Synthesis of superconductor REBa₂Cu₄O₈ phase by molten hydroxide method

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Superconducting oxide REBa₂Cu₄O₈ (RE124; RE=Y, Sm, Eu, Gd, Dy, Ho, Er, Tm and Yb) were synthesized by a molten hydroxide method under an ambient pressure. Rare earth oxide, barium carbonate and copper oxide powder were used as starting materials and potassium hydroxide (KOH) was used as a solvent material. The synthesis was carried out by a heating treatment at 715°C. XRD peaks of RE124 using small ionic radius elements such as Y and Dy-Yb were obtained to be intense and sharp. The effect of RE substitution in superconductivity and lattice constant was investigated by SQUID and XRD. Superconducting critical temperature (*T_c*) increased and c-axis length decreased as the ion radius decreased. In order to investigate relationship between heating temperature and synthesized phases, Y124 were prepared at different heating temperature from 500°C to 800°C. Y124 phase appeared in the range between 600°C and 800°C, and the most intense at 700°C. No Y124 phase was observed at 500°C. From these results, it was considered that small ion radius elements such as Y and Dy-Yb are appropriate to easily synthesize RE124 by this method, and the optimal heating temperature is about 700°C.

Key words: Y124, superconductor, YBa₂Cu₄O₈, synthesis

1. Introduction

The high temperature superconducting oxide of YBa₂Cu₄O₈ (Y124) was discovered as a stacking fault in YBa₂Cu₃O_{7-x} (Y123) film.¹ Because Y124 has consisted of the double Cu-O chain, Y124 structure is hard to yield an oxygen deficiency in the crystal. The critical temperature (*T_c*) of Y124 is approximately 80 K, however, when Y site is replaced with a bit of Ca, *T_c* value increases to 90 K.² There are many reports about the preparation of Y124, for example, a high oxygen pressure method,³ a nitrate method,⁴ a sol-gel method,⁵ and others. Most of these methods are needed a long reaction time and particular equipments or particular chemicals, for instance, a high-pressure equipment or organic metals. Among a number of methods, a hydroxide flux method is relatively an easier route to synthesize RE124 in a short reaction time under the ambient pressure.⁶⁻⁷ There are only two reports on the synthesis of RE124 (RE=Y, Eu) by this method. Therefore, we tried to prepare RE124 using different rare earth elements from La to Lu, and investigated the substitution effect in phase formation, superconductivity and lattice constant.

We also investigate a relationship between heating temperature and synthesized phase to reveal the optimal temperature condition for Y124 synthesis.

2. Experimental

Rare earth oxide (RE = Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb and Lu), barium carbonate and copper oxide powders were used as starting materials, and potassium hydroxide (KOH) was used as a solvent. The starting materials were weighed in a molar ratio of RE:Ba:Cu = 1:2:4, mixed and put into an alumina crucible with the solvent of 60wt% of the raw materials. Then the mixture was heat-treated using a muffle furnace in air. Synthesized specimens were washed in distilled water and ethanol to remove the remained KOH. Table I summarizes the heat treatment conditions.

The phase identification and lattice parameter were investigated by X-ray powder diffraction (XRD). Temperature dependence of magnetic susceptibility was measured by superconducting quantum interference device (SQUID) to determine an existence of superconducting phases and superconducting critical

Table I, The heating treatment process condition for RE124 synthesis

Condition name	RE	Temperature (°C) Max - Minimum	Heating rate (°C/h)	Holding time (h)	Cooling rate (°C/h)	RE124 Crystals
A	Y, La~Lu	715 - 450	200	4	6.9	Obtained for Y, Sm ~ Yb
B	Y	500 - 20	140	4	Quench	No Crystals
C	Y	600 - 20	170	4	Quench	Y124
D	Y	700 - 20	200	4	Quench	Y124
E	Y	800 - 20	230	4	Quench	Y124

temperature (T_c).

3. Results and discussion

3.1 Substitution of rare earth element

The rare earth substituted RE124s were prepared by a slow cooling method from 715°C to 450°C (Condition A in Table 1). Samples with small ionic radius elements such as Y, Dy, Ho, Er, Tm, and Yb showed sharp and intense peaks of RE124 phase. Samples with Y, Nd, Sm, Gd, Ho, Er, and Yb showed not only RE124 peaks but also RE123 peaks. Samples with Dy, Ho and Yb showed a very weak peak of $\text{RE}_2\text{BaCuO}_5$ phase. These phase identifications are summarized in Table II. It is noteworthy that the samples with Dy and Tm showed almost single phase of RE124 under this experimental condition as shown in Fig.1. Ce, Pr, and Lu, the smallest ion, didn't synthesize RE124 phase.

Fig.1. XRD patterns of $\text{DyBa}_2\text{Cu}_4\text{O}_8$, showing almost single phase and $\text{GdBa}_2\text{Cu}_4\text{O}_8$, showing coexistence of 124 and 123 phases.

Fig.2. Temperature dependence of magnetic susceptibility of $\text{REBa}_2\text{Cu}_4\text{O}_8$ (RE = Y, Nd, Sm, Gd, Dy, Er, Ho, Tm and Yb). The measurements were carried out with increasing temperature in the constant field of 10 Oe.

