

The Effect of Ionic Radius Difference of RE^{3+} and Ba^{2+} on the Shock Synthesis of $\text{REBa}_2\text{Cu}_3\text{O}_y$ ($\text{RE} = \text{Y, Eu, La}$)

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Shock-synthesis experiments of $\text{REBa}_2\text{Cu}_3\text{O}_y$ ($\text{RE} = \text{Y, Eu, and La}$) were carried out for the mixture of component oxides as starting materials using a 25 mm-bore propellant gun. Both tetragonal $\text{EuBa}_2\text{Cu}_3\text{O}_y$ with $c/a = 3.00$ and cubic $\text{LaBa}_2\text{Cu}_3\text{O}_y$ were successfully synthesized by shock compression, but $\text{YBa}_2\text{Cu}_3\text{O}_y$ was synthesized only partly. The optimum condition for obtaining maximum yield of shock-synthesized $\text{EuBa}_2\text{Cu}_3\text{O}_y$ and $\text{LaBa}_2\text{Cu}_3\text{O}_y$ was shock compression of the starting materials with 40% porosity to 30 GPa. $\text{La}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_y$ could also be synthesized, but $\text{Eu}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_y$ could not. Shock-synthesized $\text{EuBa}_2\text{Cu}_3\text{O}_y$ and $\text{LaBa}_2\text{Cu}_3\text{O}_y$ were in a metastable phase in which RE^{3+} and Ba^{2+} were not ordered perfectly; they converted to the phase synthesized by conventional solid state reaction when annealed above 900°C . Only after annealing above 900°C , followed by oxidation at 400°C , did $\text{EuBa}_2\text{Cu}_3\text{O}_y$ exhibit superconductivity with $T_c \cong 71$ K. These results suggest that shock synthesis of $\text{REBa}_2\text{Cu}_3\text{O}_y$ becomes easier with a decrease in the difference between ionic radii of RE^{3+} and Ba^{2+} . © 1998 Academic Press

INTRODUCTION

The shock compression technique has been noted as a unique method for synthesizing materials within a very short time. In the shock compression of a powder specimen, rapid chemical reaction is either directly induced or assisted by the introduction of a large concentration of defect. The residual temperature after pressure release remains for only several milliseconds, and metastable phase can be synthesized because of the highly nonequilibrium process. Shock compression method has been successfully applied to the synthesis of high-temperature oxide superconductors such as $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ (1, 2) and $\text{Tl}_2\text{Ba}_2\text{CuO}_6$ (3). We already reported the shock synthesis of $\text{EuBa}_2\text{Cu}_3\text{O}_y$, which was found to be a metastable tetragonal phase with $c/a = 3.00$, in contrast to the high T_c phase synthesized by conventional solid state reaction (4). This difference has been explained as incomplete ordering among the metal ions of the A site because of the short duration of the shock process. $\text{Eu}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_y$ with $0.1 \leq x \leq 0.5$ could not be synthesized by shock compression.

In the present study, we have synthesized $\text{REBa}_2\text{Cu}_3\text{O}_y$ ($\text{RE} = \text{Y, Eu, and La}$) by shock compression and compared the effect of ionic radius of RE^{3+} on synthesis conditions and resulting crystal structure. Shock synthesis of $\text{RE}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_y$ was also carried out for $\text{RE} = \text{Eu}^{3+}$ and La^{3+} , where a wide solid solution range for $0 \leq x \leq 0.5$ exists (5). Furthermore, the effect of annealing shock-synthesized $\text{EuBa}_2\text{Cu}_3\text{O}_y$ and $\text{LaBa}_2\text{Cu}_3\text{O}_y$ was examined.

EXPERIMENTAL

Powder materials of component oxide, RE_2O_3 ($\text{RE} = \text{Y, Eu, and La}$), CuO , and BaCuO_2 were mixed in a stoichiometric ratio by ball milling for 3 h to give $\text{RE}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_y$. The mixture was pressed into a pellet 13 mm in diameter and 1 mm in thickness. The pellet was encapsulated in a SUS304 stainless steel container. Shock loading experiments were carried out using a powder gun with 25 mm bore (6). The specimen assembly was impacted by a SUS304 stainless steel flyer with 3 mm thickness in the flyer velocity range 1.0–1.7 km/s. The shock pressure in the container was calculated to be 20–40 GPa from the measured flyer velocity on the basis of the impedance match concept (7). The shock pressure achieved in the specimen container was taken to represent the shocked state of the sample by assuming equilibration with the container via multiple reflection across the specimen–container boundaries. The shock-synthesis conditions were controlled by the shock pressure and porosity of the starting materials in the range of 50–70% of theoretical density.

