we estimate the onset point as 92.2 K (onset $T_c$) and 2.1 mΩ cm (onset resistivity, abbreviated as onset $R$). Next, we estimate the temperature where the resistivity shows just half of the onset $R$ as midpoint $T_c$ (90.2 K for the sample sintered at 900 °C). And finally, we estimate the offset $T_c$ where the resistivity becomes zero (87.5 K for the sample sintered at 900 °C).

In figure 3 we present thus obtained transition temperature $T_c$'s in the pure YbBa₂Cu₃O₇₋δ as a function of the sintering temperature $T_s$. Although the highest onset $T_c$ is obtained when the pellet was sintered at 920 °C, the pellet was partially melted and the transition towards zero resistivity showed rather long tail. Thus we conclude that the optimum sintering temperature is 890 °C for the pure YbBa₂Cu₃O₇₋δ, resulting in the highest offset (zero resistivity) $T_c$ of 90.4 K. Figure 4 indicates the onset $R$ as a function of $T_s$. The resistivity in the sample sintered at 890 °C is fairly low, but the lowest resistivity was obtained when sintered at 905 °C. Scattered values of the offset $T_c$ and the onset $R$
probably reflect difficulty in preparing the pure \( \text{YbBa}_2\text{Cu}_3\text{O}_{7-\delta} \) which is easily melted at rather low sintering temperatures, resulting only in insufficient solid state reaction. Thus, we seek to raise the sintering temperature by the Gd substitution.

Figure 3. Variation of superconducting transition temperature \( T_c \)'s against the sintering temperature \( T_s \) in Yb-pure sample.

3.2. \( \text{Yb-10\%Gd} \)

In figure 5 we next show temperature dependent resistivity in 10\%Gd-substituted ceramics; \( \text{Yb}_{0.9}\text{Gd}_{0.1}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta} \) (Yb-10\%Gd). Similarly to the previous subsection, we estimate the transition temperature \( T_c \)'s and onset \( R \) as a function of the sintering temperature \( T_s \), the results being given in figures 6 and 7, respectively. From the results we can conclude that the optimum sintering temperature is 900°C for the Yb-10\% Gd sample with the highest zero resistivity \( T_c \) of 91.1 K and very low onset \( R \) of 0.35 m\( \Omega \)cm.

Figure 4. Variation of onset resistivity (Onset \( R \)) against the sintering temperature \( T_s \) in Yb-pure sample.

Figure 5. Electrical resistivity in 10\%Gd-substituted ceramics; \( \text{Yb}_{0.9}\text{Gd}_{0.1}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta} \) (Yb-10\%Gd) as a function of temperature.

Figure 6. Variation of superconducting transition temperature \( T_c \)'s against the sintering temperature \( T_s \) in Yb-10\%Gd.

It should be noted that when compared with the pure sample the zero resistivity \( T_c \) has increased by 0.7 K according to increased sintering temperature by the 10\%Gd substitution. It is also noted that
significant variations of $T_c$'s and onset $R$ in the pure sample have been drastically suppressed by the 10%Gd substitution. We infer the origin of these improvements as due to improved stability of the 123 structure by larger ion (Gd) substitution, which then enabled higher temperature sintering.

3.3. *Yb-20%Gd*

In figure 8 we show temperature dependent resistivity in Yb-20%Gd ceramics. Estimated transition temperature $T_c$'s and onset $R$ as a function of the sintering temperature $T_s$ is given in figures 9 and 10, respectively. As can be seen from the figures, the optimum sintering temperature is 905°C for the Yb-20%Gd sample with the highest zero resistivity $T_c$ of 91.2 K and the very low onset $R$ of 0.28 mΩcm.

It is noted that the optimum sintering temperature has been even increased by the 20%Gd substitution, compared to 10%Gd substitution. Significant variations of $T_c$'s and onset $R$ in the pure sample have been again drastically suppressed by the 20%Gd substitution. In fact, onset $R$ for all 8 samples falls between 0.2 and 0.6 mΩcm, in spite of the wide variation of the sintering temperature from 900°C to 940°C.

