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Additional effect of Ag and 211 phase on thermal expansion of REBaCuO bulk superconductor (RE = Sm, Y)

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Abstract

The anisotropic thermal expansion $\Delta L/L$ was examined for melt-processed REBaCuO(Ag) bulk composites (RE = Sm, Y) as functions of not only the contents of the RE_2BaCuO_5 second phase but also Ag metal added to the highly oriented $REBa_2Cu_3O_7$ matrix. The $\Delta L/L|_c$ values in the *c*-direction of REBaCuO(Ag) bulks are about 1.5–1.8 times as large as the $\Delta L/L|_{ab}$ values in the *ab*-plane. $\Delta L/L$ increases with increasing Ag content in both directions but $\Delta L/L|_c$ is by far more sensitive to the Ag content. The resultant compressive strain due to Ag particles in the *c*-direction through the melt-processing was estimated and its possible contribution for the improvement of the superconducting characteristics of the matrix was discussed.

Keywords: Thermal expansion; REBaCuO bulk superconductors; RE_2BaCuO_5; Silver

1. Introduction

Because of the high critical current density J_c and the high magnetic flux trapping ability, the melt-processed REBaCuO bulk superconductors (RE: rare earth ions) have widely been exploited for the applicational use, such as the high-field bulk magnets, power current leads for liquid-He-free superconducting magnets and so on [1–3]. Through the melt-processing, RE_2BaCuO_5 (RE211) particles precipitate in the $REBa_2Cu_3O_7$ (RE123) superconducting main phase and act as efficient pinning centers in the bulk materials [1]. The amount of the RE211 particles can be controlled by adjusting the composition of the starting materials.

Another standard technique to improve the superconducting characteristics of the melt-processed bulks is the addition of 10–20 wt.% silver (Ag) metal, which is believed to be effective in improving the crystalinity of the RE123 matrix, reinforcing the mechanical strength at the same time. A very small amount (<0.5 wt.%) of platinum (Pt) metal is also added to disperse the RE211 particles more finely and uniformly in the matrix. The Ag-doped melt-processed REBaCuO(Ag) bulk can be regarded as a composite superconducting material, consisting of RE123, RE211 and Ag.

We measured the thermal expansion $\Delta L/L$ of the SmBaCuO and YBaCuO composites. The amounts of Ag and the RE211 phase were systematically changed. Our main attention was placed on the SmBaCuO composites because REBaCuO(Ag) bulks with right rare-earth element (RE = Nd, Sm) were reported to achieve higher J_c values than REBaCuO bulks with heavy RE or YBaCuO, especially in high magnetic fields. Therefore, the SmBaCuO(Ag) bulk is a very useful material for the applications. The YBaCuO composites have also been measured for comparison. We have already reported the thermal conductivity $\kappa(T)$, the thermal diffusivity $\alpha(T)$ and the thermoelectric power $S(T)$ on the SmBaCuO(Ag) and YBaCuO(Ag) systems [4,5]. The abundant and methodical database of the thermal properties, however, has not yet been completed for these bulk superconductors. In this paper, the effect of the induced strain due to Ag addition was elucidated from the viewpoint of the thermal expansion.