The recovered specimens were examined by X-ray powder diffraction (XRD) analysis with $\text{CuK}\alpha$ radiation. The oxygen content was determined by iodometric titration. Magnetic susceptibility measurements were carried out using a SQUID magnetometer.

RESULTS AND DISCUSSION

X-ray powder diffraction analysis of the shock-recovered specimen of $\text{REBa}_2\text{Cu}_3\text{O}_y$ showed the formation of a

perovskite-based phase. The shock conditions, pressure and porosity, were changed over a wide range to identify the best shock-synthesis conditions for $\text{REBa}_2\text{Cu}_3\text{O}_y$. It was considered that the reaction took place with shock-induced temperature increases when powder material was shock-loaded. Figure 1 shows the relationship between apparent yield of shock-synthesized $\text{REBa}_2\text{Cu}_3\text{O}_y$ and shock temperature, which was estimated from shock pressure and porosity of starting materials by assuming the Hugoniot of BaTiO_3 (8) with the perovskite structure. The small yield of $\text{YBa}_2\text{Cu}_3\text{O}_y$ hardly changed when the shock temperature was varied. The shock-synthesis yield of $\text{YBa}_2\text{Cu}_3\text{O}_y$ did not increase above 17%. The yield of both $\text{EuBa}_2\text{Cu}_3\text{O}_y$ and $\text{LaBa}_2\text{Cu}_3\text{O}_y$ increased with increasing shock temperature above 1000°C , and maximum yield was obtained at around 1500°C . There was no appreciable difference between optimum shock temperature for the synthesis of $\text{EuBa}_2\text{Cu}_3\text{O}_y$ and $\text{LaBa}_2\text{Cu}_3\text{O}_y$. The best shock-synthesis conditions were achieved by shock compression to 30 GPa for a 60% packing density pellet, which corresponds to shock temperature of around 1500°C .

Figure 2 shows XRD patterns of shock-recovered specimens of $\text{REBa}_2\text{Cu}_3\text{O}_y$ with the best shock conditions. In the XRD pattern of $\text{YBa}_2\text{Cu}_3\text{O}_y$, diffraction lines due to a triple-perovskite phase were observed, indicating the synthesis of $\text{YBa}_2\text{Cu}_3\text{O}_y$, although a considerable portion of

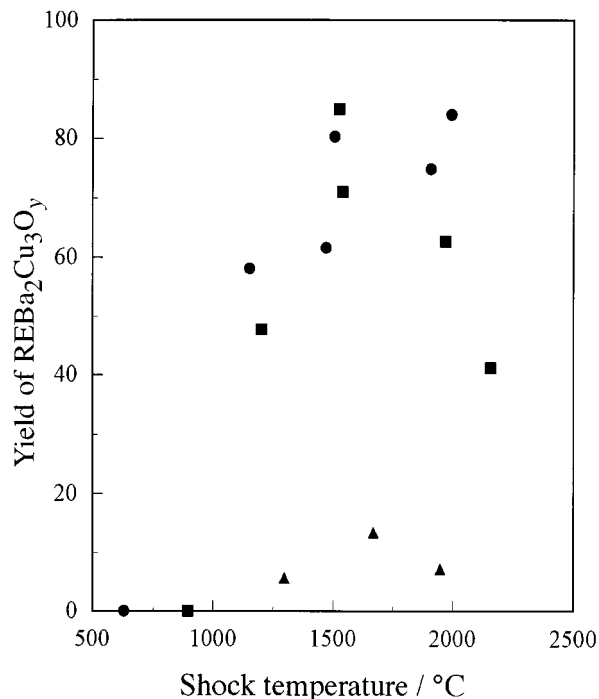


FIG. 1. Yield of shock-synthesized $\text{REBa}_2\text{Cu}_3\text{O}_y$ plotted as a function of shock temperature. Triangles, circles, and squares indicate $\text{YBa}_2\text{Cu}_3\text{O}_y$, $\text{EuBa}_2\text{Cu}_3\text{O}_y$, and $\text{LaBa}_2\text{Cu}_3\text{O}_y$, respectively.

