Effects of N_2O Gas on Electrical Properties of $Eu_{1+x}Ba_{2-x}Cu_3O_y$

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$Eu_{1+x}Ba_{2-x}Cu_3O_y$ の電気特性への N_2O ガスの影響

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The temperature dependence of electrical resistance of $Eu_{1+x}Ba_{2-x}Cu_3O_y$ ($x=0, 0.2$, and 0.5) was measured in N_2O and 5 % N_2O-N_2 . Kinks were observed in the temperature-resistance curves of $EuBa_2Cu_3O_y$ in N_2O and 5 % N_2O-N_2 . This behavior was considered to be related to the order-disorder transition of oxygen vacancy (oxygen ion). Substitution of Eu ions for Ba ions affects the decomposition of N_2O and the migration of oxygen ions, that is, the local rearrangement of oxygen ions in $Eu_{1+x}Ba_{2-x}Cu_3O_y$.

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1. Introduction

Since the discovery of high- T_c oxide superconductor was reported by Bednorz and Müller,¹⁾ a number of studies have been made on high- T_c superconducting materials. In processing oxide superconductors, high temperature treatment in O_2 and stability in various gases are required. There are a few reports on the effects of gaseous species on the electrical properties of RE-Ba-Cu-O systems. We reported changes in resistances of $Eu_{1+x}Ba_{2-x}Cu_3O_y$ in $NO-N_2$, NO_2-N_2 , or N_2O gas around 473 K.²⁾ The resistance in N_2O scarcely varied for $EuBa_2Cu_3O_y$ and $Eu_{1.2}Ba_{1.8}Cu_3O_y$, and increased remarkably for $Eu_{1.5}Ba_{1.5}Cu_3O_y$ around 473 K. This behavior was considered to be related with the adsorption and surface decomposition of N_2O , which caused the increase of the resistance of $Eu_{1.5}Ba_{1.5}Cu_3O_y$ due to the recombination of the electrons and holes. The decomposition of N_2O may contribute to oxidation of the oxides at higher temperatures.

In this letter, we report the effects of N_2O on electrical properties of $Eu_{1+x}Ba_{2-x}Cu_3O_y$ at high temperatures and discuss the substitution effects of the Eu ions for the Ba ions on the electrical property in N_2O gas.

2. Experimental procedure

$Eu_{1+x}Ba_{2-x}Cu_3O_y$ compounds were prepared by the solid-state reaction method. The samples A, B, and C with nominal compositions

$Eu_{1+x}Ba_{2-x}Cu_3O_y$ ($x=0.0, 0.2$, and 0.5), respectively, were prepared by mixing powders of Eu_2O_3 , $BaCO_3$, and CuO . The samples were sintered at 1208 K for 6 h in air. Details of synthesis were described in the previous paper.^{2),3)} The sample A was identified to be orthorhombic and the samples B and C to be tetragonal by X-ray diffraction with $CuK\alpha$ radiation.

Electrical measurement was carried out by the usual DC four-point probe method. The samples were cut into about $2 \times 2 \times 8 \text{ mm}^3$ from the disk. A silver paste (Dupont 4929) was used for electrical contacts. The electrical resistances of the samples at high temperatures were measured in N_2O and 5 % N_2O-N_2 . Details of the electrical measurement were described elsewhere.⁴⁾

3. Results and discussion

Figures 1, 2, and 3 show the temperature dependences of the electrical resistances of the samples A, B, and C in N_2O , 5 % N_2O-N_2 , and air respectively. The resistances of the samples in N_2O were lower than in 5 % N_2O-N_2 . Those of the samples A and B in N_2O were larger than in air and that of sample C was smaller than in air above 973 K, which suggested that the samples were oxidized by N_2O gas.

The oxidation due to the decomposition of N_2O and the reduction due to the release of oxygen are considered to contribute to the changes in the resistances of the samples. This oxidation-reduc-

Fig. 1. Temperature dependence of resistances of EuBa₂Cu₃O_y in N₂O, 5 % N₂O-N₂, and air.

Fig. 2. Temperature dependence of resistances of Eu_{1.2}Ba_{1.8}Cu₃O_y in N₂O, 5 % N₂O-N₂, and air.

tion process is described by using Kröger-Vink notation as follows :

and

where V_O, O_O, and h denote oxygen vacancy, oxygen ion on lattice, and hole, respectively. The valence of the oxygen ion was assumed to be -2 on the lattice site, to simplify the discussion. The resistance of Eu_{1+x}Ba_{2-x}Cu₃O_y in N₂O is

Fig. 3. Temperature dependence of resistance of Eu_{1.5}Ba_{1.5}Cu₃O_y in N₂O, 5 % N₂O-N₂, and air.

considered to depend on the competition between oxidation and reduction process shown by Eqs. (1) and (2). Equation (1) means the move of the oxygen vacancies (oxygen ions) to react to N₂O gas. It is important that the reaction of Eq. (1) is dominated by oxygen vacancy.