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2. Experimental

The SmBaCuO(Ag) bulk samples were prepared at the laboratory of DOWA Mining Co., Ltd. through the following procedure [6,7]. A mixture of $BaCO_3$ and CuO powders was calcined at 880 °C for 30 h to obtain the $BaCuO_2$ and CuO mixture. The calcined powder was mixed with Sm_2O_3, 10–19.7 wt.% Ag and 0.42 wt.% Pt, which were sintered at 900 °C for 20 h. The resultant sintered polycrystal consisted of the Sm123 matrix, additional X mol Sm211 phase, y wt.% Ag and 0.42 wt.% Pt. We express this composite by the formula, $Sm_{1+2X}Ba_{2+X}Cu_{3+X}O_{7+5X}$ (Ag:y). The sintered polycrystals were pulverized and pressed into disks (53∅×18 mm). The disks were partially melted at 1100 °C in a 2-zone furnace for 30 min and cooled at a speed of 10 °C/min down to 1020 °C, keeping temperature gradient of 5 °C/cm between the top (low temperature side) and bottom of the disk. A seed SmBaCuO (Ag:0) crystal was attached to the top-center of the disks to realize highly oriented bulk-disks. The bulk-disks were cooled down at a speed of 1 °C/h from 1020 to 870 °C and at a speed of 40 °C/h from 870 °C to the room temperature. The process essentially follows the one for high-J_c commercial base products of Dowa Mining Co., Ltd. The sizes of the Sm211 phase and the Ag particles in the bulks were 1–5 and 20–30 μm, respectively, both of which were dispersed uniformly as confirmed by the optical microscope observation. The X-ray diffraction analyses confirmed that the Sm123 matrix was crystallographically highly oriented with the surface of the grown bulks parallel to the *ab*-plane. In the *ab*-plane, however, the bulk crystals had highly disordered *a*- and *b*-axis alignment. $Y_{1+2X}Ba_{2+X}Cu_{3+X}O_{7+5X}$ (Ag:y) bulks were fabricated through almost the same process. On the other hand, we could not observe any preferred orientations of Ag particles and 211 phases in the RE123 matrix. The grown bulks were cut into pillars with edges parallel to the *ab*-plane and to the *c*-axis for the measurements. The typical size of the pillar samples was $4.0\times4.0\times25.0$ mm^3. The density of the samples was about 95% of the ideal ones, which was determined by measuring the size and the weight. The Sm211 ceramic was also fabricated by the solid-state reaction at 1150 °C in air in order to compare the $\Delta L(T)/L$ value with those of the melt-processed bulks. The density of the Sm211 ceramic was 6.18 g/cm^3, which was 94% of the ideal one. The thermal expansion $\Delta L(T)/L$ was automatically measured between 20 and 300 K using a strain-gage method. The strain-gages (KFL-1-120-C1-16: Kyowa Electronic Instruments Co., Ltd.) with the size of ~2 mm were adhered along the *ab*-plane and along the *c*-axis of the samples using the gage cement (PT-6). We observed no orientation dependence of $\Delta L(T)/L$ in the *ab*-plane probably because of the highly disordered *a*- and *b*-axis alignment. The accuracy of the $\Delta L(T)/L$ measurement was better than 10^{-6}.

3. Results and discussion

Fig. 1 shows the temperature dependence of the *ab*-plane and *c*-axis thermal expansion $\Delta L(T)/L$ of the $Sm_{1+2X}Ba_{2+X}Cu_{3+X}O_{7+5X}$ (Ag:10) bulk composites for a fixed Ag content of 10 wt.%. In this study, the thermal expansion is normalized with respect to the sample length at 20 K and is defined by $\Delta L(T)/L = (L(T) - L(20\text{ K}))/L(20\text{ K})$, $L(T)$ being the sample length at the temperature T. As shown in Fig. 1, $\Delta L/L$ increases with increasing temperature for both directions. The temperature dependence of the *c*-axis thermal expansion $\Delta L(T)/L|_c$ is roughly 1.5 times larger than that in the *ab*-plane. The $\Delta L(T)/L$ values of the Sm211 polycrystal, also given in Fig. 1, are almost the same as those of $\Delta L(T)/L|_{ab}$ and pretty smaller than those of $\Delta L(T)/L|_c$ of the Sm-bulk composites. The $\Delta L/L|_c$ values and the anisotropy ratio, $\Delta L/L|_c/\Delta L/L|_{ab}$, of the bulk composites decrease with increasing the Sm211 content X.

Fig. 2 shows $\Delta L/L$ of $Sm_{1+2X}Ba_{2+X}Cu_{3+X}O_{7+5X}$ (Ag:10) at 200 and 300 K as a function of the volume fraction f_{211} of the Sm211 phase. Very roughly, the linear extrapolation of data points of $\Delta L/L|_c$ from the region of $f_{211} < 0.25$ to $f_{211} = 1.0$ falls on the $\Delta L/L|_{211}$ data point of the Sm211 polycrystal. Thus, a kind of the addition theorem holds for the case of Sm211 addition, i.e.,

$$\Delta L/L|_c = \Delta L/L|^c_{123'} f_{123'} + \Delta L/L|_{211} f_{211}, \quad (1)$$

where $\Delta L/L|^c_{123'}$ is the *c*-axis thermal expansion of the Sm123 main phase containing 10 wt.% Ag, and $f_{123'}$ is the total volume fraction of the Sm123 and Ag ($f_{123'} = f_{123} + f_{Ag}$). It should be noticed that the addition

