Change on the Surface of Superconducting Oxide $\text{Ba}_2\text{EuCu}_3\text{O}_{7-x}$ under Various Humid Atmospheres

Kazuo SAKAI, Tomoko SUENAGA* and Toshiyuki SATA

(Department of Industrial Chemistry, Kumamoto Institute of Technology, 1-22-4, Ikeda, Kumamoto-shi 860)
(* Kumamoto Industrial Research Institute, 3-11, Higashi-machi, Kumamoto-shi 862)

超伝導酸化物 $\text{Ba}_2\text{EuCu}_3\text{O}_{7-x}$ の湿度雰囲気下における表面状態の変化

堺 一男・末永知子*・佐多敏之

(熊本工業大学工業化学科, 860 熊本市池田 4-22-1)
(* 熊本県工業技術センター, 862 熊本市東町 3-11)

The stability of the superconducting phase of $\text{Ba}_2\text{EuCu}_3\text{O}_{7-x}$ was studied under various humid atmospheres at 25°C by XRD, SEM and EPMA. The superconducting oxide completely disintegrated within 1400 h above 80% RH, while it remained stable for a long time below 60% RH. The superconducting oxide would disintegrate by forming BaCO_3 via $\text{Ba}(\text{OH})_2$ above 80% RH. It formed only a small amount of precipitate which was considered to be $\text{BaCu}(\text{OH})_2$ below 60% RH.

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1. Introduction

Since the discovery of new superconducting oxides, a lot of researches have been rapidly performed and some properties of these superconducting oxides are gradually being clarified. The superconducting oxides are characteristically known to have the following chemical properties⁽¹⁾⁻⁽⁹⁾; (1) they are soluble in hot water, (2) they are attacked by a humid atmosphere, (3) they react together with CO_2 . A fatal defect is that they gradually disintegrate with humidity in industrial uses, because these superconducting compounds may be exposed in the moisture of the atmosphere. The chemical stability under a humid atmosphere, however, has not been systematically investigated yet. Thus in the present study, the superconducting oxide having over 90 K of T_c was synthesized and research on the stability under various humid conditions was carried out at fixed times, paying attention to the precipitate produced on the surface of the sample.

2. Experimental

BaCO_3 of purity 99.99%, Eu_2O_3 of 99.9% and CuO of 99.99% were weighed as the compositional ratio of Ba : Eu : Cu = 2 : 1 : 3 and mixed for about 2 h with ethanol. Then the mixed powder was calcined in Al_2O_3 boat for about 12 h at 920°C in flowing dry air. After the calcined powder was finely crushed and mixed again for about 2 h with

ethanol, it was molded to pellets with 13.5 mm in diameter and about 2 mm in thickness under 100 MPa. The pellets were fired for about 12 h at 950°C in flowing dry air, annealed for 4 h at 700°C in flowing O_2 gas and then the furnace temperature was gradually lowered to 200°C. Shrinkages of these samples were about 10%.

The electrical resistivity and magnetic susceptibility were measured by a conventional dc four-probe method and by an ac-inductance method, respectively. Typical changes with temperature are shown in Fig. 1. The onset temperature of the synthesized $\text{Ba}_2\text{EuCu}_3\text{O}_{7-x}$ was 93 K and the resistivity became completely zero at 92 K. The susceptibility began to drop diamagnetically at 95 K.

These samples were placed on watch glasses over H_2SO_4 solutions which were prepared to have relative humidities (RH) of 0, 20, 40, 60, 80 and 100%. The water used for dilution was pre-experimentally boiled to remove CO_2 gas. Their humid-controlled bottles were set in a thermostatic chamber of 25°C. The structural and compositional changes on the surface of the samples under several humid atmospheres were investigated during a period of 1-1400 h. The structural change on the surface was observed by X-ray diffraction method (XRD : Rigaku Electronics RAD-B ; $\text{CuK}\alpha$ 35 kV, 20 mA). The precipitate produced on the process of disintegration by H_2O

Fig. 1. Typical temperature dependence of resistivity and diamagnetic susceptibility in $\text{Ba}_2\text{EuCu}_3\text{O}_{7-x}$ used for the experiment under the humid atmosphere. Scale on the right side is denoted for resistivity ($\circ$), while on the left side for diamagnetic susceptibility ($\triangle$).

vapor was observed by a scanning electron microscope (SEM : Shimadzu Workshop) and the concentration change of each element was analyzed by an electron probe of microanalysis (EPMA : JEOL JXA-733 ; 3×10^{-7} A of an irradiation current and $5 \mu\text{m}$ of a probe diameter). Moreover, ICP analysis was performed to compare the results with the compositional data obtained by EPMA.