Temperature dependence of magnetic susceptibility is shown in Fig.2. Superconducting transition temperature was determined at which abrupt drop of susceptibility occurred. Because some samples contain both RE124

and RE123 phases, two drops were observed at about 90 K (T_c of RE23 phase) and about 80 K (T_c of RE124 phase) in such samples. The estimated T_c values for various rare earth elements are listed in Table II.

T_c of RE124 phase appeared approximately 70-80K for the samples with Y, Sm, Eu, Gd, Dy, Ho, Er, Tm and Yb. Because specimens with Y, Ho, Er and Yb contained RE123 phase with RE124 phase, 90-K transition was also observed with 80-K transition. According to the XRD measurement, the samples with Gd, Eu, Sm and Nd contained RE123 phase. However, these RE123 peaks corresponded to not $\text{REBa}_2\text{Cu}_3\text{O}_7$ but rather $\text{REBa}_2\text{Cu}_3\text{O}_6$. Therefore, these samples did not show 90-K transition. In addition, second T_c appeared at around 50K on Eu, Sm and Nd samples. The second transition may result from RE123 phase with oxygen deficiency or rare earth element substitution for Ba site.

Lattice parameter of c-axis of RE124 and T_c as a function of RE ion radius⁸ are shown in Fig.3. T_c increased and c-axis parameter decreased with decrease of RE ion radius. (These behaviors may occur because double Cu-O chains are compressed with decrease of c-axis parameter.) The both relationships correspond to the reported ones of Morris et al.⁹ and Adachi et al.¹⁰.

Fig.3. Lattice parameter of c-axis of RE124 and T_c as a function of RE ionic radius.

3.2 Y124 synthesis at different temperature

In order to investigate stable phases at high temperatures, rapid cooling experiments were conducted under the conditions of B, C, D and E in Table 1. The relationships between maximum temperature of the heating process and the intensity of characteristic XRD peak of each detected phase are shown in Fig.4.

Y124 phase appeared at 600°C, had a sharp peak at 700°C and was diminished at 800°C. No Y124 trace was detected at 500°C. On the other hand, Y123 was not detected below 600°C, recognized at 700°C and the intensity significantly increased at 800°C. The intensity crossover of Y124 and Y123 phase indicates that Y124 decomposed to Y123 at the high temperatures above 700°C. From these results, the optimal temperature for synthesis and crystal growth of Y124 phase is near 700°C.

Table II. Phase identification and REBa₂Cu₄O₈ parameter

RE	Obtained phase by XRD				124 phase parameter		
	124	123	Other phase		c lattice constant (Å)	T _c (K)	
						124	Other
Y	main peak	contained			CuO, BaCO ₃	27.251	80.6 91.5
La	no	no	(unknown)		CuO, BaCO ₃		
Ce	no	no	BaCeO ₃	CeO ₂	CuO, BaCO ₃		
Pr	no	no	Pr ₆ O ₁₁		CuO, BaCO ₃		
Nd	no	contained			CuO, BaCO ₃		57
Sm	weak peak	contained			CuO, BaCO ₃	71.8	40
Eu	weak peak	contained			CuO, BaCO ₃	74.0	54
Gd	weak peak	contained			CuO, BaCO ₃	27.271	73.4
Dy	main peak	no	Dy ₂ BaCuO ₅		CuO, BaCO ₃	27.253	74.5
Ho	main peak	contained	Ho ₂ BaCuO ₅		CuO, BaCO ₃	27.243	76.0 90.1
Er	main peak	contained			CuO, BaCO ₃	27.221	80.0 91.0
Tm	main peak	no			CuO, BaCO ₃	27.197	80.2
Yb	main peak	contained	Yb ₂ BaCuO ₅		CuO, BaCO ₃	27.188	80.5 89.5
Lu	no	no	Lu ₂ O ₃	(unknown)	CuO, BaCO ₃

Fig.4. Relationship between heating temperature and XRD peak intensity of the detected phase.

4. Summary

The molten potassium hydroxide method, which is a kind of flux method, was applied to synthesize various rare earth substituted RE124 phase. Rare earth oxide, barium carbonate and copper oxide as starting materials, and potassium hydroxide as the flux material were used. RE124 phase was obtained for RE=Y, Sm, Eu, Gd, Dy, Ho, Tm and Yb. T_c increased and c-axis length decreased with decrease of RE ionic radius. The light-weight elements of La, Ce, Pr and Nd and the smallest ionic radius element of Lu did not form RE124 structure. The results of this study revealed that the molten hydroxide method is effective not only Y but also various rare earth elements especially with small ionic radius from Dy to Yb.

The rapid cooking experiment has revealed the temperature region for Y124 phase stable. Y124 phase is stable from about 600°C to near 700°C. The XRD intensity of Y124 had a peak at 700°C. At higher temperatures Y124 decomposes to Y123. Therefore, the optimal temperature for the synthesis of Y124 is near 700°C.

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7. References

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