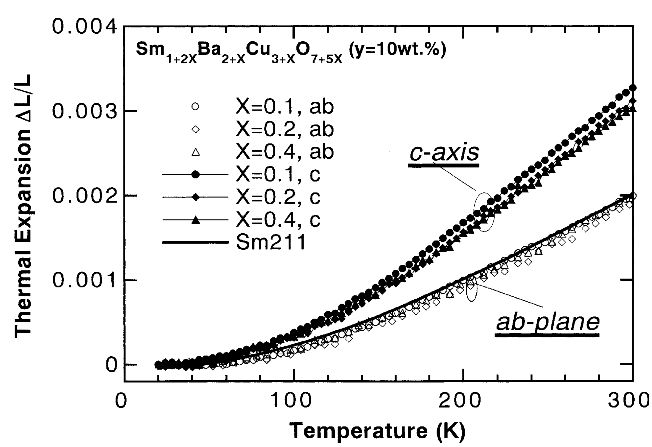

Fig. 1. The temperature dependence of the *ab*-plane and *c*-axis thermal expansion $\Delta L(T)/L$ of $Sm_{1+2X}Ba_{2+X}Cu_{3+X}O_{7+5X}$ (Ag:10) superconducting bulk composites with various Sm211 second phase contents X. The Ag content is fixed to $y = 10$ wt.%. $\Delta L(T)/L$ of the Sm211 polycrystal is also presented.

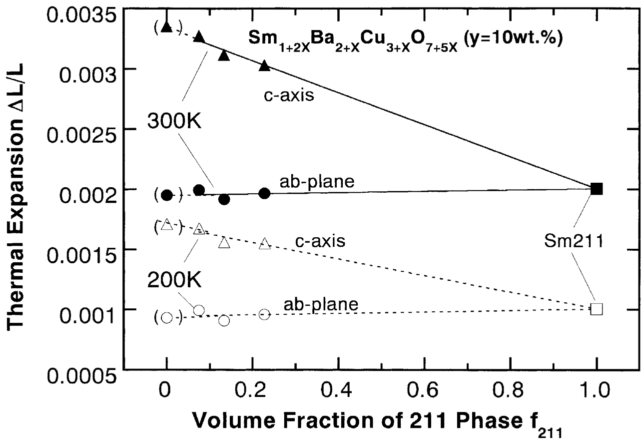

Fig. 2. $\Delta L/L$ at 300 and 200 K as a function of Sm211 volume fraction f_{211}. The linear lines correspond to the addition theorem (Eq. (1) in the text).

theorem based on Eq. (1) implicitly assumes independent expansion (or contraction) of each component, exerting negligible additional strains one another. Thus the results in Fig. 2 suggest that the induced strain by Sm211 is not serious even in the *c*-direction of the matrix lattice. The $\Delta L/L|_{ab}$ values show only a very slight f_{211} dependence, which is reasonable from the viewpoint of the addition theorem because $\Delta L/L|_{123'}^{ab}$ and $\Delta L/L|_{211}$ values are almost in agreement one another. The induced strain due to Sm211 addition should be negligibly small in this direction.

Fig. 3 shows the temperature dependence of the *ab*-plane and *c*-axis $\Delta L/L$ of $Sm_{1+2X}Ba_{2+X}Cu_{3+X}O_{7+5X}$ (Ag:*y*) as a function of the Ag content *y* for a fixed *X* (=0.2). The measured expansion of Ag metal ($\Delta L/L|_{Ag}$) is also presented for comparison. $\Delta L/L$ is the largest for Ag and $\Delta L/L$ of the SmBaCuO bulks increases with increasing *y* in both directions. What is a novel and characteristic feature is the behavior of $\Delta L/L|_c$; the *y* dependence of $\Delta L/L|_c$ is far stronger than that of