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**Figure 7.** Variation of onset $R$ against the sintering temperature $T_s$ in Yb-10%Gd sample.

**Figure 8.** Electrical resistivity in Yb-20%Gd ceramics as a function of temperature.

**Figure 9.** Variation of superconducting transition temperature $T_c$'s with the sintering temperature $T_s$ in Yb-20%Gd sample.

**Figure 10.** Variation of onset $R$ with the sintering temperature $T_s$ in Yb-20%Gd sample.
3.4. Yb-30%Gd

Figure 11 shows temperature dependent resistivity in Yb-30%Gd ceramics. Estimated transition temperature $T_c$’s and onset $R$ as a function of the sintering temperature $T_s$ is given in figures 12 and 13, respectively. In this case, the optimum sintering temperature is 930°C for the Yb-30%Gd sample with the highest zero resistivity $T_c$ of 91.8 K and very low onset $R$ of 0.34 mΩcm. It should be remarkable that the zero resistivity $T_c$ has increased by 1.4 K when compared with the pure sample.

![Figure 11](image1.png)

**Figure 11.** Electrical resistivity in Yb-30%Gd ceramics as a function of temperature.

![Figure 12](image2.png)

**Figure 12.** Variation of superconducting transition temperature $T_c$’s against the sintering temperature $T_s$ in Yb-30%Gd.

3.5. oxygen contents $7$-$\delta$

In figure 14 we indicate estimation of oxygen contents $7$-$\delta$ by the thermogravimetry (TG) measurements. Rather large variation of $7$-$\delta$ in the pure sample again reflects difficulty in preparing the pure YbBa$_2$Cu$_3$O$_{7-\delta}$ which is easily melted at rather low sintering temperatures. On the other hand, $7$-$\delta$ is well above 6.9 for Gd substituted samples, inferring stabilized 123 structure and pronounced crystal growth due to higher temperature sintering. It is also verified that the above estimation of the optimum sintering temperature based on the highest $T_c$ and the lowest onset-$R$ is not affected by undesirable variation of oxygen contents depending on different sintering temperatures.

![Figure 13](image3.png)

**Figure 13.** Variation of onset $R$ against the sintering temperature $T_s$ in Yb-30%Gd sample.

![Figure 14](image4.png)

**Figure 14.** Oxygen contents $7$-$\delta$ in Yb-pure, 10%Gd and 20%Gd ceramics as a function of sintering temperature $T_s$. 
3.6. crystal morphology observed by SEM
Such pronounced crystal growth is confirmed by the SEM images as compared in figures 15 and 16. When the Yb-10%Gd sample is sintered at 890 °C, the size of microcrystals is small and the crystal facet is not clear as seen in figure 15. There are also rather many voids between crystals and the connectivity between grains is poor, too. On the other hand, when the Yb-10%Gd sample is sintered optimally at 900 °C, the crystal growth is significant with the sharp facet, and the connectivity has also improved as shown in figure 16.

Figure 15. SEM image of Yb-10%Gd sample sintered at 890 °C, showing poor crystal growth (magnification x500).

Figure 16. SEM image of Yb-10%Gd sample sintered at 900 °C, indicating pronounced crystal growth (x500).

4. Conclusions
In summary, we prepared more than 30 samples of Gd substituted Yb-123 ceramics with various Gd concentration under various sintering temperatures, seeking to raise $T_c$ in Yb-123 ceramics by increasing the sintering temperature through Gd substitution. We, in fact, succeeded to obtain the pronounced crystal growth by higher temperature solid state reaction, resulting in the highest zero-resistivity superconducting transition at $T_c = 91.8$K in Yb$_{0.7}$Gd$_{0.3}$Ba$_2$Cu$_3$O$_{7-\delta}$ ceramics, optimally sintered at 930°C. We infer that higher temperature sintering has been realized by improved stability of the 123 structure by the larger ion Gd substitution.

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