Effects of N$_2$O Gas on Electrical Properties of Eu$_{1+x}$Ba$_{2-x}$Cu$_3$O$_y$

Fumio MUNAKATA, Kazuhiko SHINOHARA and Mitsugu YAMANAKA

{Materials Research Laboratory, Central Engineering Laboratories, Nissan Motor Co., Ltd.,}
{1, Natsushima-cho, Yokosuka-shi, Kanagawa 237}

Eu$_{1+x}$Ba$_{2-x}$Cu$_3$O$_y$の電気特性への N$_2$O ガスの影響

宗像文男・細原和彦・山中貢
(日産自動車（株）中央研究所材料研究所，237 神奈川県横須賀市夏島町1)

The temperature dependence of electrical resistance of Eu$_{1+x}$Ba$_{2-x}$Cu$_3$O$_y$ (x=0.0, 0.2, and 0.5) was measured in N$_2$O and 5% N$_2$O-N$_2$. Kinks were observed in the temperature-resistance curves of EuBa$_2$Cu$_3$O$_y$ in N$_2$O and 5% N$_2$O-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$_2$O and the migration of oxygen ions, that is, the local rearrangement of oxygen ions in Eu$_{1+x}$Ba$_{2-x}$Cu$_3$O$_y$.

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1. Introduction

Since the discovery of high-\(T_c\) oxide superconductor was reported by Bednorz and Muller, 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$_3$O$_y$ in NO-N$_2$, NO$_2$-N$_2$, or N$_2$O gas around 473K. The resistance in N$_2$O scarcely varied for EuBa$_2$Cu$_3$O$_y$ and Eu$_{1.5}$Ba$_{1.5}$Cu$_3$O$_y$, and increased remarkably for Eu$_{1.5}$Ba$_{1.5}$Cu$_3$O$_y$. This behavior was considered to be related with the adsorption and surface decomposition of N$_2$O, which caused the increase of the resistance of Eu$_{1.5}$Ba$_{1.5}$Cu$_3$O$_y$ due to the recombination of the electrons and holes. The decomposition of N$_2$O may contribute to oxidation of the oxides at higher temperatures.

In this letter, we report the effects of N$_2$O on electrical properties of Eu$_{1+x}$Ba$_{2-x}$Cu$_3$O$_y$ at high temperatures and discuss the substitution effects of the Eu ions for the Ba ions on the electrical property in N$_2$O gas.

2. Experimental procedure

Eu$_{1+x}$Ba$_{2-x}$Cu$_3$O$_y$ 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$_3$O$_y$ (x=0.0, 0.2, and 0.5), respectively, were prepared by mixing powders of Eu$_2$O$_3$, BaCO$_3$, and CuO. The samples were sintered at 1208K for 6h in air. Details of synthesis were described in the previous paper. 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 2x2x8 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$_2$O and 5% N$_2$O-N$_2$. Details of the electrical measurement were described elsewhere.

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$_2$O, 5% N$_2$O-N$_2$, and air respectively. The resistances of the samples in N$_2$O were lower than in 5% N$_2$O-N$_2$. Those of the samples A and B in N$_2$O were larger than in air and that of sample C was smaller than in air above 973K, which suggested that the samples were oxidized by N$_2$O gas.

The oxidation due to the decomposition of N$_2$O 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-
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The reaction process is described by using Kröger-Vink notation as follows:

\[ \text{N}_2\text{O}(g) + V_{O}^{+} \rightarrow O_{O}^{2-} + 2h^+ + \text{N}_2(g) \]  

(1)

and

\[ O_{O}^{2-} + 2h^+ \rightarrow V_{O}^{+} + (1/2)\text{O}_2(g) \]  

(2)

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$_{2-x}$Cu$_3$O$_y$ in N$_2$O is 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 N$_2$O 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 N$_2$O and 5 % N$_2$O-N$_2$, 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$_{2-x}$Cu$_3$O$_y$ 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$_{2-x}$Cu$_3$O$_y$ were arranged regularly in the orthorhombic phase and irregularly in the tetragonal phase as YBa$_2$Cu$_3$O$_y$. 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 Ca$_2$Fe$_2$O$_5$ and Sr$_2$Fe$_2$O$_5$, and pointed out that disordering of oxygen vacancies in the perovskite lattice played an important role in decomposition of NO. These two similar behaviors suggest that the migration of the oxygen ion (oxygen vacancy) contributes significantly to decomposition of N$_2$O or NO over these oxides. The notable kink in the
temperature dependence of the resistance of EuBa$_2$Cu$_3$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$_2$O, according to the previous report. 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$_2$O 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 Eu$_{1+x}$Ba$_{2-x}$Cu$_3$O$_y$ on the decomposition of N$_2$O can be discussed taking account of the relation between oxygen partial pressure and resistivity in the previous paper. The apparent oxygen partial pressures are summarized in Table 1. We obtained the following results; at 1076 K,

$$P_{o_2}^c > P_{o_2}^a > P_{o_2}^b,$$

and at 774 K,

$$P_{o_2}^c > P_{o_2}^b > P_{o_2}^a,$$

where $P_{o_2}^a$, $P_{o_2}^b$, and $P_{o_2}^c$ denote the apparent oxygen partial pressures of the samples A, B, and C, respectively. In the previous paper, 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 Eu$_{1+x}$Ba$_{2-x}$Cu$_3$O$_y$. The apparent oxygen partial pressure due to decomposition of N$_2$O 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. $P_{o_2}^b > P_{o_2}^a$ in relation (4) suggests the ordering of oxygen vacancies (oxygen ions) in the orthorhombic phase.

### Table 1. Apparent oxygen partial pressures due to decomposition of N$_2$O on Eu$_{1+x}$Ba$_{2-x}$Cu$_3$O$_y$ compounds.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Sample A</th>
<th>Sample B</th>
<th>Sample C</th>
</tr>
</thead>
<tbody>
<tr>
<td>N$_2$O</td>
<td>774</td>
<td>0.006</td>
<td>0.010</td>
</tr>
<tr>
<td>5N$_2$O-N$_2$</td>
<td>1076</td>
<td>0.21</td>
<td>0.15</td>
</tr>
<tr>
<td>5N$_2$O-N$_2$</td>
<td>774</td>
<td>0.0008</td>
<td>0.0008</td>
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<tr>
<td>1076</td>
<td>0.025</td>
<td>0.015</td>
<td>0.020</td>
</tr>
</tbody>
</table>

4. Conclusion

Temperature dependence of the electrical resistance of Eu$_{1+x}$Ba$_{2-x}$Cu$_3$O$_y$ was measured in N$_2$O and 5% N$_2$O-N$_2$. The notable kinks in the temperature dependence of the resistance of EuBa$_2$Cu$_3$O$_y$ were observed in N$_2$O and 5% N$_2$O-N$_2$. This behavior was considered to be due to order-disorder transition of the oxygen vacancy (oxygen ion). The decomposition of N$_2$O 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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### References