Kinks in the temperature dependence of the resistances of the sample A were observed at the vicinity of 823 K and 773 K in N₂O and 5 % N₂O-N₂, respectively, as shown in Fig. 1. However, the change in the resistance of the sample B in Fig. 2 did not show any kinks above 573 K. The difference in the temperature dependence of the resistance is explained in relation to the crystallographic properties, i. e., ordering or disordering of the oxygen vacancies (oxygen ions) in Eu_{1+x}Ba_{2-x}Cu₃O_y system, taking account of the reactions of Eqs. (1) and (2). The order of the oxygen vacancy is related to the orthorhombic-tetragonal phase transition. We showed that the oxygen vacancies (oxygen ions) in Eu_{1+x}Ba_{2-x}Cu₃O_y were arranged regularly in the orthorhombic phase and irregularly in the tetragonal phase as YBa₂Cu₃O_y.⁵⁾ The decomposition of NO is another example of the catalytic decomposition in relation to order-disorder phase transition of the oxygen vacancy (oxygen ion). Shin et al. reported the catalytic decomposition of NO over Ca₂Fe₂O₅ and Sr₂Fe₂O₅, and pointed out that disordering of oxygen vacancies in the perovskite lattice played an important role in decomposition of NO.⁶⁾ These two similar behaviors suggest that the migration of the oxygen ion (oxygen vacancy) contributes significantly to decomposition of N₂O or NO over these oxides. The notable kink in the

temperature dependence of the resistance of $\text{EuBa}_2\text{Cu}_3\text{O}_y$ is considered to be related to the oxygen diffusion mechanism in the lattice. The oxygen diffusion in disordered phase (tetragonal phase) may be faster than that in ordered phase (orthorhombic phase).

The temperature dependence of the resistance of the sample C was different from those of the samples A and B. The complicated behavior below 573 K is considered to be due to the adsorption and surface decomposition of N_2O , according to the previous report.²⁾ A kink in the temperature dependence of the resistance was observed in the temperature region from 823 K to 923 K. There is no report of the phase transition in this region to our knowledge. This behavior shows that the reaction of the decomposition of N_2O through the process of Eq. (1) proceeds simultaneously with the adsorption and surface decomposition.

The effects of the substitution of Eu ions for Ba ions of $\text{Eu}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_y$ on the decomposition of N_2O can be discussed taking account of the relation between oxygen partial pressure and resistivity in the previous paper.³⁾ The apparent oxygen partial pressures are summarized in Table 1. We obtained the following results; at 1076 K,

$$P_{\text{O}_2}^{\text{C}} > P_{\text{O}_2}^{\text{A}} > P_{\text{O}_2}^{\text{B}} \quad (3)$$

and at 774 K,

$$P_{\text{O}_2}^{\text{C}} > P_{\text{O}_2}^{\text{B}} > P_{\text{O}_2}^{\text{A}} \quad (4)$$

where $P_{\text{O}_2}^{\text{A}}$, $P_{\text{O}_2}^{\text{B}}$, and $P_{\text{O}_2}^{\text{C}}$ denote the apparent oxygen partial pressures of the samples A, B, and C, respectively. In the previous paper,³⁾ we showed that the substituting Eu ions for Ba ions caused the local rearrangement of oxygen ions and affected the relation between oxygen pressure and oxygen solubility in $\text{Eu}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_y$. The apparent oxygen partial pressure due to decomposition of N_2O was changed by the substitution of Eu ions for Ba ions, which affected the local rearrangement of oxygen ions, that is, the migration of oxygen ions, because all the samples were tetragonal at 1076 K. $P_{\text{O}_2}^{\text{B}} > P_{\text{O}_2}^{\text{A}}$ in relation (4) suggests the ordering of oxygen vacancies

Table 1. Apparent oxygen partial pressures due to decomposition of N_2O on $\text{Eu}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_y$ compounds.

gas	T(K)	$\text{EuBa}_2\text{Cu}_3\text{O}_y$	$\text{Eu}_{1.2}\text{Ba}_{1.8}\text{Cu}_3\text{O}_y$	$\text{Eu}_{1.5}\text{Ba}_{1.5}\text{Cu}_3\text{O}_y$
		sample A	sample B	sample C
		Apparent oxygen partial pressure (atm)		
N_2O	774	0.006	0.010	0.017
	1076	0.21	0.15	0.30
5% N_2O - N_2	774	0.0008	0.0006	0.0015
	1076	0.025	0.015	0.020

(oxygen ions) in the orthorhombic phase.

4. Conclusion

Temperature dependence of the electrical resistance of $\text{Eu}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_y$ was measured in N_2O and 5 % N_2O - N_2 . The notable kinks in the temperature dependence of the resistance of $\text{EuBa}_2\text{Cu}_3\text{O}_y$ were observed in N_2O and 5 % N_2O - N_2 . This behavior was considered to be due to order-disorder transition of the oxygen vacancy (oxygen ion). The decomposition of N_2O was affected by the substitution of Eu ions for Ba ions. The substitution was considered to affect the local rearrangement of oxygen, that is, the migration of oxygen.

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