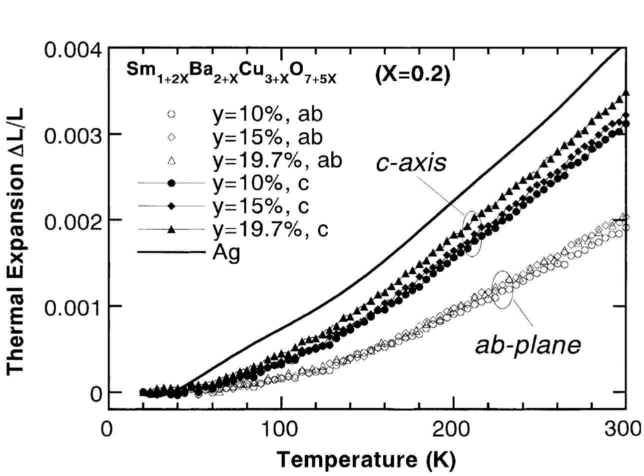

Fig. 3. The temperature dependence of the *ab*-plane and *c*-axis thermal expansion $\Delta L(T)/L$ of $Sm_{1+2X}Ba_{2+X}Cu_{3+X}O_{7+5X}$ (Ag:*y*) for $X = 0.2$ (fixed) and for various Ag wt.% *y*.

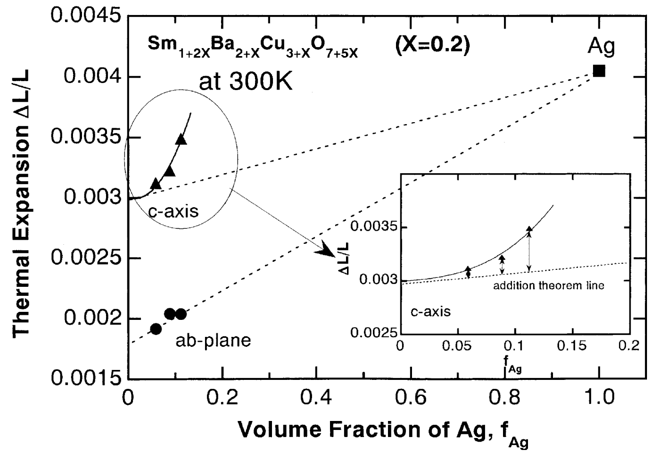

Fig. 4. $\Delta L/L$ of the SmBaCuO(Ag) bulks at 20 K as a function of Ag volume fraction f_{Ag}. The Sm211 content is fixed at $X = 0.2$. The inset shows the *c*-axis $\Delta L/L$ in a magnified scale for $f_{Ag} < 0.2$. The vertical arrows indicate the sizes of the forced strains. The dotted linear lines correspond to the addition theorem.

$\Delta L/L|_{ab}$ in spite of the far smaller difference between $\Delta L/L|_c$ and $\Delta L/L|_{Ag}$ in comparison with that between $\Delta L/L|_{ab}$ and $\Delta L/L|_{Ag}$. The $\Delta L/L|_c$ values are significantly enhanced and the anisotropy ratio $\Delta L/L|_c/\Delta L/L|_{ab}$ also rather increases with increasing *y*, which makes a marked contrast with the *X* dependence. Fig. 4 shows $\Delta L/L$ of the Sm-based bulk composites at 300 K as a function of the volume fraction f_{Ag} of Ag metal. As can be seen, $\Delta L/L|_c$ increases rapidly and nonlinearly with increasing f_{Ag} while the f_{Ag} dependence of $\Delta L/L|_{ab}$ is roughly in accord with the addition theorem. The characteristic layered crystal structure of the Sm123 main phase should be the origin of this anisotropic behavior of $\Delta L/L$ against the Ag addition.

Now let us briefly discuss the strain in the Sm123 main phase induced by Ag particles. Anisotropic Young's moduli *E* of melt-processed YBaCuO bulks ($X = 0.2$, $y = 0$) were measured by Katagiri [8] as $E_{ab} \sim 125$ GPa and $E_c \sim 40$ GPa for in the *ab*-plane and in the *c*-direction, respectively. Although we have not the *E* value data for SmBaCuO bulks, it may be reasonable to assume that the *E* values are not much different between YBaCuO and SmBaCuO bulks prepared by the same melt process. The Young's modulus of Ag is $E_{Ag} \sim 100$ GPa [9], which is intermediate between E_{ab} and E_c of the present REBaCuO bulks. Because of the smaller E_c of REBaCuO than E_{Ag}, the RE123 phase in bulk systems should be subjective to the significant *c*-direction strains introduced by the added Ag particles. In contrast, E_{ab} is larger than E_{Ag} and induced in-plane strain in the bulk composites should not be significant.