The compositions of the samples estimated by EPMA were $\text{Ba}_{2.00 \pm 0.03}\text{Eu}_{1.00}\text{Cu}_{3.00 \pm 0.26}\text{O}_{6.71-6.95}$ and the compositional fluctuation of each element on the surface was within 3%. Both values of Cu and Eu evaluated by EPMA were approximately in agreement with those by ICP analysis, but the content of Ba atom by EPMA was evaluated a little lower than that by ICP.

3. Results and discussion

3.1 In 100% RH

Figures 2(a)-(d) show photographs of $\text{Ba}_2\text{EuCu}_3\text{O}_{7-x}$ specimen at fixed times to the 54 h under 100% RH atmosphere. SEM photograph in Fig. 2(a) indicates that the precipitate appears already after 1 h. This precipitate is a spherical one of $10\text{--}50 \mu\text{m}$ in diameter, magnified by 2000 times in Fig. 2(b). This completely covered the surface of the sample after 16 h as shown in Fig. 2(c). X-ray patterns under 100% RH after 30 h and 240 h are shown in Figs. 3(a) and (b), respectively. The main precipitate after 30 h was determined to be BaCO_3 as shown in Fig. 3(a). This

BaCO_3 cannot be formed through the following, direct reaction with CO_2 in the bottle, that is,

because (i) the contents of CO_2 dissolved in H_2SO_4 solution are negligible in boiled water, (ii) only a little amount of the carbon content remains in the sample, compared to the respective components of the superconducting oxide. Therefore, it is considered that BaCO_3 was formed via a rapid reaction between $\text{Ba}(\text{OH})_2$ and CO_2 in air due to the temporal removal of the samples in air ($\text{RH} < 50\%$) from the bottle for XRD measurement. The needle-like precipitate was also observed inside the spherical particle of BaCO_3 after 54 h as shown in Fig. 2(d), and was considered to be the unreacted $\text{Ba}(\text{OH})_2 \cdot n\text{H}_2\text{O}$ ($n = 1, 3$ or 8) with CO_2 in air as described below.

The concentration ratios between each element according to the time lapse under various humid atmospheres by EPMA are summarized in

Table 1. Compositional ratios of typical precipitates caused from $\text{Ba}_2\text{EuCu}_3\text{O}_{7-x}$ are summarized under various humid atmospheres with the process of time. The content of Ba atom is taken to be 1.00 as a standard. For example, $\text{Ba}_2\text{EuCu}_3\text{O}_{7-x}$ becomes $\text{Ba}_{1.00}\text{Eu}_{0.5}\text{Cu}_{1.50}\text{O}_{3.5-\delta}$.

Passed time (h)	RH (%)	Composition (atomic ratio)			
		Eu	Ba	Cu	O
1	100	0.16	1.00	0.61	1.34
	80	0.40	1.00	1.87	4.55
8	100	0.04	1.00	0.21	1.30
	80	0.28	1.00	1.02	4.55
16	100	0.02	1.00	0.00	1.45
	80	0.43	1.00	1.44	4.95
	20	0.46	1.00	1.66	3.43
54	100	0.04	1.00	0.01	0.97
	80	0.31	1.00	0.99	4.48
	20	0.52	1.00	1.95	3.87
83	80	0.04	1.00	0.61	3.04
	20	0.58	1.00	2.52	6.25
102	80	0.03	1.00	0.78	2.15
	20	0.03	1.00	0.88	1.05
126	80	0.05	1.00	1.40	2.90
	20	0.07	1.00	1.47	3.16
174	80	0.03	1.00	0.25	1.93
	0	0.22	1.00	1.23	2.55
660	60	0.26	1.00	1.25	3.38
	20	0.05	1.00	1.39	3.22

Fig. 2. SEM photographs under 100% RH.

(a) 1 h, $\times 500$, (b) 1 h, $\times 2000$, (c) 16 h, $\times 500$, (d) 54 h, $\times 5000$

Fig. 3. X-ray diffraction patterns under 100%.

