Synthesis using molten KOH and properties of rare earth substituted REBa$_2$Cu$_4$O$_8$ phases

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Abstract. Rare-earth-substituted REBa$_2$Cu$_4$O$_8$ phases (RE124) are synthesized by using molten KOH to investigate phase formation and superconductivity. RE124 phases with small and heavy rare-earth elements of Yb, Er, Ho, Dy, Gd and Y are easily producible with good superconducting properties and crystallinity. Superconducting transition temperature and superconducting volume fraction decrease with increasing ion radius of the rare-earth elements. Samples using large rare-earth elements show broad peaks of RE124 pattern in x-ray diffraction also with broad peaks probably originating from RE123 and other related phases.

1. Introduction

First recognized in YBa$_2$Cu$_3$O$_{7-δ}$ (Y123) thin films as a stacking fault structure, YBa$_2$Cu$_4$O$_8$ (Y124) crystal [1-3] has an analogous crystalline structure to that of Y123 crystal and is more stable in a lower temperature and higher oxygen pressure region of the phase diagram than Y123 phase is [3–7]. The original superconducting transition temperature ($T_c$) is approximately 80 K; however, it increases to about 90 K by Ca substitution for Y, which is comparable to that of Y123 phase [8].

124 phase has a rigorous stability of oxygen stoichiometry and no structural phase transition as temperature changes. Accordingly, it has no twin structure formation, which is typically introduced into 123 superconductor. It resists H$_2$O exposure and is stable in the ambient atmosphere. These characteristics are suitable for device processing of thin film superconductors. They are especially important for superconducting circuits such as flux single quantum circuits because they can simplify production processes of multilayered structures and increase reliability of a series of Josephson junctions.

Many preparation methods of 124 thin film have been reported: chemical vapor deposition [9, 10], sputtering [11], electron-beam evaporation [12, 13], pulsed laser deposition [14, 15], chemical vapor deposition [16], metal-organic decomposition [17], and others. Some amount of 123 and 247 phase is often formed in 124 film. Single phases and single crystals of bulk 124 phase are prepared under high oxygen pressures about 400 atms and temperatures more than 1000°C [18].
preparation is possible [19, 20, 22] not only with addition of reaction enhancement reagents, but also by simple solid state reactions. However, a long annealing time is needed.

Preparation of 124 phase is not as simple as that of 123 phase. Therefore, few relevant studies have been conducted despite the derivative structure of 123 phase. Investigation of the effect of rare earth (RE) element substitution for the Y site in 124 phase showed that the transition temperature ($T_c$) depends on the substituted ion radius [20-22]. However, possible substitution elements for the synthesis of 124 phase depend on the preparation method, which prevents systematic investigation including all the rare earth elements of La–Yb.

The preparation method of single crystalline RE124 compound is reported using molten alkali hydroxide in ambient atmosphere [23, 24]. Sandford et al. described synthesis of Eu124 single crystal from molten potassium hydroxide and Song et al. reported a more feasible process for Y124 growth. Different from other 1-atm preparations, the molten hydroxide method is a kind of solution growth and can provide 124 single crystals. Therefore, the process is expected to be applicable to liquid phase epitaxial (LPE) growth of 124 films with high quality for a superconducting device substrate. However, the RE element substitution effect on 124 superconductivity has not been investigated for this process.

This study therefore specifically examines rare-earth-substitution dependence of superconducting properties and formation characteristics of 124 phases synthesized by using a molten potassium hydroxide solution.

2. Experimental procedure
Using RE oxide (RE=Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er and Yb), barium carbonate, and copper oxide as starting raw materials and potassium hydroxide as a solvent, RE-substituted 124 phases were synthesized. The raw materials were weighed stoichiometrically as RE:Ba:Cu=1:2:4 and put into an aluminum oxide crucible, which causes no deteriorative contamination [25], with 60 wt% of KOH to the raw materials. The crucible was heated to 715°C and kept at that temperature for 4 h; it was then cooled to 450°C at 7°C/h. The obtained samples were washed using water and ethanol to remove the KOH.

The obtained powders were investigated using X-ray diffraction (XRD) to identify the phase and determine the lattice constants. Magnetic susceptibility was measured using a superconducting quantum interference device (SQUID) to determine the superconducting transition temperature and superconducting volume fraction by application of an external field of 10 Oe.