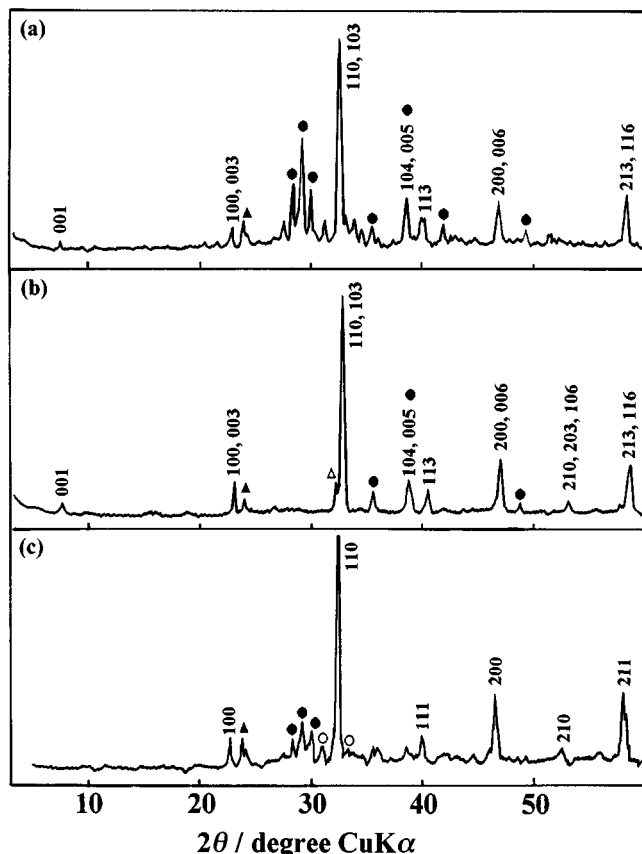


FIG. 2. X-ray powder diffraction patterns of $\text{REBa}_2\text{Cu}_3\text{O}_y$ shock-synthesized at 30 GPa: (a) $\text{YBa}_2\text{Cu}_3\text{O}_y$ (closed circles and solid triangles indicate raw materials and BaCO_3); (b) $\text{EuBa}_2\text{Cu}_3\text{O}_y$ (open triangles indicate Eu_2CuO_4); and (c) $\text{LaBa}_2\text{Cu}_3\text{O}_y$ (open circles indicate La_2CuO_4).

unreacted starting materials remained and BaCO_3 was formed. We considered that BaCO_3 was formed after the shock-loaded sample was taken out of the capsule. BaCuO_2 was partially decomposed to BaO and CuO when shock-loaded. BaO was not stable in air; therefore the reaction $\text{BaO} + \text{CO}_2 \rightarrow \text{BaCO}_3$ could occur. The shock-synthesized phase was indexed with tetragonal indices with $c/a = 3.00$, which is smaller than that of $\text{YBa}_2\text{Cu}_3\text{O}_y$ synthesized by conventional solid state reaction. The XRD pattern of shock-synthesized $\text{EuBa}_2\text{Cu}_3\text{O}_y$ indicated an almost single phase of triple-perovskite $\text{EuBa}_2\text{Cu}_3\text{O}_y$, which was also indexed with a tetragonal cell with $c/a = 3.00$. Cell constants of shock-synthesized $\text{EuBa}_2\text{Cu}_3\text{O}_y$ were smaller than those of the high T_c phase synthesized by conventional solid state reaction. In the case of La^{3+} , which has the largest ionic radius among rare earth ions, an almost single phase of $\text{LaBa}_2\text{Cu}_3\text{O}_y$ was synthesized, as in the case of $\text{EuBa}_2\text{Cu}_3\text{O}_y$. However, the XRD pattern of shock-synthesized $\text{LaBa}_2\text{Cu}_3\text{O}_y$ was indexed with a cubic cell, and a period three times that of the basic perovskite unit was not observed in the electron diffraction pattern in $\text{LaBa}_2\text{Cu}_3\text{O}_y$,

unlike $\text{EuBa}_2\text{Cu}_3\text{O}_y$. These results suggest that all shock-synthesized phases are metastable phase whose metal ions of the A site are not ordered perfectly, because of the short duration of the shock process. Shock synthesis of $\text{REBa}_2\text{Cu}_3\text{O}_y$ became easier with a decrease in the difference between the ionic radii of RE^{3+} and Ba^{2+} because of easier disordering.