(a) after 30 h, (b) after 1400 h

Each compound is indicated by the following initial in figure.

B : BaCO_3 , C : CuO , E : Eu(OH)_3 , U : EuOOH

Table 1. The composition of the precipitate after 1 h under 100% RH is $\text{Ba}_{1.00}\text{Cu}_{0.61}\text{O}_{1.34}\text{C}_{0.45}$, and no Eu atom was detected in the precipitate. The composite image of EPMA becomes darker in the radius region of $100\text{ }\mu\text{m}$ around a precipitate than that observed on the pre-experimental surface. This suggests that the heavier atom such as Eu or Cu is lacking in this region. The composition of the precipitate after 16 h under 100% RH was $\text{Ba}_{1.00}\text{Cu}_{0.00}\text{O}_{1.45}\text{C}_{0.39}$, in which neither Eu nor Cu atom was included. As indicated in Table 1, the content of Cu in the precipitate under 100% RH tended to decrease gradually with time. EPMA shows that the content of Ba atom in the precipitate is higher than that in BaCO_3 , so that the precipitate would not consist of only BaCO_3 . An unattributable peak in the vicinity of 15° appears in X-ray diffraction patterns as shown in Fig. 3 (a). This peak does not come from the Eu- or Cu-oxides, hydroxides and carbonates, except for Ba-compounds and EuOOH . EuOOH cannot be considered because the Eu atom was lacking. Though it is difficult to justify correctly from only one peak, this peak may be caused from $\text{Ba}(\text{OH})_2 \cdot n\text{H}_2\text{O}$, considering that some strong peaks for $\text{Ba}(\text{OH})_2 \cdot n\text{H}_2\text{O}$ overlap those for BaCO_3 . The number of H_2O in the polyhydrate, however, could not be determined. After 240 h, as shown in Fig. 3(b), the sample was finally disintegrated to powders. These peaks are attributed as coming from BaCO_3 , CuO , EuOOH and $\text{Eu}(\text{OH})_3$. This agrees with results of other works^{(2), (3), (9)} in dipping the superconducting oxide into water. However, $\text{Eu}_2\text{BaCuO}_5$, which corresponds to Y_2BaCuO_5 described by Yan et al.,⁽²⁾ and Barns and Laudise⁽³⁾ could not be observed in the similar way to Yoshimura et al.⁽⁷⁾ Ba atom on the surface initially forms the hydroxide, $\text{Ba}(\text{OH})_2$, under the condition of the higher vapor pressures of water such as 100% RH and then BaCO_3 forms, through reacting with CO_2 . It is considered that Ba-hydroxide or carbonate would completely disintegrate the oxygen-deficient perovskite structure with a superconducting property.

3.2 In 80% RH

SEM photograph and EPMA analysis show that the precipitate is the same spherical BaCO_3 as that under 100% RH, although the speed formed the precipitation under 80% RH is slower than that under 100% RH. The precipitates covered the whole surface of the sample after 174 h. Judging from the result by EPMA in Table 1, the concentration ratio between each element in the precipitate under 80% RH gradually approaches to that under 100% RH with time. In order to obtain the average distribution of Cu,

Ba and O atoms on the surface of the sample at fixed times under 80% RH, about $1 \times 1\text{ mm}^2$ region of the surface was scanned, expanding the probe diameter of EPMA to $50\text{ }\mu\text{m}$. The distribution of respective atoms remained approximately homogenous after 2 h. Ba atoms homogenously covered the surface by forming BaCO_3 , whereas Cu atoms remarkably distributed inhomogenously after 126 h and Cu atoms locally assembled.

X-ray diffraction patterns with the process of time under 80% RH are shown in Fig. 4. The

Fig. 4. X-ray diffraction patterns with the process of time under 80%.

Fig. 5. The intensity ratio of the peaks from (111) of BaCO_3 and from (103) of Eu-superconducting oxide, and FWHM in their peaks under 80% RH. Scale on the right side denotes full width, while the one on the left side denotes the intensity ratio.