![Figure 1](image.png)

**Figure 1.** Temperature dependence of susceptibility of as-synthesized samples using various rare-earth elements.
Table 1. Transition temperature, volume fraction, and lattice constant of c of the various rare-earth-element-substituted 124 phases.

| Rare-earth elements | $T_c$ (K) | Volume Fraction at 10 K (%) | Lattice constant c (nm) |
|---------------------|-----------|-----------------------------|------------------------|
| Y                   | 80.5      | 112                         | 2.724                  |
| Yb                  | 80.5      | 92                          | 2.718                  |
| Er                  | 79.5      | 62                          | 2.721                  |
| Ho                  | 75.5      | 85                          | 2.724                  |
| Dy                  | 74.5      | 51                          | 2.725                  |
| Gd                  | 73.5      | 28                          | 2.730                  |
| Eu                  | 74.5      | 23                          | -                      |
| Sm                  | 72        | 2                           | -                      |
| Nd                  | 54        | 11                          | -                      |
| La                  | 33        | 0.15                        | -                      |

3. Results and discussion

The temperature dependence of susceptibility of the as-synthesized specimens is presented in Fig. 1. Marked diamagnetism is observed at approximately 80 K, which corresponds to the 124 phase transition temperature, indicating the formation of superconductive RE124 phase. The superconducting volume fraction estimated by the susceptibility at 15 K is presented in Table 1. The theoretical density of each rare-earth-substituted 124 phase was assumed in the estimation. As might be readily apparent, small ion radius elements provide a large fraction near 100%, meaning that almost the entire volume changed to the superconductor. It is noteworthy, however, that Y, Ho, Er, and Yb showed a small amount of diamagnetism at about 90 K, reflecting the co-existence of 123 phases. The corresponding fractions are approximately 5–10%. Transition temperatures of RE124 phases are plotted in Fig. 2 as a function of the rare-earth ion radius. These temperatures decreased as the ion radius increased, which is the same tendency as previously reported [20-22]. Specimens with large ion radius elements show broad transition and small fraction of the superconducting volume. In fact, La-sample, with the largest ion of rare earths, showed only obscured diamagnetism around 30 K, even though some XRD peaks correspond to 124 lattice periodicity. No superconductivity or conventional superconducting phase was detected on Pr-substituted and Ce-substituted specimens.

Figure 2. Transition temperature of RE124 phases as a function of ionic radius.
XRD patterns of the synthesized samples with various rare-earth elements are displayed in Fig. 3. They revealed that the samples with smaller ionic radius elements of Yb, Er, Ho, Dy and Y showed intense diffraction patterns originating from the 124 structure, confirming that it is the main phase. Furthermore, samples with Yb, Er, Ho, and Y showed weak peaks of the 123 diffraction, corresponding to the 90-K transition. On the other hand, XRD patterns observed on the samples with large ionic elements of Gd, Eu, Sm, Nd, and La showed broader diffraction peaks of some phases such as 124, 123 and undefined phases, meaning that the synthesis process was not completed under the condition of this experiment.

Figure 4. Lattice constant of c as a function of ionic radius
Lattice parameters of RE-substituted 124 phases were derived from the obtained 124 XRD pattern. Fig. 4 shows the lattice constant of the c-axis as a function of the ion radius. As reported previously [20-22], the c-lattice constant increases concomitantly with the increase of RE ionic radius.

Relatively large grains of a few hundred µm in size were contained in the samples with smaller ionic radius elements. The shape of such large 124 grains was cubic or hexahedral observed using the scanning electron microscope. This implies that each grain was grown in the molten KOH solution, as reported [24].

4. Conclusion
RE124 phases with high transition temperature, large superconducting volume fraction and good crystallinity was obtained by the molten KOH method when using small rare earth elements of Yb, Er, Ho, Dy and Gd as well as Y. Accordingly, the molten KOH method is suitable for the production of RE124 phases with smaller ionic radius elements and has a promising potential to produce superconducting RE124 crystals and thin films with high crystalline perfection, which is an indispensable feature for reliable oxide superconducting devices. On the other hand, the obtained samples synthesized with large ionic radius elements of Eu, Sm, Nd and La show complicated broad peaks of x-ray diffraction probably originating from 124, 123 and other related phases. The transition temperature of RE124 phase has a tendency of monotonous decrease as the ionic radius increased. Transition temperature of Yb124, the smallest element examined, was 80.5 K. The La-substituted sample, the largest element, only showed weak diamagnetism at about 30 K. No superconducting phase was synthesized when using Pr and Ce. The obtained RE124 crystals by this method were synthesized as grown crystals through the molten KOH solution.

