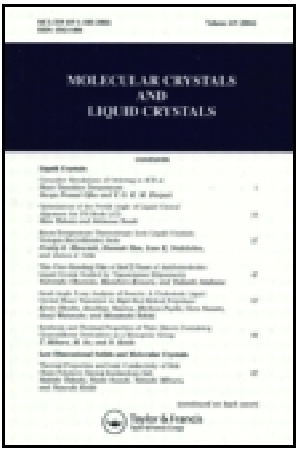

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High T^{C} Superconducting Oxides and Solid State Chemistry

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High T_c Superconducting Oxides and Solid State Chemistry

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Abstract The valences of copper,cerium and bismuth and the oxygen content of $(La_{1-x}M_x)_2CuO_{4-\delta}$ (M=Sr,Ba and Ca),$Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ and $Bi_{2.00}Sr_{1.88}Ca_{1.00}Cu_{2.14}O_y$ systems were determined by the chemical analysis and thermogravimetry. Also the relationship between the copper valence and the critical temperature T_c was revealed. The δ vs. log Po_2 curves of $(La_{1-x}M_x)_2CuO_{4-\delta}$ had a sigmoid-like shape which was characteristic of perovskite type oxides. The copper valence at a constant oxygen partial pressure increased proportionally with the increase in x and deviated from the linear relationship above a certain value of x.This deviation arised from the formation of oxygen deficit δ . The chemical analysis on $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ revealed that the cerium valence was 3.84, irrespective of temperature and patial pressure of oxygen.The oxygen deficit δ increased with the increase in the oxygen deficit. The copper valence was given as contour in the T - log Po_2 diagram. The critical temperature appeared below the copper valence of 1.84. The measurement of oxygen deficit on $Bi_{2.00}Sr_{1.88}Ca_{1.00}Cu_{2.14}O_y$ revealed the difference in y - log Po_2 between above and below 800°C. Above 800°C, the y -log Po_2 relation resembled those of other kinds of high T_c superconducting oxides. However, below 800°C y only depended on temperature, that is, y was independent of oxygen partial pressure. The tailing of resistivity - temperature curve in the vicinity of critical temperature seemd to be due to the existence of neutral oxygen species confirmed by the chemical analysis and microthermogravimetry.

INTRODUCTION

In transition metal oxides, the superconductivity as well as the electric conductivity is controlled by the concentration of electronic defects. So, it is of essential importance to regulate and determine the defect concentration as accurately as possible, in order to elucidate the superconduction mechanism and to improve the superconducting properties. Control of the defect concentration in transition metal oxides is usually effected by controlling the valence of transition metal ion, and the valence control is made by doping with other kinds of *cations and changing the oxygen content.*

Although most of studies carried out so far on the superconducting oxides have reported the mixing ratio of starting raw materials, mention has not been made on the composition and copper valence of superconducting oxides. Also the annealing was often made, but the valence change due to annealing scarcely has determined. The purpose of this paper is to determine the copper valence of superconducting oxides by the thermomicrogravimetry and chemical analysis in order to elucidate the relationship between the copper valence and the critical temperature.

$(La_{1-x}M_x)_2CuO_{4-\delta}$ (M=Sr,Ba and Ca)

Preparation and method of chemical analysis

Nitrate aqueous solutions of La, M and Cu were mixed in a desired ratio, and an oxalic acid-ethanol solution was added under the controlled pH condition to prepare the coprecipitate. After the filtration the precipitate was dried at 100°C, calcined at 400°C to convert into the oxide, and fired at 1000°C for 12 hours for homogenization. After the annealing at a predetermined temperature and oxygen partial pressure, the oxide was subjected to the two-step iodometry to determine the average copper valence. In the two-step iodometry, the total valence change from Cu^{3+} to Cu^{+} and from Cu^{2+} to Cu^{+} was determined from the amount of iodine liberated by the dissolution of sample oxide in a hydrochloric acid solution containing potassium iodide, and the amount of copper was determined from the amount of iodine liberated by adding potassium iodide to the solution after the dissolution of oxide in a hydrochloric acid solution.

Determination of oxygen nonstoichiometry by microbalance technique

An amount of oxide sample of which copper valence was known was placed in a platinum basket and suspended from a beam of Shimazu microbalance the sensitivity of which was 1μg. The equilibrium weight was determined as functions of oxygen partial pressure and temperature. Figure 1 shows the plot of the oxygen deficit againt the logarithm of oxygen partial pressure, for $(La_{0.88}Sr_{0.12})_2CuO_{4-\delta}$. If the chemical formula is expressed by $(La_{1-x}Sr_x)_2CuO_{4-\delta}$ and the copper valence is denoted by (2+z), the electroneutrality condition gives

$$z=2x-2\delta \qquad (1)$$

Therefore , the copper valence can be calculated from x and δ.