—○— the intensity ratio,
□..... the full width in half maximum for BaCO_3 ,
 - - -△- - - the full width in half maximum for $\text{Ba}_2\text{EuCu}_3\text{O}_{7-x}$

superconducting phase remains stable until 360 h and coexists with BaCO_3 and then it gradually decreases with time. All of the peak intensities in Fig. 4 become weaker with time due to the roughness on the surface caused by the production of the spherical BaCO_3 . Thus, the intensity ratio and the full width in half maximum (FWHM) of the (111) peak of BaCO_3 to the (103) peak of Eu-superconducting oxide are respectively shown in Fig. 5. After the precipitate of BaCO_3 increases until about 540 h, it reaches to a saturated state. FWHM of BaCO_3 becomes narrower with time, while that of the superconducting phase becomes inversely broader. This indicates that the superconducting phase gradually disintegrated via the tetragonal phase with a loss of the oxygen contents as BaCO_3 was homogeneously formed on the surface of the sample. Finally, the sample was disintegrated to powders after 1400 h.

3.3 In RH=60, 40 and 20%

X-ray diffraction patterns under 20% RH are depicted in Fig. 6 and no great change is observed. The superconducting phase remains until 650 h under RH=20%, 40% and 60%, and a part of this phase after 860 h transforms to the tetragonal one with a loss of the oxygen contents. Only a small amount of precipitates are detectable by SEM. The composition of this precipitate under 20% RH after 97 h is $\text{BaCu}_{1.00}\text{O}_{3.4}$ by EPMA. The precipitate may be $\text{BaCu}(\text{OH})_4$ or BaCuO_2 . $\text{BaCu}(\text{OH})_4$ might be constituted by the reaction with a little amount of moisture. BaCuO_2 , which is a stable compound, is pro-

duced by removing partly the oxygen content from the superconducting oxide under the dry atmosphere. No BaCO_3 , however, was formed, which differs from the results of 100% or 80% RH. This fact suggests that Ba atom cannot react with CO_2 in the case of no H_2O vapor and support the speculation described earlier under the condition of above 80% RH. This precipitate could not be observed by X-ray diffraction on account of only the small amount of precipitate present. This result is different from that of Hyde et al.⁴⁾ where the decomposed compound is $\text{Ba}_2\text{Cu}(\text{OH})_6$, because the content of Ba was never observed to be twice as much as that of Cu under any condition by EPMA. After 1400 h, T_c of three samples under 20% RH, 40% RH and 60% RH were 90 K, 92 K and 90 K, respectively. The observations revealed that the samples would not suffer any effect of moisture when ignoring the slight decrease of T_c in dry atmosphere, and also that the superconducting phase is stable for long periods (>1400 h).

3.4 Characteristic behavior in various humid atmospheres

The experimental facts described above can be summarized as follows:

(i) the decomposition process of the superconducting oxide extremely differs in accordance with RH. BaCO_3 is formed in the region of RH > 80%, while not in the region of RH < 60% in spite of temporarily taking out the sample in air (RH < 50%) from the bottle for XRD measurement.

(ii) A peak based on $\text{Ba}(\text{OH})_2 \cdot n\text{H}_2\text{O}$ ($n=1, 3$ or 8) is observed by XRD.

Judging from these facts, the most probable reaction for forming BaCO_3 in RH > 80% at 20°C is,

Namely, in the first step the H_2O vapor in the bottle condenses on the surface of the sample and the condensed water attacks the A-site of $\text{Ba}_2\text{EuCu}_3\text{O}_{7-x}$ structure. Then Ba atom precipitates on the surface of the sample to form a large amount of BaCO_3 . Consequently, it leads to the disintegration of the superconducting phase. The considerable reactions for Ba atom are generally,

and

and

The progression observed in reactions (2)–(4) occurs, when we considered from the differences of the standard free energies (enthalpies) for the

Fig. 6. X-ray diffraction patterns after several hours under 20% RH.

respective compounds. In a similar way, the reaction (5) also proceeds, but Ba atom in the $\text{Ba}_2\text{EuCuO}_{7-x}$ is stable against the attack of CO_2 without water, because BaCO_3 was not formed in the region of $\text{RH} < 60\%$. H_2O vapor in air could not condense on the surface of the sample in the case of $\text{RH} < 60\%$. Thus, the superconducting phase would remain stable for a long time.

4. Conclusion

The decomposition process of the superconducting oxide was investigated under various humid atmospheres at 25°C . It was found that it takes a long time under below 60% RH to disintegrate and that the superconducting phase remains. However, the precipitate of BaCO_3 is mainly produced when vapor atmosphere of above 80% RH through the process of producing $\text{Ba}(\text{OH})_2$ and it leads to the disintegration of the superconducting oxide body.

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