There was not much difference in shock synthesis of $\text{EuBa}_2\text{Cu}_3\text{O}_y$ and $\text{LaBa}_2\text{Cu}_3\text{O}_y$. However, a remarkable difference between $\text{RE} = \text{La}$ and Eu was observed in the case of shock synthesis of $\text{RE}_{1.5}\text{Ba}_{1.5}\text{Cu}_3\text{O}_y$, as shown in the XRD patterns of the recovered specimen (Fig. 3). A large amount of Eu_2CuO_4 was found in the shock-loaded product, and no $\text{Eu}_{1.5}\text{Ba}_{1.5}\text{Cu}_3\text{O}_y$ phase was formed. On the other hand, $\text{La}_{1.5}\text{Ba}_{1.5}\text{Cu}_3\text{O}_y$ was successfully synthesized as an almost single phase by shock compression and its XRD pattern was indexed with a cubic cell, the same as $\text{LaBa}_2\text{Cu}_3\text{O}_y$. Furthermore $\text{La}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_y$ was found to be synthesized for $x = 0.1, 0.3,$ and 0.4 . This result can be explained by the smaller differences between the ionic radii of La^{3+} (1.18 Å) and Ba^{2+} (1.42 Å) than between those of Eu^{3+} (1.07 Å) and Ba^{2+} . The cubic cell constants of all the shock-synthesized $\text{La}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_y$ are plotted against La^{3+} content in Fig. 4. The cell constants of both shock-synthesized $\text{La}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_y$ and the specimens synthesized by conventional solid state reaction decreased with increasing La^{3+} content. However, the cell constants of the former were considerably smaller than those of the latter. This result suggests that all shock-synthesized

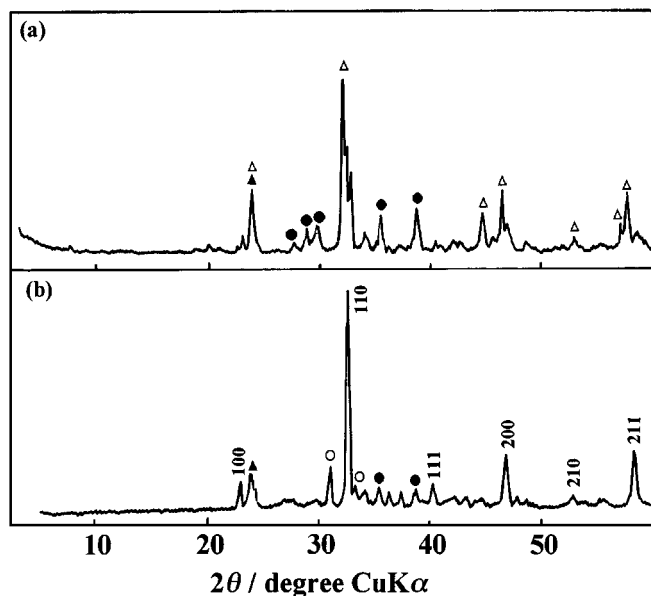


FIG. 3. X-ray powder diffraction patterns of $\text{RE}_{1.5}\text{Ba}_{1.5}\text{Cu}_3\text{O}_y$ shock-synthesized at 30 GPa: (a) $\text{Eu}_{1.5}\text{Ba}_{1.5}\text{Cu}_3\text{O}_y$ (closed circles, solid triangles, and open triangles indicate raw materials, BaCO_3 , and Eu_2CuO_4); and (b) $\text{La}_{1.5}\text{Ba}_{1.5}\text{Cu}_3\text{O}_y$ (open circles indicate La_2CuO_4).