The result is given on the ordinate of right hand side in Fig.1. From Fig.1 it is easily seen that asymptotically approaches to a line of $\delta=0$ as log Po_2 increases, whereas it approaches to a line of z=0 as log Po_2 decreases. The δ-log Po_2 curves show a sigmoid like shape which is often observed for the perovskite type oxides . Figure 2 is the plot of copper valence vs. x for $(La_{1-x}M_x)_2CuO_{4-\delta}$ with M = Sr, Ba and Ca. The dotted line represents a relation of copper valence and x, obtained form eq(1) by putting $\delta=0$. In a range where x is small, the copper valence linearly increases along the dotted line and the copper valence gradually deviates from the dotted line as x becomes large.

The x value at which the deviation from the dotted line begins depends on the kind of alkaline earth metal. The critical value is highest for strontium and lowest for calcium.

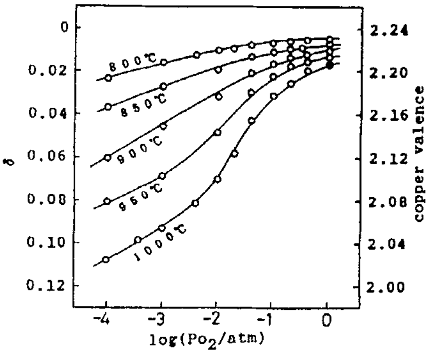

Fig.1. Oxygen nonstoichiometry of $(La_{0.88}Sr_{0.12})_2CuO_{4-\delta}$

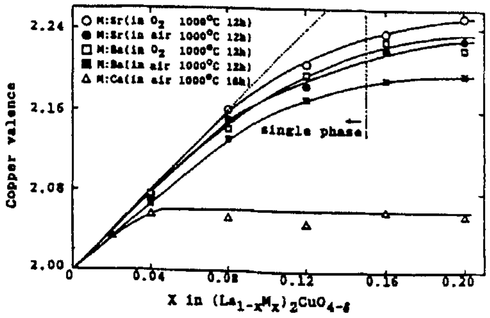

Fig.2. Relationship between copper valence and x for $(La_{1-x}M_x)_2CuO_{4-\delta}$

$Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$

Preparation and method of chemical analysis

The oxide sample was prepared by the coprecipitation method in a similary way as $(La_{1-x}M_x)_2CuO_{4-\delta}$. The oxide was dissolved in a nitric acid solution and the total amount of Nd+Ce was determined by the chelate titration method. The amount of cerium in solution was determined by the permanganate titration method after the whole cerium ion was oxidized to tetra-valent state with potassium peroxosulfate. The amount of ceric ion in oxide was determined by the permanganate titration method[1] after the oxide was dissolved in a 0.1N $MnSO_4$ - 1N HNO_3 aqueous solution at 60 70°C. The iodometric titration method was employed to determine the valence change corresponding to $Ce^{4+} \rightarrow Ce^{3+}$, $Cu^{3+} \rightarrow Cu^{+}$ and $Cu^{2+} \rightarrow Cu^{+}$. The valences of cerium and copper were obtained by the combination of results of chemical analysis.

Stability region of $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$

Figure 3 gives the stability region of $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ on a T-log Po_2 plane. Symbol ▽ indicates the melting point determined by the TGA-DTA method. Symbol △ gives the boundary determined by the EMF measurement using a solid state electrochemical cell. The boundary line represents

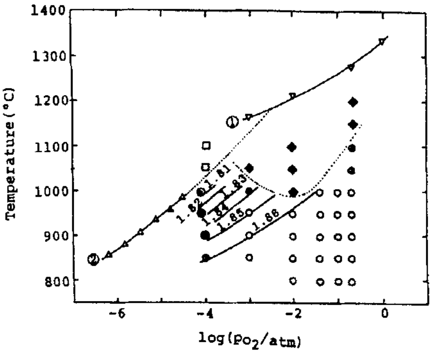

Fig.3. Stability region of $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$

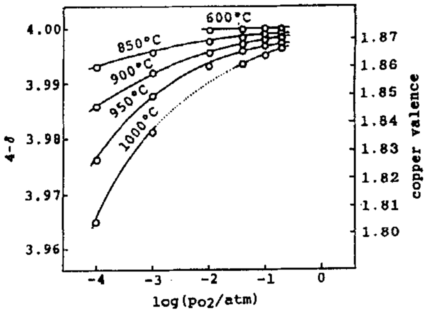

Fig.4. Oxygen nonstoichiometry of $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$

the equilibrium condition for the reaction

$$Nd_{1.85}Ce_{0.15}CuO_{4-\delta} = 0.925Nd_2O_3 + 0.15CeO_2 + 0.5Cu_2O + (0.213-\delta/2)O_2 \quad (2)$$