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References
[1] H. W. Zandbergen, R. Gronski, K. Wang, and G. Thomas, Nature 331, 596 (1988).
[2] A. F. Marshall, R. W. Barton, K. Char, A. Kapitulnik, B. Oh, R. H. Hammond, and S. S. Laderman Phys. Rev. B 37, 9353 (1988).
[3] H. W. Zandbergen and G. Thomas, phys. stat. solidi A 105, 207 (1988).
[4] D. M. Pooke, R. G. Buckley, M. R. Preshand, and J. L. Tallon, Phys. Rev. B 41, 6616 (1990).
[5] T. Wada, N. Suzuki, A. Ichinose, Y. Yaegashi, H. Yamauchi, and S. Tanaka, Jpn. J. Appl. Phys. 29, L915 (1990).
[6] H. Murakami, T. Suga, T. Noda, Y. Shiohara, and S. Tanaka, Jpn. J. Appl. Phys. 29, 2720 (1990).
[7] D. E. Morris, A. G. Markelz, B. Fayn, and J. H. Nickel, Physica C 168, 153 (1990).
[8] T. Miyataka, S. Goto, N. Koshizuka, and S. Tanaka, Nature 341, 41 (1989).
[9] H. Hayashi, Y. Yamada, K. Sugawara, Y. Shiohara, and S. Tanaka, Jpn. J. Appl. Phys. 30, L352 (1991).
[10] H. Sakai, Y. Shiohara, and S. Tanaka, Physica C 228 259 (1994).
[11] A. F. Marshall, R. W. Barton, K. Char, A. Kapitulnik, B. Oh, R. H. Hammond, and S. S. Ladermann, Phys. Rev. B 37, 9353 (1988).
[12] K. Char, Mark Lee, R. W. Barton, A. F. Marshall, R. H. Hammond, M. K. Beasley, T. H. Geballe, A. Kapitulnik, and S. S. Ladermann, Phys. Rev. B 38, 5031 (1988).
[13] K. Char, M. Lee, R. W. Barton, A. F. Marshall, I. Bozovic, R. H. Hammond, M. R. Beasley, T. H. Geballe, A. Kapitulnik, and S. S. Ladermann, Phys. Rev. B 38, 834 (1988).
[14] R. Kita, S. Kawamoto, K. Ohata, H. Izumi, R. Itti, T. Morishita, and S. Tanaka, Physica C 170, 500 (1990).
[15] M. Badaye, Y. Kanke, K. Fukushima, and T. Morishita, Physica C 231, 335 (1994).
[16] H. Hayashi, Y. Yamada, T. Sugimoto, Y. Shiohara, S. Tanaka, Jpn. J. Appl. Phys. 30, L725 (1991).
[17] T. Manabe, Y. Yajima, I. Yamaguchi, T. Kumagai, T. Shimizu, and S. Mizuta, Physica C 53 (1998).
[18] J. Karpinski, E. Kaldis, E. Julek, S. Rusiecki, and B. Bucher, Nature 336, 660 (1988).
[19] R. J. Cava, J. J. Krajewski, W. F. Peck Jr, B. Batlog, L. W. Rupp Jr., R. M. Fleming, A. C. W. P. James, and P. Marsh, Nature 338, 328 (1989).
[20] S. Adachi, H. Adachi, K. Setsune, and K. Wada, Physica C 175, 523 (1991).
[21] D. E. Morris, J. H. Nickel, Y. T. Wei, N. G. Asmar, J. S. Scott, J. E. Post, P. J. Heaney, D. R. Veblen, and R. M. Hazen, Phys. Rev. B 39, 7347 (1989).
[22] Masakazu Tatsumi, Makoto Kawazoe, and Seika Yamamoto, Physica C 262, 261 (1996).
[23] D. Sandford, L. N. Marquez, and A. M. Stacy, Appl. Phys. Lett. 67, 422 (1995).
[24] Y. T. Song, J. B. Peng, X. Wang, G. L. Sun, and C. T. Lin, J. Cryst. Growth 300, 263 (2007).
[25] G. L. Sun, Y. T. Song and C. T. Lin, Supercond. Sci. Technol. 21, 125001 (2008)