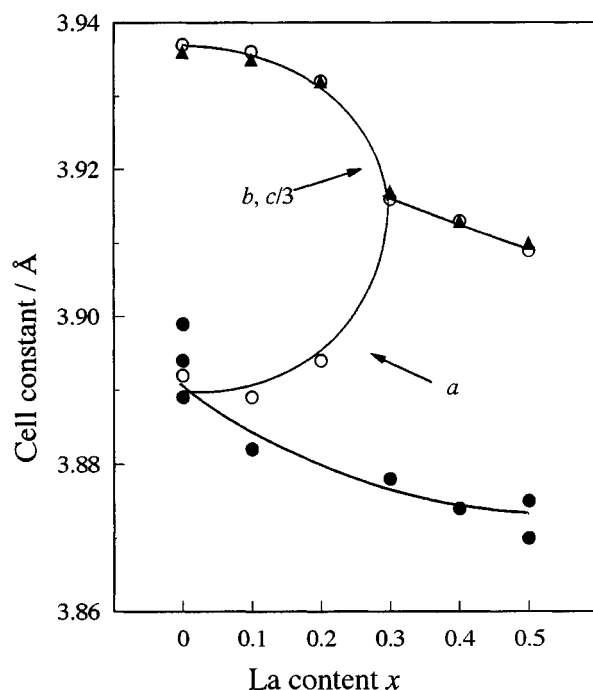


FIG. 4. Cell constant of $\text{La}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_y$ plotted as a function of La^{3+} content. Closed circles indicate a -axis of shock-synthesized specimen. Open circles and solid triangles indicate a -, b -axes and c -axis of the specimen synthesized by conventional solid state reaction.

$\text{La}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_y$ are metastable phase, probably due to incomplete order among La^{3+} and Ba^{2+} .

The shock-synthesized phases were not superconductors, and an annealing treatment was necessary to achieve superconductivity. The annealing experiments of shock-synthesized $\text{EuBa}_2\text{Cu}_3\text{O}_y$ and $\text{LaBa}_2\text{Cu}_3\text{O}_y$ were carried out. Figure 5 shows the change of the c/a ratio of shock-synthesized $\text{EuBa}_2\text{Cu}_3\text{O}_y$ plotted as a function of annealing temperature in O_2 for 2 h. The c/a ratio of $\text{EuBa}_2\text{Cu}_3\text{O}_y$ remained at 3.00 for annealing below 900°C . Above 900°C the c/a ratio began to increase and reached 3.05, which is the c/a value of $\text{EuBa}_2\text{Cu}_3\text{O}_y$ synthesized by conventional method. Annealing of shock-synthesized $\text{EuBa}_2\text{Cu}_3\text{O}_y$ at 400°C in O_2 did not indicate superconductivity, although the oxygen content increased to 6.77 and Cu valence increased to 2.18, which should show superconductivity. However, the shock-synthesized specimen annealed above 900°C exhibited superconductivity with $T_c \approx 71$ K (Fig. 6) if its oxygen content was increased to 6.77 by annealing at 400°C in O_2 . Shock-synthesized $\text{EuBa}_2\text{Cu}_3\text{O}_y$ consisted of domains whose c -axes were orthogonal to each other from HRTEM image observation (4). These results suggest that the complete CuO_2 plane has not been achieved in the shock-synthesized $\text{EuBa}_2\text{Cu}_3\text{O}_y$ because of oxygen disordering originating from a partial disorder between Eu^{3+} and Ba^{2+} , and the perfect ordering necessary for achieving

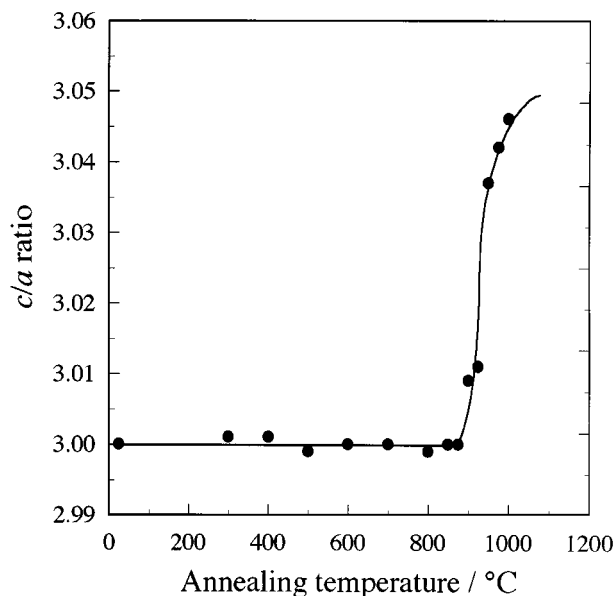


FIG. 5. The c/a ratio of shocked $\text{EuBa}_2\text{Cu}_3\text{O}_y$ annealed in O_2 for 2 h plotted as a function of annealing temperature.

superconductivity is considered to be established above 900°C , where cation migration takes place.