Circles indicate the condition under which the single phase of $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ was found to be stable by using the X-ray diffraction and microgravimetric methods. Symbol ◆ gives the condition under which the oxide lost its weight slowly. The X-ray diffraction study on the surface showed the existence of new oxide phase. The superconduction was observed on samples annealed under the condition represented by symbol ⊙, but only the onset temperature was observed under the condition with symbol ● . Samples annealed under the condition represented by ◑ showed the semiconducting property. A set of lines with figures from 1.86 to 1.81 gives the contour of copper valence. The explanation will be given later.

Oxygen nonstoichiometry and copper valence

Figure 4 gives the plot of against log P_{O_2} for $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$. Chemical analysis has revealed that the cerium valence was 3.85 irrespective of the annealing condition. So using the electroneutrality

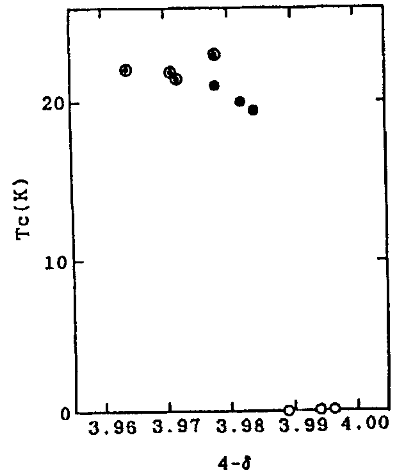

Fig.5(a). Relationship between Tc and oxygen content of $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$

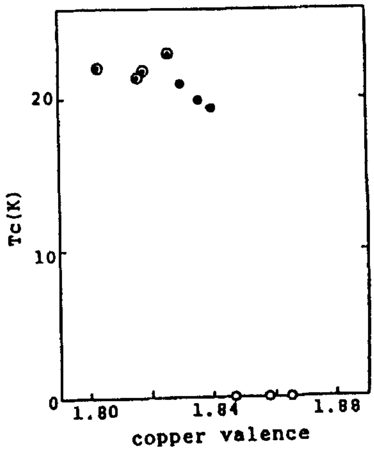

Fig.5(b). Relationship between Tc and copper valence of $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$

condition, the calculation was made on the copper valence, which is given on the ordinate of right hand side in Figure 4. The T- log Po_2 relation at a constant copper valence was read from the figure and plotted in Fig.1 as contour.

Figure 5(a) shows the plot of T_c against oxygen content $4-\delta$ and Figure 5(b) gives the relationship between T_c and copper valence.

Below the copper valence of 1.83, the superconductivity was observed.

$Bi_{2.00}Sr_{1.88}Ca_{1.00}Cu_{2.14}O_y$

Preparation and method of chemical analysis

The oxide was prepared in a similar way as $(La_{1-x}M_x)_2CuO_{4-\delta}$ and $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$. The chelate titration method was employed for the determination of Bi and Sr+Ca. The ratio of Sr to Ca was determined by the ICP method, and the respective amounts of Sr and Ca were calculated. The amount of Bi^{5+} in oxide was determined by the permanganate titration after the oxide was dissolved in 0.1N $MnSO_4$ - 1N HNO_3 solution. The copper valence was determined by the two-step iodemetric titration .

Oxygen nonstoichiometry

The oxygen content y of $Bi_{2.00}Sr_{1.88}Ca_{1.00}Cu_{2.14}O_y$ was determined by means of a microbalance. The results are given in Fig.6 In the figure, the dotted line represents the melting point determined by the gravimetric method.The oxygen content y ranges from 8.15 to 8.33, which is much narrower than that of $YBa_2Cu_3O_{7-\delta}$[2]. The shape of y-log Po_2 curves below 800°C is quite different from that above 800°C. That is, the shape resembles that of the perovskite type oxides[3] and can be interpreted by the incorporation of oxygen into oxide to form or annihilate ionic and electronic defects. However, below 800°C, the oxygen content is independent of the oxygen partial pressure and it only depends on the temperature . Within the author's knowledge such a dependence has not been reported so far.