In Fig. 4, we can notice that $\Delta L/L|_c$ nonlinearly increases as a function of Ag volume fraction f_{Ag} deviating heavily from the addition theorem line. As we have already mentioned, the addition theorem corresponds to the case of the independent expansion of the constituents of the bulk composites. Accordingly, the deviation from the addition theorem line may roughly correspond to the net induced c-direction strain in the Sm123 (+20 mol.% Sm211) phase due to added Ag particles. The inset of Fig. 4 shows the c-axis $\Delta L/L$ at 300 K in a magnified scale for $f_{Ag} < 0.2$. The smooth interpolation of the c-axis $\Delta L/L$ to $y = 0$ and the deviation of the data points from the addition theorem line suggest that Sm123 main phase is under the influence of forced compressive strain of about 0.9×10^{-4}, 1.5×10^{-4} and 3.7×10^{-4} in the c-direction for $y = 10$ wt.% ($f_{Ag} = 0.058$), 15 wt.% ($f_{Ag} = 0.088$) and 19.7 wt.% ($f_{Ag} = 0.112$), respectively. We performed the thermal expansion measurement only below 300 K but the melt-process to prepare the SmBaCuO(Ag) bulk starts above the Ag melting point ($T_{melt}^{Ag} \sim 1230$ K). By linearly extrapolating the $\Delta L/L$ data to 1230 K, the total induced c-direction strain may be roughly 4 times as large as the above given values. Actually, this strain results in a forced compressive stress for the Sm123 superconducting phase during the cooling process after the sample melting. The resultant strain may affect the crystal quality and the superconducting properties of the Sm123 main phase as well as possible other factors such as a small amount of Ag solution into the matrix phase or oxygen content variation. Fig. 5 shows resistive superconducting transition for the same samples as in Fig. 4. The superconducting transition temperature T_c of the ab-plane samples is enhanced from $y = 10.0$ to 15.0 wt.% and degraded from $y = 15.0$ to 19.7 wt.%. This result suggests that the total c-axis compressive strain of $\sim4\times1.5\times10^{-4}$ corresponding to $y = 15.0$ wt.% is suitable to realize the best superconducting characteristics of the Sm123 phase and that too heavy strain exceeding 10^{-3}, which corresponds to $y = 19.7$ wt.%, degrades the superconducting characteristics. Measurements in a previous paper on the critical current densities and residual magnetic flux densities of the SmBaCuO(Ag) bulk composites supported that the added Ag content of 10–15 wt.% corresponded to the best condition to improve the superconducting characteristics [6].

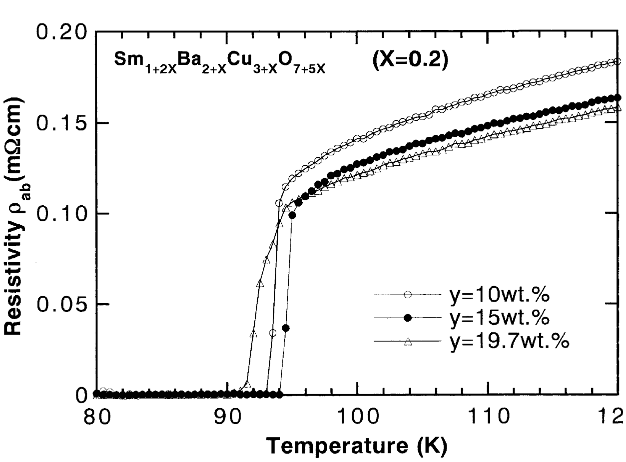

Fig. 5. The temperature dependence of the ab-plane electrical resistivity $\rho_{ab}(T)$ for the same samples as in Fig. 4.