Figure 7 shows the change of cell constant of shock-synthesized $\text{LaBa}_2\text{Cu}_3\text{O}_y$ plotted as a function of annealing temperature in O_2 . The cell constant of $\text{LaBa}_2\text{Cu}_3\text{O}_y$ began to increase from 800°C . The crystal system changed from cubic to tetragonal above 900°C . These results also suggest that La^{3+} and Ba^{2+} began to order above 900°C . However, the c/a ratio remained 3.00 even with annealing at 1050°C , indicating that the ordering between La^{3+} and Ba^{2+} was less complete than between Eu^{3+} and Ba^{2+} because of smaller differences in ionic radii.

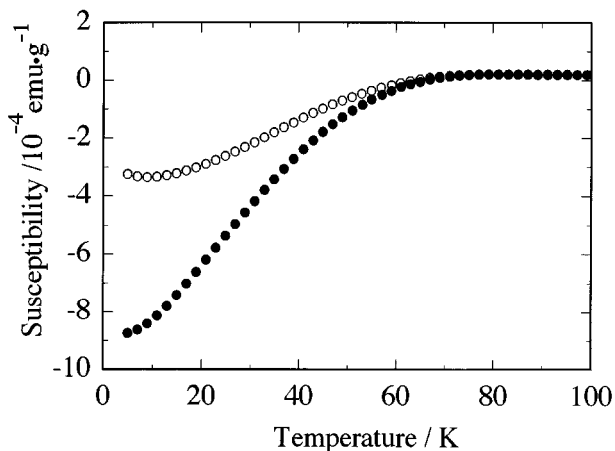


FIG. 6. Temperature dependence of DC susceptibility of $\text{EuBa}_2\text{Cu}_3\text{O}_{6.77}$ shock-synthesized and annealed at 900°C , for zero-field cooling (closed circles) and field cooling (open circles) ($H = 20 \text{ Oe}$).

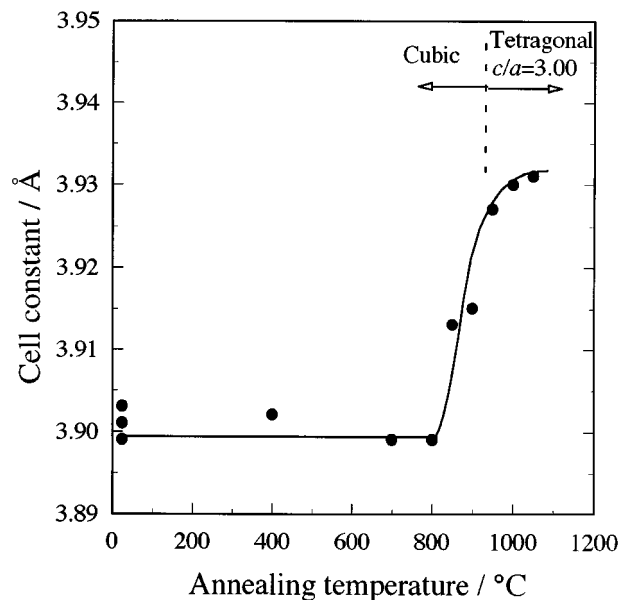


FIG. 7. The cell constant of shocked $\text{LaBa}_2\text{Cu}_3\text{O}_y$ annealed in O_2 for 2 h plotted as a function of annealing temperature.

CONCLUSION

Tetragonal $\text{EuBa}_2\text{Cu}_3\text{O}_y$ and cubic $\text{La}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_y$ were successfully synthesized as an almost single phase by shock compression, but $\text{YBa}_2\text{Cu}_3\text{O}_y$ was synthesized only partly. Shock-synthesized phases seemed to be a metastable phase whose RE^{3+} and Ba^{2+} were not perfectly ordered, and the degree of disordering increased with a decrease in the difference between ionic radii of RE^{3+} and Ba^{2+} . The shock-synthesized phase was considered to have an incomplete CuO_2 plane because of incomplete ordering between RE^{3+} and Ba^{2+} , and did not show superconductivity simply by oxygen treatment. Only after annealing above 900°C did the shock-synthesized $\text{EuBa}_2\text{Cu}_3\text{O}_y$ and $\text{LaBa}_2\text{Cu}_3\text{O}_y$ become superconductors, because RE^{3+} and Ba^{2+} began to order completely. Shock synthesis of $\text{REBa}_2\text{Cu}_3\text{O}_y$ was found to be easier with the decrease in the difference between ionic radii of RE^{3+} and Ba^{2+} , because disordering became easier, which favored synthesis due to the short reaction time in the shock process.

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