Copper valence

After annealed at various temperatures and oxygen pressures and queched to liquid nitrogen, the samples were subjected to the chemical analysis. The results are summarized in Table 1 . The bismuth valence is not 3 but about 3.15 and the copper valence is about 2.07, irrespective of the annealing condition . Also y is the oxygen content calculated from the valences, and y' is the one determined by means of a microbalance. For the oxides annealed above 800°C , the difference $\Delta y(=y-y')$ is positive. The positive value is considered to be due to the oxygen absorption during quenching . However, Δy is negative for oxides annealed below 800°C . This fact suggests that a portion of oxygen contained in oxide does not contribute the oxidation of copper and/or bismuth and remains as neutral species. The high T_c superconducting oxides have the layer stucture and act as the intercalation compounds. For example, $YBa_2Cu_3O_{7-\delta}$ absorbs 1-2 moles of CO or NO per one mole of the oxide[4]. Accordingly, there is a possibility of absorbing oxygen as neutral species.

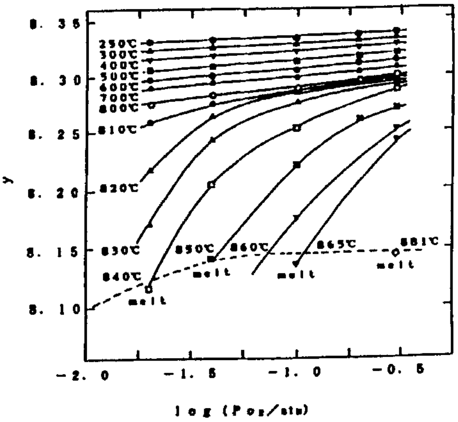

Fig.6 Oxygen nonstoichiometry of $Bi_{2.00}Sr_{1.88}Ca_{1.00}Cu_{2.14}O_y$

Table 1 Characterization of $Bi_{2.00}Sr_{1.88}Ca_{1.00}Cu_{2.14}O_y$

Annealing Temp (°C)	Po_2 (atm)	Valence Bi	Cu	y	y'	Δy [y-y']	T_c(on) (K)	T_c(0) (K)
865	0.2	3.12	2.08	8.22	8.214	0.01	98	74
860	0.1	3.12	2.07	8.22	8.178	0.04	101	78
830	0.02	3.12	2.08	8.21	8.171	0.04	97	70
800	0.2	3.14	2.07	8.23	8.294	-0.06	99	74
700	0.2	3.15	2.08	8.24	8.302	-0.06	98	71
600	0.2	3.16	2.06	8.23	8.309	-0.08	92	55
500	0.2	3.16	2.07	8.25	8.316	-0.07	90	14
400	0.2	3.17	2.08	8.25	8.322	-0.07	84	15
300	0.2	3.17	2.08	8.27	8.328	-0.06	76	8
850*	0.2	3.17	2.07	8.26	8.260	0.00	90	78

Annealing Time = 48hr.

*)Sample was quenched to room temperature.

Annealing condition and T_c

Figures 7 and 8 show the resistivity-temperature curves of samples annealed under various conditions given in Table 1. The critical temperatures T_c(onset) and T_c(zero) are listed in Table 1. The onset critical temperature T_c(onset) appears to be independent of annealing condition, but T_c(zero)is strongly dependent. Namely, the samples annealed below about 800°C give the resistivity-temperature curves with a remarkable tailing. The tailing becomes remarkable with the decrease in annealing temperature. However, the samples annealed above 800°C do not show tailing.

As mentioned above, the samples annealed below 800°C contain the neutral oxygen species as a part. So, it is concluded that the neutral species of oxygen incorporated into oxide seems to have an effect of lowering the critical temperature of this kind of superconducting oxides.

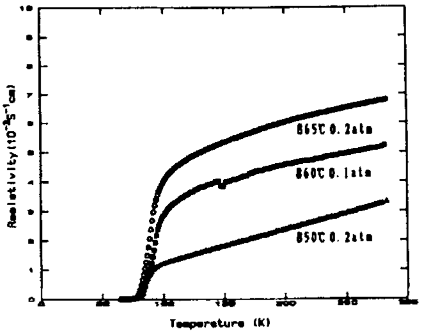

Fig.7 Resistivity-Temperature curves of $Bi_{2.00}Sr_{1.88}Ca_{1.00}Cu_{2.14}O_y$

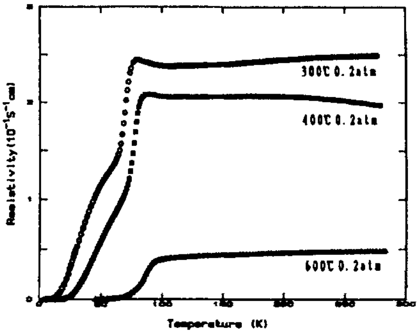

Fig.8 Resistivity-Temperature curves of $Bi_{2.00}Sr_{1.88}Ca_{1.00}Cu_{2.14}O_y$

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