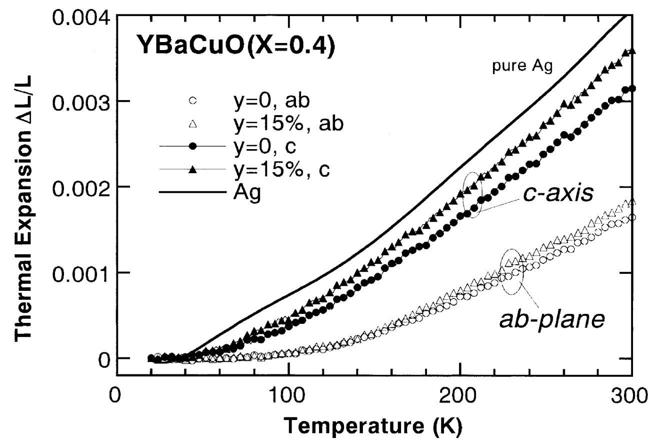

Fig. 6. The temperature dependence of the ab-plane and c-axis $\Delta L(T)/L$ of the $Y_{1+2X}Ba_{2+X}Cu_{3+X}O_{7+5X}$ ($X = 0.4$) superconducting bulks for the Ag content $y = 0$ and 15 wt.%.

Finally, Fig. 6 presents the temperature dependence of the thermal expansion of the $Y_{1+2X}Ba_{2+X}Cu_{3+X}O_{7+5X}$ ($X = 0.4$) bulk composites with the Ag content of $y = 0$ and 15 wt.%. The ab-plane and the c-axis $\Delta L/L$ show an anisotropic behavior. $\Delta L/L$ of an $YBa_2Cu_3O_7$ single crystal has been investigated by Maingast et al. [10], and the reported $\Delta L/L$ values from 300 to 10 K are 0.0015 in the ab-plane and 0.0036 along the c-axis. Comparing with these values, $\Delta L/L|_c$ of the present Ag-nondoped $Y_{1+2X}Ba_{2+X}Cu_{3+X}O_{7+5X}$ ($X = 0.4$) bulk crystals is somewhat smaller, possibly because of the presence of the Y211 particles (see Fig. 1). Both $\Delta L/L|_c$ and $\Delta L/L|_{ab}$ increase by addition of Ag, but the increase in $\Delta L/L|_c$ is more distinct, showing the similar tendency to the SmBaCuO(Ag) bulk composites. The large compressive stress effect in the c-direction caused by addition of Ag metal is a peculiar but a common feature in the high-T_c cuprates with the layered crystal structures.

4. Summary

The ab-plane and c-direction thermal expansion $\Delta L/L$ were measured for $Sm_{1+2X}Ba_{2+X}Cu_{3+X}O_{7+5X}$ (Ag:y) bulk composites, which consisted of the superconducting $SmBa_2Cu_3O_7$ (Sm123) main phase, X mol $Sm_2Ba_1Cu_1O_5$ (Sm211) second phase and added y wt.% silver (Ag) metal. Main results obtained in this study are summarized in the following.

(i) The thermal expansion measured along the ab-plane and the c-axis of the Sm123 phase showed anisotropy, reflecting the layered lattice structure of the main Sm123 phase. The $\Delta L/L|_c$ values in the c-direction were 1.5–1.8 times larger than those of $\Delta L/L|_{ab}$ in the ab-plane.

(ii) The $\Delta L/L|_c$ values and the anisotropy ratio $\Delta L/L|_c/\Delta L/L|_{ab}$ of SmBaCuO(Ag) composites decreased with increasing content X of the Sm211 second phase. The addition theorem, which assumes that the thermal expansion of the composite is given by the sum of the independent contributions proportional to the volume fractions of the constituents, roughly explained the X dependence of $\Delta L(T)/L$.

(iii) In contrast, the addition of Ag metal particles drastically enhanced the $\Delta L/L|_c$ values of the composites, far deviating from the addition theorem, while the addition theorem remained roughly valid for $\Delta L/L|_{ab}$. The different behavior of $\Delta L/L|_{ab}$ and $\Delta L/L|_c$ on Ag addition can be understood on the basis of the anisotropic Young's modulus of the RE123 main phase with the layered lattice structure. Through the cooling process in the melt-processing procedure, the Ag addition forces a considerable compressive stress in the c-direction of the Sm123 phase. The resultant strain seems to make an important factor in improving the superconducting characteristics of the bulk composite for Ag content range, $y \leqslant 15$ wt.%.

(iv) $\Delta L/L$ of YBaCuO(Ag) bulk composites also showed a similar behavior for Ag metal addition. The forced compressive strain due to Ag particles in the c-direction of the main phase is a common feature of the REBaCuO bulk composites.

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